

**OPTICAL AND INFRARED SPECTRA
OF SOME UNSTABLE MOLECULES**

by

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ABSTRACT

Some unstable gaseous molecules, cobalt oxide (CoO), niobium nitride (NbN) and aminoborane (NH₂BH₂), were studied by high resolution optical spectroscopy. A portion of the "red" system of CoO, from 7000 Å to 5800 Å, was measured using laser induced fluorescence techniques. Three bands of the system, with origins at 6338 Å, 6411 Å and 6436 Å, were rotationally analyzed. The lower levels of these parallel bands are the $\Omega = 7/2$ and $5/2$ spin-orbit components of a $^4\Delta_i$ electronic state. Available evidence indicates that this is the ground state of the molecule; its bond length is 1.631 Å. This work completes the determination of the ground state symmetries for the entire series of first row diatomic transition metal oxides. The hyperfine structure in the ground state is very small, supporting a $\sigma^2\delta^3\pi^2$ electron configuration. The upper state, assigned as $\sigma\delta^3\pi^2\sigma^*$, has large positive hyperfine splittings that follow a case (a_β) pattern; it is heavily perturbed, both rotationally and vibrationally.

The sub-Doppler spectrum of the $^3\Phi$ - $^3\Delta$ system of NbN was measured by intermodulated fluorescence techniques, and the hyperfine structure analyzed. Second order spin-orbit interactions have shifted the $^3\Phi_3$ - $^3\Delta_2$ subband 40 cm⁻¹ to the blue of its central first order position. The perturbations to the spin-orbit components were so extensive that five hyperfine constants, rather than three, were required to fit the data to the case (a) Hamiltonian. The $^3\Delta$ - $^3\Phi$ system of NbN is the first instance where this has been observed. The magnetic hyperfine constants indicate that all components of

the $^3\Delta$ and $^3\Phi$ spin orbit manifolds may be affected, though the $^3\Delta$ state interacts most strongly, presumably by the coupling of the $^3\Delta_2$ component with the $^1\Delta$ state having the same configuration. The Fermi contact interactions in the $^3\Delta$ substates are large and positive, consistent with a $\sigma^1\delta^1$ configuration. In the $^3\Phi$ state the (b + c) hyperfine constants are negative, as expected from a $\pi^1\delta^1$ configuration. The $^3\Delta$ and $^3\Phi$ bond lengths are 1.6618 Å and 1.6712 Å, respectively, which are intermediate between those of ZrN and MoN.

The Fourier transform infrared spectrum of the ν_7 BH₂ wagging fundamental of NH₂BH₂ was rotationally analyzed. A set of effective rotational and centrifugal distortion constants was determined, but the band shows extensive perturbations by Coriolis interactions with the nearby ν_5 and ν_{11} fundamentals. A complete analysis could not be made without an analysis of the ν_5 - ν_7 - ν_{11} Coriolis interactions, which is currently not possible because the very small dipole derivative of the ν_5 vibration has prevented its analysis.

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CHAPTER I

ELECTRONIC TRANSITIONS IN HETERONUCLEAR DIATOMIC MOLECULES

I.A. Some Properties of Angular Momenta.

In a non-rotating molecule, the angular momentum operators \mathbf{J} , \mathbf{S} and \mathbf{L} have the following diagonal matrix elements:¹

$$\langle J\Omega | \hat{J}_z | J\Omega \rangle = \hbar\Omega \quad (1.1)$$

$$\langle S\Sigma | \hat{S}_z | S\Sigma \rangle = \hbar\Sigma \quad (1.2)$$

$$\langle L\Lambda | \hat{L}_z | L\Lambda \rangle = \hbar\Lambda \quad (1.3)$$

$$\langle J\Omega | \hat{J}^2 | J\Omega \rangle = \hbar^2 J(J+1) \quad (1.4)$$

$$\langle S\Sigma | \hat{S}^2 | S\Sigma \rangle = \hbar^2 S(S+1) \quad (1.5)$$

$$\langle L\Lambda | \hat{L}^2 | L\Lambda \rangle = \hbar^2 L(L+1) \quad (1.6)$$

J , S and L are the total, spin and orbital angular momenta, respectively; J , S and L are their respective quantum numbers, and Ω , Σ and Λ are the projection quantum numbers in diatomic molecules (i.e., along the molecular z axis).

The ladder operator \hat{L}_{\pm} of a general angular momentum $\hat{\mathbf{L}}$ has the Cartesian form²

$$\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y \quad (1.8)$$

It has the property of transforming state $|L, m\rangle$ into state $|L, m\pm 1\rangle$, where m is the quantum number of L . For $\hat{\mathbf{J}}$ and $\hat{\mathbf{S}}$ the laddering operations are written:¹

$$\langle J, \Omega\pm 1 | \hat{J}_{\mp} | J\Omega \rangle = \hbar[J(J+1) - \Omega(\Omega\pm 1)]^{1/2} \quad (1.9)$$

$$\langle S, \Sigma\pm 1 | \hat{S}_{\pm} | S\Sigma \rangle = \hbar[S(S+1) - \Sigma(\Sigma\pm 1)]^{1/2} \quad (1.10)$$

J_{\mp} in equation (1.9) is not expressed as J_{\pm} because the commutation relations are different in the space-fixed and molecule-fixed axis systems:³

$$J_x J_y - J_y J_x = i J_z \quad \text{SPACE} \quad (1.11)$$

$$J_x J_y - J_y J_x = -i J_z \quad \text{MOLECULE} \quad (1.12)$$

This leads to a sign reversal upon transformation from the space-fixed to molecule-fixed systems (the anomalous sign of i):

$$J_{\pm} |JM\rangle = \hbar [J(J+1) - M(M\pm 1)]^{1/2} |J, M\pm 1\rangle \quad \text{SPACE} \quad (1.13)$$

$$J_{\mp} |JK\rangle = \hbar [J(J+1) - K(K\pm 1)]^{1/2} |J, K\pm 1\rangle \quad \text{MOLECULE} \quad (1.14)$$

Although the motion of the electrons about the axis defines a good quantum number Λ , L itself is not a good quantum number because a diatomic molecule is not a spherical system. Thus \hat{L}_x and \hat{L}_y do not obey the usual operator equations, and \hat{L}_{\pm} is left in the form $\langle \hat{L}_+ \hat{L}_- + \hat{L}_- \hat{L}_+ \rangle / 2$, or $\langle \hat{L}_{\perp}^2 \rangle$, with the quantity $B \langle L_{\perp}^2 \rangle$ appearing on the diagonal of the rotational Hamiltonian matrix as a minor, constant electronic isotope shift incorporated into the effective vibrational energy.¹

The dot product of two general angular momentum operators $\hat{\mathbf{A}}$ and $\hat{\mathbf{B}}$ is:

$$\hat{\mathbf{A}} \cdot \hat{\mathbf{B}} = A_z B_z + (A_+ B_- + A_- B_+) / 2 \quad (1.15)$$

The addition of angular momenta j_1 and j_2 to form j results in the coupled eigenfunction $|jm\rangle$:

$$|jm\rangle = \sum_{m_1 m_2} (-1)^{j_1 - j_2 + m} \sqrt{2j+1} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix} |j_1 m_1\rangle |j_2 m_2\rangle \quad (1.16)$$

where $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$ are the uncoupled eigenfunctions, the first term is a phase factor, and $\sqrt{2j+1}$ is a normalization factor. The term in brackets is a coefficient called a Wigner 3-j symbol. Its definition is given by equation (1.16) rearranged as:⁴

$$\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix} = \frac{(-1)^{j_1-j_2+m}}{\sqrt{2j+1}} \langle j_1 j_2 m_1 m_2 | jm \rangle \quad (1.17)$$

According to the angular momentum commutation relations for j_1 , j_2 and j ,⁵ the algebraic form for the 3-j symbol is determined by the requirement that $m_1 + m_2 = m$ and $|j_1 - j_2| \leq j \leq (j_1 + j_2)$ (the triangle, or vector addition, rule)⁴. If these conditions are not satisfied, the vector coupling coefficient $\langle j_1 j_2 m_1 m_2 | jm \rangle$ is 0.

I.B. Spherical Harmonics and Spherical Tensor Operators.

Spherical harmonics, $Y_{lm}(\theta, \phi)$, are orbital angular momentum eigenfunctions normalized to unity on a unit sphere. To be exact they are the eigenfunctions of the differential operators \hat{L}^2 and \hat{L}_z , corresponding to the eigenvalues $l(l+1)$ and m :^{6,7}

$$\hat{L}^2 Y_{lm}(\theta, \phi) = l(l+1) Y_{lm}(\theta, \phi) \quad (1.17)$$

$$\hat{L}_z Y_{lm}(\theta, \phi) = m Y_{lm}(\theta, \phi) \quad (1.18)$$

The angles θ and ϕ are the usual polar coordinates as illustrated in Figure 1.1. The differential operators \hat{L}^2 and \hat{L}_z , defined in units where $\hbar = 1$, are⁶

$$\hat{L}_z = \partial/\partial\phi \quad (1.19)$$

$$\hat{L}^2 = -[(\sin \theta)^{-1}(\partial/\partial\theta)(\sin \theta \partial/\partial\theta) + (\sin^2\theta)^{-1}\partial^2/\partial\theta^2] \quad (1.20)$$

Expressed in terms of the orbital angular momentum functions of θ and ϕ on the unit sphere, a spherical harmonic is:⁸

$$Y_{lm}(\theta, \phi) = c_l (-1)^{l+m} [(l-m)!/(l+m)!]^{1/2} (\sin\theta)^m [\partial/\partial(\cos\theta)]^{l+m} \times (\sin\theta)^{2l} e^{im\phi} \quad (1.21)$$

where c_l is a normalization factor:

$$|c_l| = [(2l+1)!]^{1/2}/(4\pi)^{1/2} 2^l l! \quad (1.22)$$

Associated Legendre polynomials, $P_l^m(\cos \theta)$, are commonly exploited in quantum mechanics because of their connection to spherical harmonics:⁶

$$Y_{lm}(\theta, \phi) = (-)^m [(2l+1)(l-m)!/4\pi(l+m)!]^{1/2} P_l^m(\cos \theta) e^{im\phi} \quad (1.23)$$

where⁶

$$P_l^m(x) = (1-x^2)^{m/2}/2^l l! [d^{l+m}/dx^{l+m}](x^2-1)^l \quad (1.24)$$

When the component $m = 0$, the spherical harmonic and Legendre polynomial differ only by a constant⁹

$$Y_{l0}(\theta, \phi) = [(2l+1)/4\pi]^{1/2} P_l(\cos \theta) \quad (1.25)$$

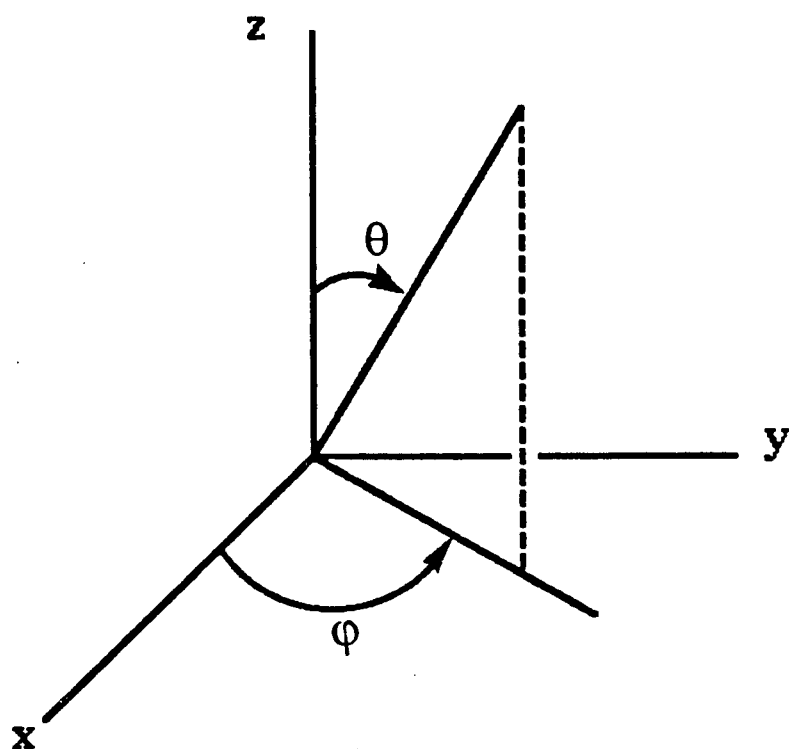


Fig. 1.1. Polar and Cartesian coordinates, in which $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, $z = r\cos\theta$.⁸

The derivation of expressions describing the coupling of angular momenta, particularly those for the magnetic hyperfine and quadrupolar hyperfine interactions, is often best approached using irreducible spherical tensors. A brief explanation of spherical tensor operators, and the expressions required for their manipulation, follows. Spherical tensor methods are then applied where necessary in subsequent sections to derive the forms employed in the Hamiltonian representing the diatomic molecules in the present work.

The spherical components of a vector, or first rank tensor, operator acting on an angular momentum \mathbf{A} are related to their Cartesian counterparts by:^{2,4}

$$T^1_0(\mathbf{A}) = A_z \quad (1.26)$$

$$T^1_{\pm 1}(\mathbf{A}) = \mp(A_x \pm iA_y)/\sqrt{2} \quad (1.27)$$

A spherical tensor \mathbf{T} of rank k is defined as a set of $2k+1$ quantities ("components") which transform into one another upon rotation from one coordinate system to another (for example, between molecule- and space-fixed axis systems):^{10,11}

$$T^k_q = \sum_p T^k_p D_{pq}^{(k)}(\alpha\beta\gamma) \quad (1.28)$$

where q and p are the components of the tensor in the molecule- and space-fixed axis systems, respectively, and $D_{pq}^{(k)}(\alpha\beta\gamma)$ is the Wigner rotation matrix. The angles α , β and γ are the Euler angles corresponding to the three successive axis rotations required to transform between two coordinate systems. In spectroscopy, a beam of photons (in the space-fixed axis system) induces a change in the molecule in the molecule-fixed system. Wigner rotation

matrices function to project from one axis system to another in order to put the photon beam and the molecules being altered by the photons into the same frame of reference. In the reverse direction, from space- to molecule-fixed coordinates, the relation is:

$$T_p^k = \sum_q D_{pq}^{k*}(\alpha\beta\gamma) T_q^k \quad (1.29)$$

where the complex conjugation of a rotation matrix is given by

$$D_{MK}^{k*}(\alpha\beta\gamma) = (-1)^{M-K} D_{-M,-K}^k(\alpha\beta\gamma) \quad (1.30)$$

The complex conjugation is required to account for the anomalous sign of i .

A Wigner rotation matrix is a matrix describing how the eigenfunctions of \hat{J}^2 and \hat{J}_z , i.e., a spherical harmonic $|jm\rangle$, transform on coordinate rotation into other functions $|jm\rangle$:¹²

$$D(\alpha\beta\gamma)|jm\rangle = \sum |jm'\rangle D_{m'm}^{(j)}(\alpha\beta\gamma) \quad (1.31)$$

Premultiplying equation (1.31) by $|jm'\rangle^*$ (i.e., $\langle jm'|$) and integrating reduces the right hand side to $D_{m'm}^{(j)}$ due to the orthogonality of spherical harmonic functions:¹²

$$D_{m'm}^{(j)}(\alpha\beta\gamma) = \langle jm'|D(\alpha\beta\gamma)|jm\rangle \quad (1.32)$$

A D matrix element with one of its projections equal to zero collapses to a spherical harmonic, which depends on only two angles:¹²

$$D_{p0}^l(\alpha\beta\gamma) = (-1)^p [4\pi/(2l+1)]^{1/2} Y_{lp}(\beta,\alpha) \quad \text{SPACE} \quad (1.32)$$

$$D_{0q}^l(\alpha\beta\gamma) = [4\pi/(2l+1)]^{1/2} Y_{lq}(\beta,\gamma) \quad \text{MOLECULE} \quad (1.33)$$

If both projections are zero, the Wigner rotation matrix collapses to a Legendre polynomial:^{9,12}

$$D_{00}^l(\alpha\beta\gamma) = P_l(\cos \beta) = [4\pi/(2l+1)]^{1/2} Y_{l0}(\beta,0) \quad (1.34)$$

The Legendre polynomial $P_l(\cos\theta)$ is also related to the spherical harmonics by the spherical harmonic addition theorem:

$$P_l(\cos \theta) = (4\pi/2l+1) \sum_m Y_{lm}^*(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2) \quad (1.35)$$

where $Y_{lm}^*(\theta, \phi) = (-)^m Y_{l, -m}(\theta, \phi)$.^{6,9,13,14} The angles $\theta_1, \theta_2, \phi_1$ and ϕ_2 are as defined by Fig. 1.1 for vectors \mathbf{r}_1 and \mathbf{r}_2 , and θ is the angle between directions (θ_1, ϕ_1) and (θ_2, ϕ_2) . Using Racah's modified spherical harmonics to eliminate the factor of $[4\pi/(2l+1)]^{1/2}$:¹⁶

$$C_{lm}(\theta, \phi) = [4\pi/(2l+1)]^{1/2} Y_{lm}(\theta, \phi) \quad (1.36)$$

the spherical harmonic addition theorem becomes^{13,15}

$$P_l(\cos \theta) = \sum_m C_{lm}^*(\theta_1, \phi_1) C_{lm}(\theta_2, \phi_2) \quad (1.37)$$

or¹⁴

$$P_l(\cos \theta) = C_l(\theta_1, \phi_1) \cdot C_l(\theta_2, \phi_2) \quad (1.38)$$

The coupling of two tensor operators to form a compound tensor is similar to the addition of two angular momenta given in equation (1.16):¹⁰

$$[\mathbf{T}^{k_1}(1) \otimes \mathbf{T}^{k_2}(2)]_{q^k} = \sum (-1)^{k_1-k_2+q} \sqrt{2k+1} \begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & -q \end{pmatrix} \times [\mathbf{T}^{k_1}_{q_1}(1), \mathbf{T}^{k_2}_{q_2}(2)] \quad (1.39)$$

Here the tensor \mathbf{T}^{k_1} of rank k_1 , operating on system (1), is coupled to tensor \mathbf{T}^{k_2} [which operates on system (2)]. Shorter, alternative ways of denoting a compound tensor are $[\mathbf{T}^{k_1}(1), \mathbf{T}^{k_2}(2)]$ or, for a tensor of rank k_1 coupled to itself, $[\mathbf{T}^k(1,1)]$, where $k = 2k_1$. If two tensors of the same rank k are coupled to give a scalar, i.e., a quantity invariant to a coordinate rotation, the compound tensor of equation (1.39) is also a scalar, or of rank zero. The resulting expression

becomes much simpler and lacks the orientation-dependent 3-j symbol:¹⁰

$$[T^k(1) \otimes T^k(2)]_{00} = (-1)^k(2k+1)^{-1/2} T^k(1) \cdot T^k(2) \quad (1.40)$$

where the conventional scalar product $T^k(1) \cdot T^k(2)$ is given as:^{10,11}

$$T^k(1) \cdot T^k(2) = \sum_q (-1)^q T^k_q(1) T^k_{-q}(2) \quad (1.41)$$

After a compound tensor equation is written which appropriately represents a particular physical interaction and breaks it into its constituent tensors, the Wigner-Eckart theorem is applied to evaluate the matrix elements T^k_q of the constituent tensors. According to the theorem the matrix elements of a tensor operator are factored into: 1) a 3-j symbol, which contains information on the geometry or orientation of the angular momentum; 2) a reduced matrix element (denoted by double vertical bars), related to the magnitude of the angular momentum but independent of its direction; and 3) a phase factor. Expressed in terms of the eigenfunctions $|\gamma j m\rangle$, where j is the quantum number acted upon by T^k , m is the projection of j , and γ contains any remaining quantum numbers not of interest in this particular basis, the Wigner-Eckart theorem is:¹⁶

$$\langle \gamma' j' m' | T^k_q | \gamma j m \rangle = (-1)^{j'-m'} \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} \langle \gamma' j' || T^k || \gamma j \rangle \quad (1.42)$$

Note that the reduced matrix element is independent of m .

A reduced matrix element is usually worked out by evaluating the simplest type of matrix element and then substituting into the Wigner-Eckart theorem. For example to obtain $\langle J || T^1(J) || J \rangle$, where J refers to a general angular momentum, we calculate the simplest type of matrix element of $T^1(J)$, namely its $q = 0$ (or z) component:¹⁷

$$\langle J'M' | T^1_0(J) | JM \rangle = \delta_{MM'} \delta_{JJ'} M \quad (1.43)$$

This element is non-vanishing only if $J'M' = JM$. From the Wigner-Eckart theorem (equation 1.42),

$$M = (-1)^{J-M} \begin{pmatrix} J & 1 & J \\ -M & 0 & M \end{pmatrix} \langle J || T^1(J) || J \rangle \quad (1.44)$$

Substitution for the 3-j symbol¹¹ produces

$$M = (-1)^{J-M} (-1)^{J-M} M [J(J+1)(2J+1)]^{-1/2} \langle J || T^1(J) || J \rangle \quad (1.45)$$

Since J and M both have integral or half-integral values, $(-1)^{2(J-M)}$ is 1, which reduces equation (1.45) to:

$$\langle J || T^1(J) || J \rangle = [J(J+1)(2J+1)]^{1/2} \quad (1.46)$$

An important reduced matrix element is that of the rotation matrix element $D_{q^{(k)}}(\alpha\beta\gamma)$ (cf. equations 1.29 and 1.30):

$$\langle J'K' || D_{\dot{q}^{(k)}}(\alpha\beta\gamma) || JK \rangle = (-1)^{J'-K'} [(2J+1)(2J'+1)]^{1/2} \begin{pmatrix} J' & k & J \\ -K' & q & K \end{pmatrix} \quad (1.47)$$

in which the dot replacing the p indicates that no reduction has been performed with respect to space-fixed axes, so there is no dependence on the M quantum number. Another useful formula gives the matrix elements of the scalar product of two commuting tensor operators (that is, ones which act on different parts of the system) in a coupled basis:¹⁸

$$\begin{aligned} & \langle \gamma' j_1' j_2' J'M' | T^k(1) \cdot U^k(2) | \gamma j_1 j_2 JM \rangle = \\ & (-1)^{j_1+j_2+J} \delta_{J'J} \delta_{M'M} \left\{ \begin{matrix} J & j_2' & j_1' \\ k & j_1 & j_2 \end{matrix} \right\} \sum_{\gamma''} \langle \gamma' j_1' || T^k(1) || \gamma'' j_1 \rangle \langle \gamma'' j_2' || U^k(2) || \gamma j_2 \rangle \end{aligned} \quad (1.48)$$

in which T^k acts on j_1 and U^k on j_2 . The term in curly brackets is a Wigner 6-j symbol, a coefficient which arises in the coupling of three angular momenta, as compared to two in the 3-j symbol.¹⁹

I.C. Selection Rules and Hund's Coupling Cases.

An electronic transition can occur in a molecule only if there are non-zero matrix elements of the electric dipole moment operator \mathbf{M} which allow interaction with electromagnetic radiation.²⁰ The probability of such a transition occurring between electronic states n and m is proportional to the square of the transition moment, R^{nm} :

$$R^{nm} = \int \Psi_n^* \mathbf{M} \Psi_m d\tau, \quad (1.49)$$

where Ψ_n and Ψ_m are the eigenfunctions of states n and m .²⁰ The electric dipole moment \mathbf{M} for a total of N particles (electrons and nuclei) is²¹

$$\mathbf{M} = \sum_{i=1}^N e_i \mathbf{r}_i \quad (1.50)$$

where e_i is the charge on particle i which has coordinates \mathbf{r}_i . In the general case the transition moment integral vanishes unless the change in total angular momentum, J , is zero or unity, or²²

$$\Delta J = 0, \pm 1 \quad (1.51)$$

Changes in J of -1 , 0 and $+1$ are denoted by the letters P , Q and R , respectively.

The specific selection rules vary depending on the manner in which the spin, orbital and rotational angular momenta are coupled to one another and to the internuclear axis. The angular momentum coupling schemes in diatomic molecules are distinguished by sets of molecule-fixed basis functions called the Hund's coupling cases. The main property differentiating the four coupling cases described below is the number of angular momenta which have well-defined components (quantum numbers) along the internuclear axis. The

appropriate coupling case is the one which produces the smallest off-diagonal matrix elements for the rotational Hamiltonian, or diagonal elements which most closely reproduce the observed spectral pattern. The most common cases by far in molecules with no very heavy atoms are cases (a) and (b).

Hund's case (a) coupling has the maximum number of well-defined quantum numbers, such that the relations given in equations (1.1), (1.2) and (1.3) for a non-rotating molecule remain valid.^{1,23} The basis function for a case (a) coupling scheme is therefore $|(L)\Lambda\rangle|S\Sigma\rangle|J\Omega\rangle$, or $|\eta\Lambda;S\Sigma;J\Omega M\rangle$, where Λ , Σ and Ω are the eigenvalues of the z components of \hat{L} , \hat{S} and \hat{J} , with M being the space-fixed analog of Ω , and $\Omega = \Lambda + \Sigma$.¹ The semicolon separators indicate products of component wavefunctions. L is incorporated into the label η for the vibronic state, as it is not a good quantum number (cf. Section I.A). The case (a) representation is a good working approximation when there are no strong interactions in the Hamiltonian which uncouple these angular momenta from the axis. Case (a) occurs where there is a non-zero orbital angular momentum and fairly small spin-orbit coupling, where the coupling of **L** and **S** to each other is less important than the coupling of **L** to the axis.²⁴ The vector diagram for case (a) coupling is given in Fig. 1.2.

In case (b) coupling, **S** is coupled only weakly to the axis, but **L** remains strongly coupled. Given a large enough value of J, any case (a) state uncouples toward case (b) because as J increases the rotational and spin magnetic moments must ultimately be coupled more strongly to one another than **L** and **S** are. Formally it can be said that the rotation (**R**) has increased to the point where it couples

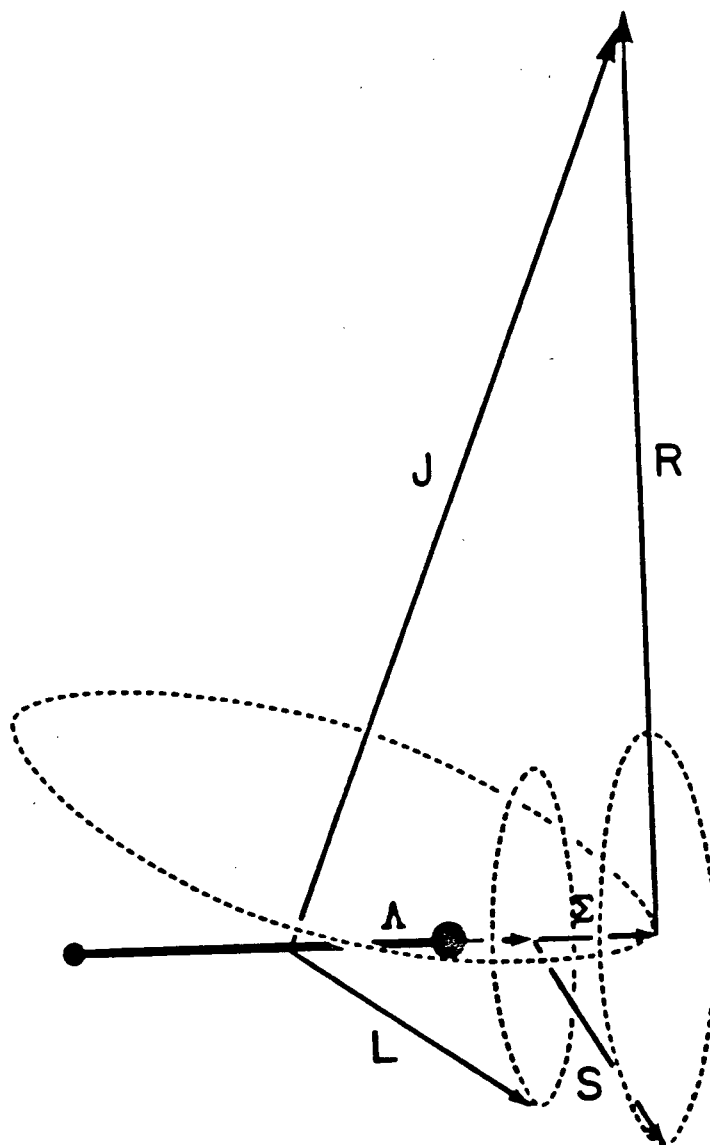


Fig. 1.2. Vector diagram of Hund's coupling case (a).²⁴

to the orbital angular momentum to form a resultant \mathbf{N} , causing \mathbf{S} to uncouple from \mathbf{L} , and therefore from the molecular axis. The effects of rotation become important when BJ becomes large compared to the separations between the spin-orbit components.¹ The transformation of a case (a) situation to case (b) occurs by way of the spin-uncoupling operator, $-B(\hat{J}_+\hat{S}_- + \hat{J}_-\hat{S}_+)$. With its selection rules ΔS and $\Delta \Lambda = 0$, and $\Delta \Omega = \Delta \Sigma = \pm 1$, this operator most commonly mixes spin-orbit components of a given $2S+1\Lambda$ state, which is consistent with the physical case (b) phenomenon of uncoupling \mathbf{L} from \mathbf{S} .²³ The case (b) representation also arises for Σ states in which there is no orbital angular momentum to couple the spin to the axis. The total angular momentum \mathbf{J} in case (b) is thus obtained as:²⁴

$$\mathbf{R} + \mathbf{L} = \mathbf{N}; \mathbf{N} + \mathbf{S} = \mathbf{J} \quad (1.52)$$

instead of the case (a) situation

$$\mathbf{R} + \mathbf{L} + \mathbf{S} = \mathbf{J} \quad (1.53)$$

The case (b) basis function, $|\eta; N\Lambda S J\rangle$, is the more physically realistic representation in those cases where the rotational angular momentum \mathbf{N} is quantized about the axis, with electron spin providing only minor corrections to the total energy. Its vector diagram appears in Fig. 1.3.

When nuclear spin is included in the basis set describing angular momentum coupling in diatomic molecules, the Hund's coupling cases (a) and (b) must be further subdivided. In the majority of diatomic molecules, including those considered in the current work, \mathbf{I} is coupled so loosely to the internuclear axis or to \mathbf{S} that the dominant coupling is to the rotational angular momentum \mathbf{J} , or

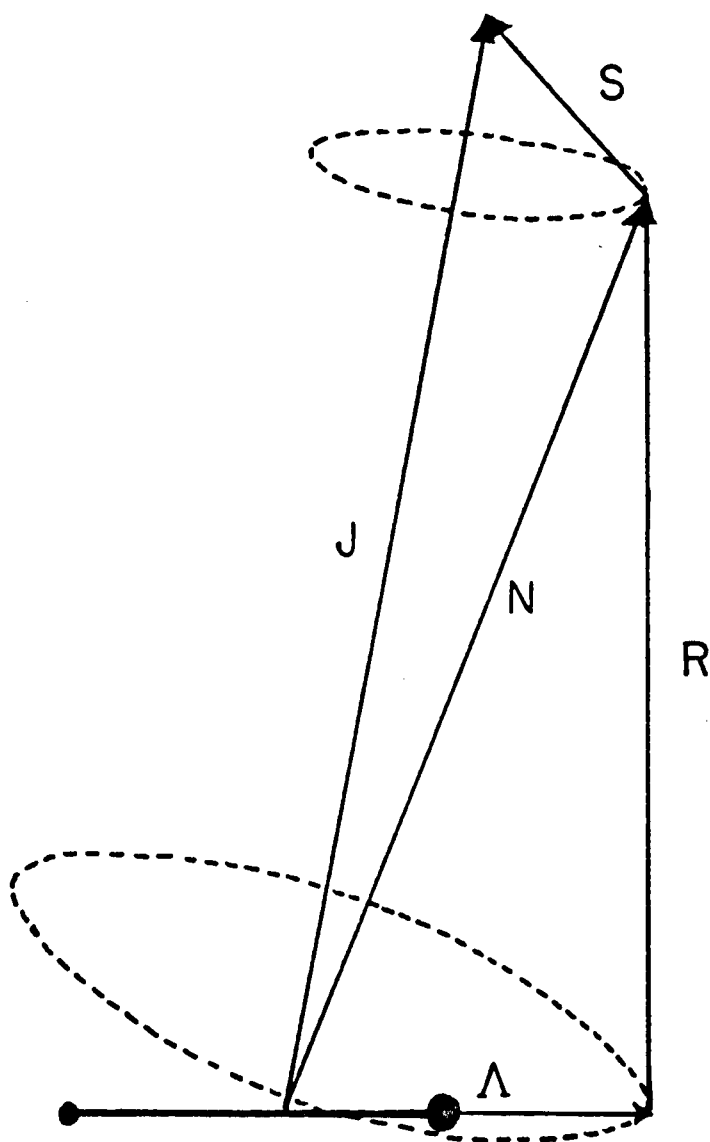


Fig. 1.3. Vector diagram of Hund's coupling case (b).²⁴

$$\mathbf{J} + \mathbf{I} = \mathbf{F} \quad (1.54)$$

By analogy with Hund's case (b), those coupling schemes following equation (1.54) are denoted by β subscripts. The extended Hund's coupling cases are called a_β and $b_{\beta J}$, corresponding to basis functions $|\Lambda S \Sigma J \Omega I F\rangle$ and $|N \Lambda S J I F\rangle$, respectively.^{25,26}

Coupling schemes in which \mathbf{I} is not coupled to \mathbf{J} are a_α , $b_{\beta N}$ and $b_{\beta S}$. In the a_α case, nuclear spin is coupled to the molecular axis with the projection quantum number I_z , though molecules exhibiting case (a_α) coupling have never been observed.²⁷ This is expected since nuclear magnetic moments are on the order of a thousand times smaller than that of the electron, making it unlikely that the dominant nuclear spin coupling will be to the internuclear axis by a magnetic interaction with the electronic and orbital angular momenta. In the $b_{\beta N}$ and $b_{\beta S}$ cases \mathbf{I} is coupled to \mathbf{N} and \mathbf{S} , respectively, rather than to \mathbf{J} as in case ($b_{\beta J}$). Case ($b_{\beta N}$) coupling is not expected to be observed, as the magnetic moment of \mathbf{N} (composed of $\mathbf{R} + \mathbf{L}$) is normally considerably less than that of either \mathbf{J} or \mathbf{S} , as \mathbf{S} has a large magnetic moment and \mathbf{J} is the sum of \mathbf{S} and \mathbf{L} .²⁷ In Hund's case ($b_{\beta S}$), \mathbf{I} couples to \mathbf{S} to form a vector \mathbf{G} , which couples to \mathbf{N} to form the total angular momentum \mathbf{F} :

$$\mathbf{I} + \mathbf{S} = \mathbf{G}$$

$$\mathbf{G} + \mathbf{N} = \mathbf{F}$$

In a nonrotating molecule, where any rotationally induced angular momenta are absent, case ($b_{\beta S}$) will be the dominant case (b) coupling scheme. In a rotating case (b) molecule, however, the coupling case that occurs depends on the relative sizes of the coupling of \mathbf{S} to \mathbf{I} and \mathbf{N} : if the $\mathbf{I} \cdot \mathbf{S}$ coupling dominates, the ($b_{\beta S}$)

case occurs. The best condition for a case ($b\beta_S$) molecule is a Σ state which originates nearly completely from an atomic s orbital. Case ($b\beta_S$) coupling is therefore rather rare, though it has been extensively described in the ground $^2\Sigma$ state of scandium oxide, ScO .^{28,29,30} This molecule is ideal because the transition metal ion and closed shell oxygen have widely differing ionization potentials. This leaves the Sc^{2+} uncontaminated by contributions from O^{2-} , and the $^2\Sigma$ state far removed from the closed state of non-spherical symmetry with which it could mix.²⁷ Other molecules that have been observed to conform to case ($b\beta_S$) coupling are the $b^3\Sigma$ and $c^3\Sigma$ states of AlF ³¹, and the ground $^2\Sigma^+$ state of LaO ³². Note that both of these molecules also adhere to the conditions required for the $b\beta_S$ coupling case.

Case (c) coupling occurs in molecules containing an atom sufficiently heavy that the spin-orbit interaction which results is so large that electron motion can no longer be defined in either the **L** or **S** representations; one of the consequences is that spin multiplicity is no longer defined. This phenomenon is expressed as an axial **J** (J_a) equal to the sum of **L** and **S**, which is then coupled to **R** to form the resultant **J**, as illustrated in Fig. 1.4.²⁴ The basis function for case (c) is therefore $|\eta J_a; J\Omega M\rangle$, where the only well-defined axial component is Ω .¹ Case(c) molecules observed so far are ^{209}BiO ($X^2\Pi_{1/2}$ state)^{33,34} and InH ($^3\Pi_1$ state)³⁵.

Case (d) coupling is normally only found in molecules where an electron has been promoted to a Rydberg orbital with higher principal quantum number n . The effect of the long distance between

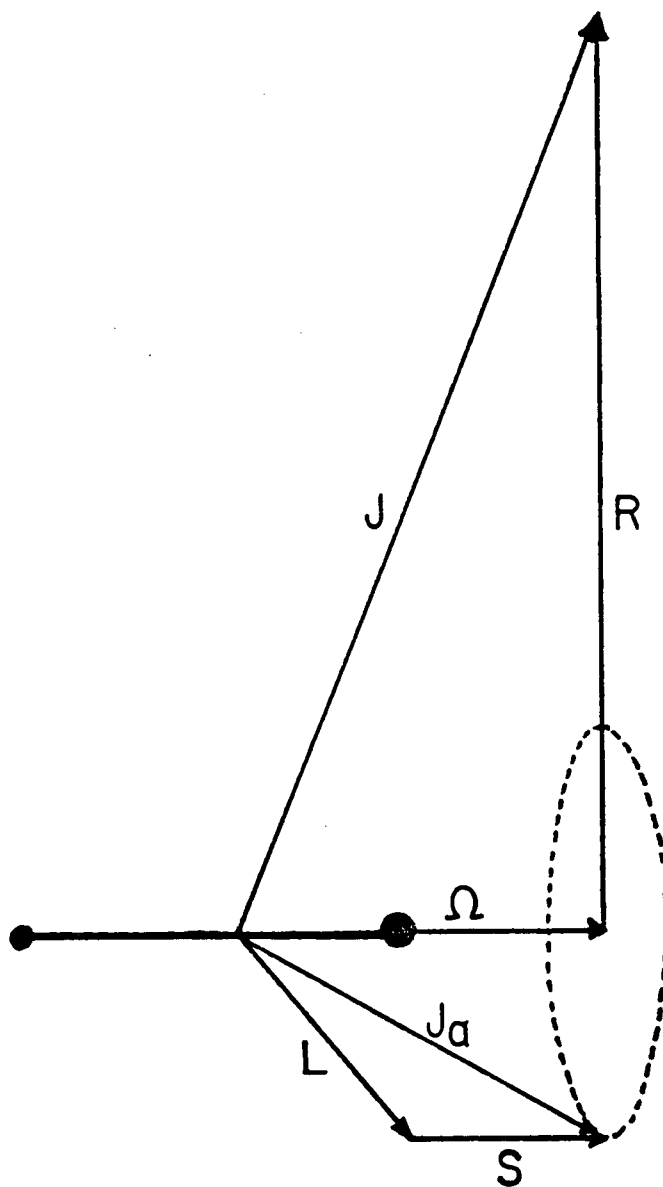


Fig. 1.4. Vector diagram for Hund's case (c).²⁴

the electron and the nuclei is that the electron orbital motion is coupled only weakly to the internuclear axis, but can instead couple more strongly to the rotational angular momentum, R .^{21,24} Case (d) is equivalent to case (b) but with the difference that L is uncoupled from the axis rather than S ; the transition from case (a) is made by the L-uncoupling operator, $-B(\hat{J}_+\hat{L}_- + \hat{J}_-\hat{L}_+)$ rather than via the S-uncoupling operator.²³

While still in the case (a) or (b) limits, the L-uncoupling operator may induce Λ -doubling, which lifts the degeneracy of the $\pm\Lambda$ states. The selection rules for interactions by this operator are $\Delta\Omega = \Delta\Lambda = \pm 1$ and $\Delta S = 0$.²³ The phenomenon of Λ -doubling is discussed in more detail in the last section of this chapter. Case (d) becomes the appropriate representation when $-2B\hat{J}\cdot\hat{L}$ makes a contribution to the energy levels that is large with respect to the separation of states with differing Λ .

The Hund's coupling cases corresponding to the niobium nitride (NbN) and cobalt oxide (CoO) molecules in this work are most appropriately described by the case (a) and, with higher rotation, case (b) coupling schemes. As Λ and S are defined in both of these cases, the following selection rules can be stated for cases (a) and (b):²⁴

$$\Delta\Lambda = 0, \pm 1 \quad (1.55)$$

$$\Delta S = 0 \quad (1.56)$$

For case (a), with Σ and Ω as good quantum numbers, there are the more specific rules:

$$\Delta\Omega = 0, \pm 1 \quad (1.57)$$

$$\Delta\Sigma = 0 \quad (1.58)$$

where equation (1.57) follows from equations (1.55) and (1.56).²⁴ The $\Delta S = 0$ and $\Delta \Sigma = 0$ rules become less strict as the spin-orbit interaction increases, because the selection rules for the spin-orbit interaction are $\Delta \Omega = 0$ with either $\Delta \Lambda = \Delta \Sigma = 0$ or $\Delta \Lambda = -\Delta \Sigma = \pm 1$.^{24,36} In case (b) neither Σ nor Ω are well-defined, so the 'rotational' selection rule becomes

$$\Delta N = 0, \pm 1 \quad (1.59)$$

I.D. The Hamiltonian.

I.D.1. Nuclear rotational Hamiltonian.

From equation (1.53) it follows that the nuclear rotational Hamiltonian $\hat{B}\hat{R}^2 - D\hat{R}^4$ should be written in the form appropriate for case (a) as:

$$\hat{H}_{\text{rot}} = B(\hat{J} - \hat{L} - \hat{S})^2 - D(\hat{J} - \hat{L} - \hat{S})^4 \quad (1.60)$$

where B is the rotational constant, and D is the centrifugal distortion constant representing the influence of centrifugal force due to rotation on bond length. Expansion of the B term of equation (1.60) gives

$$\hat{H} = B(\hat{J}^2 + \hat{L}^2 + \hat{S}^2 - 2\hat{J}\cdot\hat{L} - 2\hat{J}\cdot\hat{S} + 2\hat{L}\cdot\hat{S}) \quad (1.61)$$

Because the x and y components of \hat{L} are not defined in a non-spherical system, their effects are omitted in subsequent calculations¹. Equation (1.61) therefore simplifies to:

$$\hat{H} = B[\hat{J}^2 + \hat{L}^2 + \hat{S}^2 - 2\hat{J}_z\hat{L}_z - 2\hat{J}_z\hat{S}_z - (\hat{J}_+\hat{S}_- + \hat{J}_-\hat{S}_+) + 2\hat{L}_z\hat{S}_z] \quad (1.62)$$

The off-diagonal term, $-(\hat{J}_+\hat{S}_- + \hat{J}_-\hat{S}_+)$, is the spin-uncoupling operator discussed in Section 1.C.

The diagonal and off-diagonal rotational matrix elements are calculated by applying equations (1.1) through (1.10) and equation (1.15) to equation (1.61):

$$\langle J\Omega L\Lambda S\Sigma | \hat{H} | J\Omega L\Lambda S\Sigma \rangle = B[J(J+1) - \Omega^2 + S(S+1) - \Sigma(\Sigma+1)]^{1/2} \quad (1.63)$$

and

$$\begin{aligned} \langle JS, \Omega \pm 1, \Sigma \pm 1 | \hat{H} | JS\Omega\Sigma \rangle = & -B\{[(J(J+1) - \Omega(\Omega \pm 1))] \\ & \times [S(S+1) - \Sigma(\Sigma \pm 1)]\}^{1/2} \end{aligned} \quad (1.64)$$

The D terms are obtained by squaring the matrix of the coefficients of the B terms.

I.D.2. Spin Hamiltonian.

Spin-orbit coupling can be expressed as the scalar product of the many-electron electronic spin and orbital angular momentum operators, $\hat{\mathbf{S}}$ and $\hat{\mathbf{L}}$, which (using equations 1.8 and 1.15) is represented in Cartesian form as:

$$\begin{aligned}\hat{H}_{L \cdot S} &= A[(\hat{L}_x + i\hat{L}_y)(\hat{S}_x - i\hat{S}_y)/2 + \hat{L}_z\hat{S}_z + (\hat{L}_x - i\hat{L}_y)(\hat{S}_x + i\hat{S}_y)/2] \\ &= A\hat{L}_z\hat{S}_z + A(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+)/2\end{aligned}\quad (1.65)$$

where A is the spin-orbit coupling constant. Neglecting the terms off-diagonal in L , equation (1.65) can be shortened to:³¹

$$\hat{H}_{L \cdot S} = A\hat{L}_z\hat{S}_z \quad (1.66)$$

which has the selection rule $\Delta S = 0$, and produces diagonal matrix elements of $A\Lambda\Sigma$.

The dipolar spin-spin interaction can be represented by the classical Hamiltonian for two bar magnets, or dipoles, μ :³⁷

$$\hat{H} = (\mu_1 \cdot \mu_2)/(r_{12})^3 - 3(\mu_1 \cdot \mathbf{r}_{12})(\mu_2 \cdot \mathbf{r}_{12})/(r_{12})^5 \quad (1.67)$$

in which \mathbf{r}_{12} is the vector between dipoles μ_1 and μ_2 , or $\mathbf{r}_1 - \mathbf{r}_2$. The magnetic dipole of spin \mathbf{S} is

$$\mu = -g\mu_B\mathbf{S} \quad (1.68)$$

where g is the dimensionless electronic g factor and μ_B is the Bohr magneton (the unit on an electronic magnetic moment, equal to $e\hbar/2m$ where e and m are the charge and mass of the electron, respectively).³⁸ The dipolar interaction in terms of two electron spin vectors separated by vector \mathbf{r} is therefore:

$$\hat{H}_{S-S} = (g^2\beta^2/r^3)\{\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 - 3(\hat{\mathbf{S}}_1 \cdot \mathbf{r})(\hat{\mathbf{S}}_2 \cdot \mathbf{r})/r^2\} \quad (1.69)$$

Considering only the $q = 0$ terms (i.e., neglecting the components $q = \pm 1$ and ± 2), the interaction reduces to:³⁷

$$\hat{H}_{S-S} = (g^2\beta^2/r^3)\{\hat{S}_z^{(1)}\hat{S}_z^{(2)}(3\cos^2\theta_{12} - 1)\}$$

$$- (\hat{S}_-(1)\hat{S}_+(2) + \hat{S}_+(1)\hat{S}_-(2))(3\cos^2\theta_{12} - 1)/4 \quad (1.70)$$

Averaging over all orientations of \mathbf{r}_1 and \mathbf{r}_2 and expressed in terms of a total spin \mathbf{S} , equation (1.70) becomes:

$$\begin{aligned} \hat{H}_{S-S} &= (g^2\mu_B^2/r^3)[3\hat{S}_z^2 - \hat{S}^2 - (\hat{S}_+\hat{S}_- + \hat{S}_-\hat{S}_+)/2] \\ &= (g^2\mu_B^2/r^3)[2\hat{S}_z - (\hat{S}_x + i\hat{S}_y)(\hat{S}_x - i\hat{S}_y)] \\ &= (g^2\mu_B^2/r^3)(3\hat{S}_z - \hat{S}^2) \end{aligned} \quad (1.71)$$

or in terms of the spin-spin coupling constant λ (or zero-field splitting parameter $2\lambda^{38}$),

$$\hat{H}_{S-S} = 2\lambda(3\hat{S}_z - \hat{S}^2)/3 \quad (1.72)$$

The spin-spin interaction originates from two mechanisms: the primary contribution to λ is from the dipolar interaction of two unpaired spins, but there is also an effect due to second order spin-orbit coupling, which may in fact be considerably larger:³⁹

$$\lambda = \lambda^{SS} + \lambda^{SO} \quad (1.73)$$

Second order perturbation theory applied to the spin-orbit interaction produces a spin-spin interaction as follows. The second order contribution of the spin-orbit interaction in single particle terms is:

$$\begin{aligned} E_{SO}^{(2)} &= \sum_{\eta'\Lambda'S'} [E_{\eta\Lambda S} - E_{\eta'\Lambda'S'}]^{-1} \sum_i \langle \eta\Lambda | a_{i1} | \eta'\Lambda' \rangle \sum_j \langle \eta'\Lambda' | a_{j1} | \eta\Lambda \rangle \\ &\quad \times \sum_{\Sigma'} \langle S\Sigma | \hat{s}_i | S'\Sigma' \rangle \langle S'\Sigma' | \hat{s}_j | S\Sigma \rangle \end{aligned} \quad (1.74)$$

The term summing over Σ' produces the dipolar spin-spin term $\langle S\Sigma | \hat{s}_i \hat{s}_j | S\Sigma \rangle$, as well as other matrix elements not of interest here because they are off-diagonal in Λ .

The dipolar spin-spin interaction matrix elements are obtained by applying equations (1.2) through (1.5) to equation (1.72):

$$\langle J\Omega L A S \Sigma | \hat{H}_{S-S} | J\Omega L A S \Sigma \rangle = 2\lambda[\Sigma^2 - S(S+1)/3] \quad (1.75)$$

The states they mix have $\Delta\Sigma (= \Delta\Lambda)$ and $\Delta S = 0, \pm 1, \pm 2$.⁴⁰

Centrifugal distortion corrections to the spin-orbit and spin-spin interactions-- A_D and λ_D , respectively--must also be considered. Terms containing the parameters A_D and λ_D are therefore added to the rotational Hamiltonian (equation 1.60) as follows:⁴¹

$$\hat{H}_{\text{rot}} = B\hat{R}^2 - D\hat{R}^4 + A_D\hat{R}^2\hat{L}_z\hat{S}_z + 2\lambda_D\hat{R}^2(3\hat{S}_z - \hat{S}^2)/3 \quad (1.76)$$

Since the products of the operators in the A_D and λ_D terms are not Hermitian, a Hermitian average must be taken by symmetrizing the products with the anticommutator. The diagonal matrix elements for the A_D and λ_D parameters therefore follow the rotational constant B , but are multiplied by the elements for the spin-orbit and spin-spin interactions, respectively. The off-diagonal elements do likewise, except that since there are no off-diagonal terms in A or λ , the factor for these interactions becomes the average of the two diagonal elements. As before, the operator \hat{R}^2 is simplified by omission of the x and y components of $-2\hat{J}\cdot\hat{L} + 2\hat{L}\cdot\hat{S} + \hat{L}^2$.

The spin-rotation operator, the dot product of the spin and rotational angular momenta, is written in Cartesian form as:³¹

$$\hat{H}_{S-R} = \gamma(\hat{J} - \hat{L} - \hat{S})\cdot\hat{S} \quad (1.77)$$

Neglecting L_{\pm} terms, equation (1.77) produces the expanded Hamiltonian:

$$\hat{H}_{S-R} = \gamma[\hat{J}_z\hat{S}_z - \hat{L}_z\hat{S}_z - \hat{S}_z^2 + (\hat{J}_+\hat{S}_- + \hat{J}_-\hat{S}_+)/2] \quad (1.78)$$

with diagonal elements:

$$\langle J\Omega L A S \Sigma | \hat{H}_{S-S} | J\Omega L A S \Sigma \rangle = \gamma[\Sigma^2 - S(S+1)] \quad (1.79)$$

and off-diagonal elements equal to those given in equation (1.64), but replacing B with $-\gamma/2$.

I.D.3. Magnetic hyperfine interactions.

The magnetic hyperfine interactions include all interactions of the nuclear spin, I , with the other angular momenta in the basis set, which for the case(a) basis are J , L and S . Nuclear magnetic moments interact weakly with the rotational magnetic moment giving rise to a scalar interaction term written:²⁵

$$\hat{H}_{I,J} = c_I \hat{I} \cdot \hat{J} \quad (1.80)$$

where c_I denotes the interaction constant. From equation (1.54),

$$\mathbf{F}^2 = \mathbf{J}^2 + 2\mathbf{I} \cdot \mathbf{J} + \mathbf{I}^2 \quad (1.81)$$

so that the $I \cdot J$ interaction can be expressed in terms of \mathbf{F} as:

$$\hat{H}_{I,J} = c_I (\hat{\mathbf{F}}^2 - \hat{\mathbf{J}}^2 - \hat{\mathbf{I}}^2)/2 \quad (1.82)$$

The matrix elements can be obtained directly from equation (1.4) as:

$$\langle \Lambda S \Sigma J \Omega I F | \hat{H}_{I,J} | \Lambda S \Sigma J \Omega I F \rangle = c_I [F(F+1) - J(J+1) - I(I+1)]/2 \quad (1.83)$$

The interactions of electronic and nuclear spins are represented by the Hamiltonian:²⁶

$$\hat{H}_{I,S} = b \hat{I} \cdot \hat{S} + c \hat{I}_z \hat{S}_z \quad (1.84)$$

with

$$b = a_F - c/3 \quad (1.85)$$

where a_F and c are the isotropic (Fermi-contact) and dipolar hyperfine constants, respectively. The former interaction is directly proportional to the quantity of electron density at the spinning nucleus, while the dipolar, or bar magnet, interaction between I_z and S_z is the same as given in equation (1.67). The interaction of nuclear spin with the electronic orbital magnetic moment is a scalar product of I and L which is treated in the same manner as the $L \cdot S$ interaction described by equations (1.65) and (1.66). The resulting Hamiltonian is therefore:^{26,31}

$$\hat{H}_{I.L} = a \hat{I}_z \hat{L}_z \quad (1.86)$$

in which a is the interaction constant.

The b term of equation (1.84) is expressed in spherical tensor form as:

$$\hat{H}_{I.S} = b T^1(I) \cdot T^1(S) \quad (1.87)$$

To derive the matrix elements of the interaction, I is first uncoupled from J by application of equation (1.48):

$$\begin{aligned} \langle \eta' \Lambda S \Sigma J \Omega | F | T^1(I) \cdot T^1(S) | \eta' \Lambda S' \Sigma' J' \Omega' | F \rangle = \\ (-1)^{I+J'+F} \left\{ \begin{matrix} F & J & I \\ 1 & I & J' \end{matrix} \right\} [I(I+1)(2I+1)]^{1/2} \langle \eta' \Lambda S \Sigma J \Omega || T^1(S) || \eta' \Lambda S' \Sigma' J' \Omega' \rangle \end{aligned} \quad (1.88)$$

where the $[I(I+1)(2I+1)]^{1/2}$ term is the reduced matrix element of $T^1(I)$ according to equation (1.46). By projecting the reduced matrix element in equation (1.87) from the space-fixed axis system to the molecule-fixed system, using Wigner rotation matrices as in equation (1.47), the general matrix element can be expressed as:³¹

$$\begin{aligned} \langle \eta' \Lambda S \Sigma J \Omega | F | \hat{H}_{I.S} | \eta' \Lambda S' \Sigma' J' \Omega' | F \rangle = \\ (-1)^{I+J'+F} \left\{ \begin{matrix} F & J & I \\ 1 & I & J' \end{matrix} \right\} [I(I+1)(2I+1)(2J+1)(2J'+1)]^{1/2} \sum_q (-1)^{J-\Omega} \begin{pmatrix} J & 1 & J' \\ -\Omega & q & \Omega' \end{pmatrix} \\ \times (-1)^{S-\Sigma} \begin{pmatrix} S & 1 & S' \\ -\Sigma & q & \Sigma' \end{pmatrix} \sum_i \langle S || T^1(S) || S' \rangle \langle \eta' \Lambda S | b_i | \eta' \Lambda S' \rangle \end{aligned} \quad (1.89)$$

The $c \hat{I}_z \hat{S}_z$ and $a \hat{I}_z \hat{L}_z$ Hamiltonians are treated by the same method.

Evaluation of the 3-j and 6-j symbols with the appropriate formulae^{5,42}, yields the matrix elements for $b \hat{I} \cdot \hat{S}$, $c \hat{I}_z \hat{S}_z$ and $a \hat{I}_z \hat{L}_z$, except that the only matrix elements written for the a and c constants are those diagonal in Λ and Σ , respectively. The resulting matrix elements employed in the hyperfine analysis of NbN are as follows:

$$\langle JIF\Omega\Sigma M | \hat{H}_{hf} | JIF\Omega\Sigma M \rangle = \Omega h R(J)/[2J(J+1)] \quad (1.90)$$

$$\begin{aligned} \langle JIF\Omega\Sigma M | \hat{H}_{hf} | J-1, IF\Omega\Sigma M \rangle = \\ -h(J^2 - \Omega^2)^{1/2} P(J) Q(J) / [2J(4J^2 - 1)^{1/2}] \end{aligned} \quad (1.91)$$

$$\begin{aligned} \langle JIF\Omega\Sigma M | \hat{H}_{hf} | JIF\Omega\pm 1, \Sigma\pm 1, M \rangle = \\ b[(J+\Omega)(J\pm\Omega+1)]^{1/2} R(J) V(S) / [4J(J+1)] \end{aligned} \quad (1.92)$$

$$\begin{aligned} \langle JIF\Omega\Sigma M | \hat{H}_{hf} | J-1, IF\Omega\pm 1, \Sigma\pm 1, M \rangle = \\ \mp b[(J\mp\Omega)(J\mp\Omega+1)]^{1/2} P(J) Q(J) V(S) / [4J(4J^2 - 1)^{1/2}] \end{aligned} \quad (1.93)$$

where the following abbreviations have been used:

$$R(J) = F(F+1) - J(J+1) - I(I+1) \quad (1.94)$$

$$P(J) = [(F - I + J)(F + J + I + 1)]^{1/2} \quad (1.95)$$

$$Q(J) = [(J + I - F)(F - J + I + 1)]^{1/2} \quad (1.96)$$

$$V(S) = [S(S+1) - \Sigma(\Sigma\pm 1)]^{1/2} \quad (1.97)$$

The constant b is that given in equation (1.84), while h is used in the diagonal elements in order to incorporate the a , b and c constants into one:

$$h = a\Lambda + (b + c)\Sigma \quad (1.98)$$

I.D.3.a. The sign of nuclear hyperfine coupling constants in transition metal complexes.

I.D.3.a.i. The sign of the Fermi contact interaction.

For an isotropic (Fermi contact) interaction involving only pure s electrons, the isotropic hyperfine constant a_F is positive because the magnetic field generated at the nucleus by the interaction is in the same direction as the electronic spin. However, negative contributions to the isotropic hyperfine interaction occur when there are open shell d or p electrons which polarize s electrons in inner (filled) orbitals via an exchange interaction which promotes an

electron from an inner s orbital to an outer empty one.⁴³ For example, a ground electronic configuration with a single unpaired 3d electron,

$$\Psi_0 = (3s^+)(3s^-)(3d^+)$$

can mix with excited states resulting from the promotion of an electron from a 3s to 4s orbital to produce the three functions:⁴³

$$\Psi_1 = (4s^+)(3s^-)(3d^+)$$

$$\Psi_2 = (3s^+)(4s^-)(3d^+)$$

$$\Psi_3 = (3s^+)(4s^+)(3d^+)$$

This is known as a configuration interaction, in which the ground and excited states possess different spin distributions yet form the basis for the same irreducible representation, in keeping with the requirement that the energy of the system remains constant.⁴⁴ First order perturbation theory is applied to describe the mixing, yielding an expression for the hyperfine contribution due to configuration interaction that is a function of the product of the ns and ms orbitals evaluated at the nucleus $[ns(0)ms(0)]$, times an exchange integral $J(ms,3d,3d,ns)$, divided by the energy separation between the ms and ns orbitals:

$$\chi = 8\pi \sum_{n=1}^3 \sum_{m=4}^{\infty} [ns(0)ms(0) \times J(ms,3d,3d,ns)] / (E_m - E_n) \quad (1.99)$$

The quantity χ is independent of charge⁴³ and is related to the isotropic Fermi contact coupling constant, a_F , by:⁴⁴

$$a_F = (2/3)g_e\mu_B g_n\mu_n\chi \quad (1.100)$$

where g_e and g_n are the electronic and nuclear g factors and μ_B and μ_n are the Bohr and nuclear magnetons. The quantity $[ns(0)4s(0)]/(E_4 -$

E_n) for the $n = 1, 2, 3$ s orbitals of the neutral atoms of the first row transition metals from V to Cu was found to increase by about 20% across the series. The exchange integrals varied in the opposite sense, though more gradually, decreasing by an overall 14% from V to Cu.⁴³

An alternative approach to the configuration interaction (CI) is core (or spin) polarization, a treatment which may be easier to conceptualize but is not as theoretically sound.⁴⁴ This theory differs from CI in that the orbitals involved belong to a single configuration which originates from spin-dependent one-electron orbitals. The resulting hyperfine interaction is therefore a function of the amount of spin density of each sign. CI requires two spin-independent configurations to represent the wavefunction. The wavefunction for the core polarization model is a spin-polarized unrestricted Hartree-Fock function (UHF) where UHF differs from the conventional, or restricted, Hartree-Fock function in that the trial one-electron wavefunctions are not required to be independent of the orientation of the spin.⁴⁴ The radial functions whose spins are being polarized, corresponding to spin up and spin down, differ from one another because they couple differently with the unpaired d or p electrons. The resulting hyperfine interaction is negative because the polarized spin has the opposite sense to the unpaired electron which induces the polarization.⁴⁴

I.D.3.a.ii. The sign of the dipolar nuclear hyperfine interaction.

The sign and magnitude of the dipolar hyperfine interaction depends on the number and type of open shell d and p electrons. The interaction constant for such an electron in orbital η is⁴⁵

$$c_i = 3g_e\mu_B g_n \mu_n \langle \eta | r^{-3} (3\cos^2\theta - 1)/2 | \eta \rangle \quad (1.101)$$

where θ is the angle between the nucleus and the i th unpaired electron at a distance r ; closed shell electrons do not contribute to $\langle 3\cos^2\theta - 1 \rangle$. Using for sake of illustration the ground electronic $4\Sigma^-$ state of VO, with the configuration $(\sigma^2\pi^4\sigma_n^1\delta^2)$, there are three non-bonding $\sigma_n^1\delta^2$ open shell electrons contributing to the I-S interaction. If the assumption is made that the interacting electrons are metal centered, the hyperfine constants are:⁴⁶

$$(A_{iso})_{VO} \approx (1/3)(A_{iso})_{4s\sigma} \quad (1.102)$$

$$(A_{dip})_{VO} \approx (2/3)(A_{dip})_{3d\delta} \quad (1.103)$$

where these A parameters are related to a_F , b and c by:

$$A_{iso} = A_{\perp} + A_{dip} = a_F \quad (1.104)$$

$$A_{\perp} = b = a_F - c/3 \quad (1.105)$$

$$A_{dip} = c/3 \quad (1.106)$$

$$A_{||} = b + c \quad (1.107)$$

Combining equations (1.101), (1.103) and (1.106), the expression for c becomes:

$$c = 3g_e\mu_B g_n \mu_n (2/3) \langle 3d\delta | r^{-3} \cdot (3\cos^2\theta - 1)/2 | 3d\delta \rangle \quad (1.108)$$

Using the algebreic expression for the spherical harmonic Y_{20} (see Section I.B)⁴⁷, the matrix element portion of equation (1.108) can be written in terms of the n, l and m quantum numbers as:

$$\langle nlm | r^{-3} \cdot (3\cos^2\theta - 1)/2 | nlm \rangle = (1/2) \langle lm | 3\cos^2\theta - 1 | lm \rangle \langle n | r^{-3} | n \rangle$$

$$= \frac{3m^2 - l(l+1)}{(2l-1)(2l+3)} \langle r^{-3} \rangle_{nl} \quad (1.109)$$

For a δ orbital, equation (1.109) reduces to $(2/7)\langle r^{-3} \rangle_{nl}$, producing a value for c (in cm^{-1}) of⁴⁶

$$c = -(4/7)g_e\mu_B g_n\mu_n \langle r^{-3} \rangle_{3d} / hc \quad (1.110)$$

When an electron is promoted from the $4s\sigma$ to $4p\sigma$ orbital to produce the $C^4\Sigma^-$ excited state, all three electrons contribute to the dipolar term and c becomes (in cm^{-1}):

$$\begin{aligned} c &= 3g_e\mu_B g_n\mu_n [(2/3)\langle r^{-3} \cdot (3\cos^2\theta - 1)/2 \rangle_{3d\delta} \\ &\quad + (1/3)\langle r^{-3}(3\cos^2\theta - 1)/2 \rangle_{4p\sigma}] / hc \\ c &= g_e\mu_B g_n\mu_n [-(4/7)\langle r^{-3} \rangle_{3d\delta} + (2/5)\langle r^{-3} \rangle_{4p\sigma}] / hc \end{aligned} \quad (1.111)$$

Using this method the different values for c corresponding to the various possible electron configurations of an electronic state can be estimated, which assists in the assignment of an electronic state.

I.D.4. The nuclear electric quadrupole interaction.

The nuclear electric quadrupole interaction involves two second rank tensors, representing the electric field gradient and the nuclear quadrupole moment. A simple method by which to derive the quadrupolar Hamiltonian is with the use of spherical harmonics and Legendre polynomials.

To obtain the Hamiltonian for the electrostatic interaction of the nuclear quadrupole moment with the electric field gradient at the nucleus, a multipole expansion is made for the scalar coupling of the charges of the nucleons with those of the electrons. A multipole

expansion is a spherical harmonic expansion (or Legendre polynomial expansion) where the values of l in the spherical harmonic Y_{lm} are referred to as monopole, dipole, quadrupole and octopole for $l = 0, 1, 2$ and 3 .⁴⁸ By Coulomb's law⁴⁹, the electrostatic Hamiltonian is

$$\hat{H} = \sum_n eq_n/R_n \quad (1.112)$$

which describes the interaction between n nucleons with charge q_n and an electron with charge e , with an electron-nucleon separation of R_n . The electrostatic potential at the electron is

$$V = \sum q_n/R_n \quad (1.113)$$

The distance R_n is the resultant of the two vectors originating from the nuclear center to the n th nucleon (r_n) and to the electron (R), with the angle between vectors r_n and R denoted by θ_n . The law of cosines⁵⁰ gives the relation between R_n , r_n , R and θ_n :

$$\begin{aligned} R_n &= (R^2 + r_n^2 - 2Rr_n\cos\theta_n)^{1/2} \\ &= R[1 + (r_n/R)^2 - 2(r_n/R)\cos\theta_n]^{1/2} \end{aligned} \quad (1.114)$$

By the generating function for Legendre polynomials⁵¹,

$$[1 - 2(r_n/R)\cos\theta_n + (r_n/R)^2]^{1/2} = \sum P_l(\cos\theta_n)(r_n/R)^l \quad (1.115)$$

equation (1.113) can be written in terms of a Legendre polynomial as:⁵²

$$V = \sum_{l=0} \sum_n P_l(\cos\theta_n) q_n r_n^l / R^{l+1} \quad (1.116)$$

Each Legendre polynomial represents the scalar product of electronic and nuclear tensor operators (from the spherical harmonic addition theorem), producing from equations (1.112) and (1.116) the multipole expansion:^{48,52}

$$\begin{aligned}\hat{H}_{\text{multipole}} &= eV \\ &= \sum_{l=0} \sum_m (-1)^m \left[\sum_e (e/R^{l+1}) C_{lm}(\theta_e, \phi_e) \times \sum_n q_n r_n^l C_{l,-m}(\theta_n, \phi_n) \right] \quad (1.117)\end{aligned}$$

where the summations over e electrons and n nucleons represent terms in electronic (θ_e, ϕ_e) and nuclear (θ_n, ϕ_n) angular coordinates, respectively.

The first term in this expansion which is non-vanishing describes the quadrupolar interaction. The $l = 0$ term can be represented by $Z_e V_0$, or the Coulombic interaction between the nuclear charge and the electrons, and is included in the electronic Hamiltonian.⁵³ The dipole term, $l = 1$, is the product of the electric dipole moment of the nucleus, which is zero, and the electrostatic field of the electrons, which is invariant over the nuclear volume and therefore produces no interaction.⁵³ The $l = 2$ quadrupole term, however, is the interaction of the nuclear electric quadrupole moment, \hat{Q} , with the electric field gradient ($\hat{\nabla}E$) experienced by the nucleus due to the charge distribution of the electrons. For those nuclei possessing a quadrupole moment, then, the quadrupolar Hamiltonian is the scalar product of these two tensor quantities:⁵⁴

$$\hat{H}_Q = -T^2(\hat{\nabla}E) \cdot T^2(\hat{Q}) \quad (1.118)$$

where the minus sign is present due to the negative charge of the electron.

The quadrupole moment is a measure of how spherical the nucleus is, as indicated by the value of the nuclear spin, I . The deviation of nuclear charge distribution from spherical symmetry is given by: $3z^2_{\text{ave}} - (x^2 + y^2 + z^2)_{\text{ave}}$ or $3\cos^2\theta_n - 1$ (where θ_n is the nuclear angular coordinate).⁵⁵ This value is non-zero if I is greater than

1/2, which is dictated by the number of odd nucleons (i.e., differences in the number of neutrons with respect to protons). The mechanism giving rise to specific values of I is imperfectly understood, though it seems to approximate the same shell model that applies to electrons. Thus, zero spin results from spin-pairing if the number of protons (Z) equals the number of neutrons (N), and predictions for I can usually be made for nuclei possessing odd N or Z based on the number of particles occupying open shells.⁵⁵

By convention, the nuclear electric quadrupole moment is defined classically as¹¹

$$\hat{Q} = e \int (3z^2 - r^2) \rho(r) d\tau \quad (1.119)$$

where $\rho(r)$ is the nuclear charge density, and $d\tau$ denotes integration over the nuclear volume. Quantum mechanically the definition becomes:⁵²

$$\hat{Q} = e^{-1} \sum_n q_n r_n^2 (3 \cos^2 \theta_n - 1) \quad (1.120)$$

The quantum mechanical observable corresponding to equation (1.120) is the nuclear quadrupole moment, Q , defined by convention as⁵⁴

$$Q = \langle I, m_I = I | \hat{Q} | I, m_I = I \rangle \quad (1.121)$$

The definition of \hat{Q} was made prior to the invention of spherical tensors and therefore lacks the factor of 1/2 needed for the expressions $P_2(\cos \theta) = T^2_0(X) = (3 \cos^2 \theta - 1)/2$; \hat{Q} was also defined without the electron charge e . The spherical tensor definition is therefore

$$T^2_0(\hat{Q}) = e\hat{Q}/2 \quad (1.122)$$

with the corresponding scalar quantity

$$eQ/2 = \langle I, m_I = 1 | T^2_0(\hat{Q}) | I, m_I = 1 \rangle \quad (1.123)$$

The quadrupole tensor, from equation (1.117), is of the form

$$T^2(\hat{Q}) = \sum_n q_n r_n^2 C^2(\theta_n, \phi_n) \quad (1.124)$$

The electric field gradient (EFG) evaluated at the nucleus, $(\partial^2 V / \partial z^2)_o$, has the spherical tensor form (from equation 1.117) of:

$$-T^2(\hat{\nabla} E) = \sum_e e R^{-3} C^2(\theta_e, \phi_e) \quad (1.125)$$

with the corresponding field gradient coupling constant defined as

$$q = \langle J, m_J = J | (\partial^2 V / \partial z^2)_o | J, m_J = J \rangle \quad (1.126)$$

where $(\partial^2 V / \partial z^2)_o = e R^{-3} (3 \cos \theta_e - 1)$. Thus, with the factor of 1/2 required by the spherical harmonic definition of the quadrupole moment, the EFG tensor can be expressed as:

$$-T^2_o(\hat{\nabla} E) = q/2 \quad (1.127)$$

To derive the matrix elements for the quadrupolar interaction (equation 1.116), equation (1.48) is applied to evaluate the scalar coupling of two commuting tensor operators in a coupled basis (I must be unravelled from J):

$$\begin{aligned} & \langle \eta' \Lambda'; S' \Sigma'; J' \Omega' | F | \hat{H}_Q | \eta \Lambda; S \Sigma; J \Omega | F \rangle \\ &= (-1)^{J+I+F} \delta_{FF} \begin{Bmatrix} F & 1 & J' \\ 2 & J & I \end{Bmatrix} \langle \eta' \Lambda'; J' \Omega' || -T^2(\hat{\nabla} E) || \eta \Lambda; J \Omega \rangle \langle I || T^2(\hat{Q}) || I \rangle \end{aligned} \quad (1.128)$$

Then project $T^2(\hat{\nabla} E)$ from space- to molecule-fixed axes with equation (1.29):

$$\begin{aligned} \langle \eta' \Lambda'; J' \Omega' || -T^2(\hat{\nabla} E) || \eta \Lambda; J \Omega \rangle &= \sum_q \langle J' \Omega' || D^2_q(\alpha \beta \gamma) || J \Omega \rangle \langle \eta' \Lambda' || -T^2_q(\hat{\nabla} E) || \eta \Lambda \rangle \\ &= \sum_q (-1)^{J'-\Omega'} [(2J+1)(2J'+1)]^{1/2} \begin{pmatrix} J' & 2 & J \\ -\Omega' & q & \Omega \end{pmatrix} \langle \eta' \Lambda' || -T^2_q(\hat{\nabla} E) || \eta \Lambda \rangle \end{aligned} \quad (1.129)$$

The last term of equation (1.128) is evaluated with the Wigner-Eckart theorem, in conjunction with equation (1.123):

$$\langle l, m_l = l | T^2_o(\hat{Q}) | l, m_l = l \rangle = eQ/2 = (-1)^{l-1} \begin{pmatrix} 1 & 2 & 1 \\ -1 & 0 & 1 \end{pmatrix} \langle l || T^2(\hat{Q}) || l \rangle \quad (1.130)$$

Substituting for the 3-j symbol⁵⁷ and solving for the reduced matrix element gives

$$\begin{aligned} \langle l || T^2(\hat{Q}) || l \rangle &= eQ/2 \begin{pmatrix} 1 & 2 & 1 \\ -1 & 0 & 1 \end{pmatrix}^{-1} \\ &= eQ/2 [(2l+1)(2l+2)(2l+3)/2l(2l-1)]^{1/2} \quad (1.131) \end{aligned}$$

In terms of the molecule-fixed $T^2(\hat{V}E)$ tensor in equation (1.129), the coupling constant q is defined by the diagonal reduced element of $T^2(\hat{V}E)$:

$$\langle \Lambda || -T^2_o(\hat{V}E) || \Lambda \rangle = q/2 \quad (1.132)$$

A first order approximation was made in the current study to neglect the ± 1 and ± 2 components of $T^2(VE)$, that is, to exclude quadrupole matrix elements off-diagonal in Ω . Appropriate combination of equations (1.128), (1.129), (1.131) and (1.132) therefore yields the matrix elements

$$\begin{aligned} &\langle \eta' \Lambda'; S' \Sigma'; J' \Omega' | F | -T^2(\hat{V}E) \cdot T^2(\hat{Q}) | \eta \Lambda; S \Sigma; J \Omega | F \rangle \\ &= (1/4)eqQ(-1)^{J+l+F} \begin{pmatrix} F & 1 & J' \\ 2 & J & 1 \end{pmatrix} [(2l+1)(2l+2)(2l+3)/2l(2l-1)]^{1/2} \\ &\times \sum_q (-1)^{J'-\Omega'} [(2J+1)(2J'+1)]^{1/2} \begin{pmatrix} J' & 2 & J \\ -\Omega' & q & \Omega \end{pmatrix} \quad (1.133) \end{aligned}$$

From the triangle condition for a 3-j symbol, which states that the third J value must not lie outside the sum and difference of the first two J values¹⁸, the 3-j symbol in equation (1.133) requires ΔJ to be 0, ± 1 or ± 2 . From equation (1.133) and these selection rules, the specific matrix elements employed in this work are as follows:

$$\langle JIF\Omega\Sigma M | \hat{H}_Q | JIF\Omega\Sigma M \rangle = \frac{eQq[3\Omega^2 - J(J+1)]\{3R(J)[R(J)+1] - 4J(J+1)I(I+1)\}}{8I(2I-1)J(J+1)(2J-1)(2J+3)} \quad (1.134)$$

$$\langle JIF\Omega\Sigma M | \hat{H}_Q | J-1, IF\Omega\Sigma M \rangle = \frac{-eQq3\Omega[R(J)+J+1](J^2-\Omega^2)^{1/2}P(J)Q(J)}{2J(2J-2)(2J+2)(2I-1)(4J^2-1)^{1/2}} \quad (1.135)$$

$$\begin{aligned} \langle JIF\Omega\Sigma M | \hat{H}_Q | J-2, IF\Omega\Sigma M \rangle \\ = \frac{eQq3[(J-1)^2-\Omega^2]^{1/2}(J^2-\Omega^2)^{1/2}P(J)Q(J)P(J-1)Q(J-1)}{4I(2I-1)4J(J-1)(2J-1)[(2J-3)(2J+1)]^{1/2}} \end{aligned} \quad (1.136)$$

The terms $R(J)$, $P(J)$, $Q(J)$, $P(J-1)$ and $Q(J-1)$ are as in equations (1.93), (1.94) and (1.95).

I.D.5. Λ -Doubling.

The phenomenon of Λ -doubling results from the breakdown of the Born-Oppenheimer approximation, which allows the separation of electronic and nuclear motion.²⁶ It is the lifting of $\pm\Lambda$ degeneracy which occurs when molecular rotation interferes with the well-defined quantization of the z component of electronic orbital angular momentum about the molecular axis. The operators in the spin and rotational Hamiltonian responsible for Λ -doubling are the x and y components of the electronic orbital angular momentum operators which produce matrix elements off-diagonal in Λ . In the rotational Hamiltonian, this is the L -uncoupling operator, $-2B\hat{J}\cdot\hat{L}$. Among the spin-interaction terms of the Hamiltonian, the spin-orbit operator is used, yielding the complete Λ -doubling Hamiltonian:⁵⁷

$$V = -2B\hat{J}\cdot\hat{L} + \sum_i a_i \hat{l}_i \cdot \hat{s}_i \quad (1.137)$$

The Λ -doubling interaction is treated by degenerate perturbation theory⁵⁸, which for Δ states must be taken to fourth order in order

to connect $|\Lambda = 2\rangle$ to $|\Lambda = -2\rangle$ via states with $\Lambda = 1$ and 0 (i.e., Π and Σ states). For this reason the interaction is smaller than that in Π states, since the mixing of $|\Lambda = 1\rangle$ and $|\Lambda = -1\rangle$ states requires only second order perturbation theory.⁵⁷ The unperturbed Hamiltonian contains those terms adhering to the Born-Oppenheimer approximation which are diagonal in Λ and independent of the orbital degeneracy. The perturbation can be treated through the use of a fourth-order effective Hamiltonian, which is obtained by subtracting out the unperturbed energy from the complete Hamiltonian expression to leave an effective Hamiltonian which operates only on the vibronic state of interest, $|l_0 k\rangle$ ^{57,59}

$$\begin{aligned}\hat{H}_{\text{eff}}^{(4)} = & P_0 V(Q_0/a) V(Q_0/a) V(Q_0/a) V P_0 - P_0 V(Q_0/a^2) V P_0 V(Q_0/a) V P_0 \\ & - P_0 V(Q_0/a^2) V(Q_0/a) V P_0 V P_0 - P_0 V(Q_0/a) V(Q_0/a^2) V P_0 V P_0 \\ & + P_0 V(Q_0/a^3) V P_0 V P_0 V P_0\end{aligned}\quad (1.138)$$

The operator P_0 , extending over the k -fold degeneracy of l_0 , is defined as

$$P_0 = \sum_k |l_0 k\rangle \langle l_0 k| \quad (1.139)$$

while

$$(Q_0/a^n) = \sum_{l=l_0} \sum_k |lk\rangle \langle lk| / (E_0 - E_n)^n \quad (1.140)$$

where l denotes any vibronic state with energy E_l , E_0 is the energy of state $\langle l_0 k|$, and k labels all rotational, spin and electronic quantum numbers in a vibronic state l_0 or l .

The Hamiltonian in equation (1.137) has $2\Lambda+1$ terms of the form $(\hat{H}_{\text{rot}})^{2\Lambda-n} (\hat{H}_{\text{s.o.}})^n$, where n ranges from zero to 2Λ . In the case (a) form it is written:⁵⁷

$$\begin{aligned}
\hat{H}_{L.D.,\Delta} = & \tilde{m}_{\Delta}(\hat{S}_+^4 + \hat{S}_-^4)/2 - \tilde{n}_{\Delta}(\hat{S}_+^3\hat{J}_+ + \hat{S}_-^3\hat{J}_-)/2 \\
& + \tilde{o}_{\Delta}(\hat{S}_+^2\hat{J}_+^2 + \hat{S}_-^2\hat{J}_-^2)/2 - \tilde{p}_{\Delta}(\hat{S}_+\hat{J}_+^3 + \hat{S}_-\hat{J}_-^3)/2 \\
& + \tilde{q}_{\Delta}(\hat{J}_+^4 + \hat{J}_-^4)
\end{aligned} \tag{1.141}$$

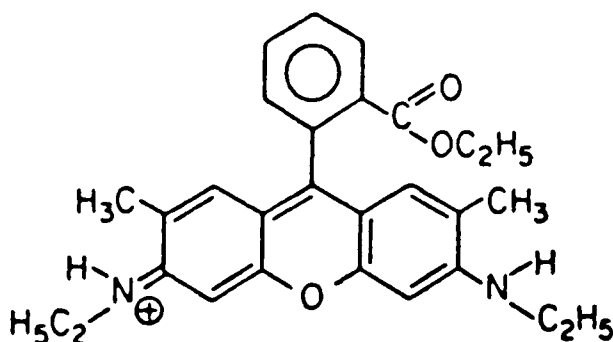
where the factors of 1/2 are included to be consistent with the notation of Mulliken and Christy⁶⁰ for Π states. Thus the \tilde{q}_{Δ} parameter accompanies $(\hat{H}_{rot})^{2\Lambda}$, \tilde{p}_{Δ} is with $(\hat{H}_{rot})^{2\Lambda-1}(\hat{H}_{s.o.})$ and so on to \tilde{m}_{Δ} with $(\hat{H}_{s.o.})^{2\Lambda}$. The number of those parameters that can be determined equals the spin multiplicity up to a maximum of 5. In a $^4\Delta$ state, for example, only four of the five parameters are included in the Λ -doubling matrix elements, with \tilde{m}_{Δ} excluded because the spin-orbit interaction need not be extended to fourth order. In a $^4\Delta$ state where there are four Ω substates, the terms appear in the 4×4 matrix as \pm terms which split a given level into two levels of different parity, labelled e and f . By convention, the e levels have parity $+(-1)^{j-k}$ and f levels have parity $-(-1)^{j-k}$, where k is 1/2 and 0 for half-integer and integer values of spin, respectively.^{61,62} The magnitude of the Λ -doubling observed in this work in the $^4\Delta_{7/2}$ - $^4\Delta_{7/2}$ transition of CoO ranged from 0.2 to 1.2 cm^{-1} , while that in the $^3\Pi_0$ state of NbN is on the order of six wavenumbers.

CHAPTER II

THE COMPUTERIZED LASER-INDUCED FLUORESCENCE EXPERIMENTS

II.A. Experimental Details.

The laser excitation experiments were performed using a Coherent Radiation model CR-599-21 scanning single frequency (standing wave) dye laser, pumped by a Coherent Radiation model Innova-18 argon ion laser operated at a wavelength of 514 nm and a power of 2.0 to 3.5 W. Output power from the dye laser was normally 100 to 150 mW. The tunability of the laser comes from selecting portions of the broad fluorescence band of an organic dye.⁶³ Two dyes were employed for both the cobalt oxide (CoO) and niobium nitride (NbN) studies. For maximum output at 590 nm (ranging from 570 to 620 nm or 17540 to 16130 cm^{-1}), the dye used was rhodamine 6G (Exciton Chemical Co.), with the structure⁶³



made to a concentration of 2×10^{-3} M in ethylene glycol. To reach the lower energy regions, the dye DCM (4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran, from Exciton Chemical Co.) was dissolved in 3:7 benzyl alcohol to ethylene glycol to form nearly saturated 2.5×10^{-3} M solutions. At a pump wavelength of 514 nm, DCM's maximum output power occurs at 640 nm, and

broadband laser operation occurs over the range 600 to 695 nm (16670 to 14390 cm^{-1}). The benzyl alcohol required to dissolve the DCM leads to bubble formation, so the solution was cooled to minimize bubbling by running the dye tubing through a $-30\text{ }^{\circ}\text{C}$ slush of dry ice mixed with a 1:3 solution of water to CaCl_2 . All chemicals were used as obtained.

A small fraction of the output beam was diverted to an iodine absorption or emission cell for absolute frequency calibration. Another fraction was sent to a Tropel fixed-length semiconfocal Fabry-Perot interferometer with a 299 MHz free-spectral range, providing a common ladder of frequency markers against which the sample and iodine spectra could be referenced. The beam containing the majority of the output power was passed down the longitudinal axis of the stream of sample molecules, with the laser-induced fluorescence (LIF) detected at right angles to the beam with a photomultiplier tube equipped with a high transmittance low pass optical filter to reduce scattered light, and powered by 300 to 500 V from a high voltage power supply. Phase-sensitive detection was achieved with a Princeton Applied Research (PAR) model 128A lock-in amplifier receiving chopped sample and reference signals, with the reference beam supplied by a Spectra-Physics model 132 Lablite He-Ne gas laser.

The resolved fluorescence experiments were performed with a 0.7 m Spex Industries model 1702 spectrometer which dispersed the spectrum onto the detector elements of a microchannel-plate intensified array detector (PAR model 1461), mounted at the output

end of the spectrometer. The spectral window of the array detector was calibrated with a Burleigh model WA-20VIS wavemeter.

II.B. Intermodulated Fluorescence.

A laser-induced fluorescence transition has a Gaussian velocity population profile forming an inhomogeneously broadened line, because of the Doppler effect, the frequency absorbed by molecules moving away from the light source appears to be lower than that absorbed by molecules moving toward it. At the center of the profile (zero velocity) the transition frequency Ω is not Doppler-shifted; that is, the molecules have zero velocity with respect to the light wave with which the molecules interact.^{65,66} In Doppler-free (or "sub-Doppler") spectroscopy, two travelling waves (laser beams) with frequency ω propagate in opposite directions through the sample gas molecules. Molecules moving with velocity v along the axis of the laser beams absorb radiation from one beam at a frequency $\Omega = \omega(1 + v/c)$, and from the other beam at $\Omega = \omega(1 - v/c)$. These opposite Doppler shifts cause each beam to depopulate a portion of the lower state velocity profile symmetrically about the profile center at $v = c(\Omega \pm \omega)/\Omega$ (see Fig. 2.1). This depletion is termed "burning a Bennet hole", creating a homogeneous profile in the lower state.⁶⁶ As the laser is scanned, and the laser frequency approaches the non-Doppler-shifted resonance frequency, the two Bennet holes converge until they meet at the center, or zero velocity (see Fig. 2.1). The resulting lower state population depletion causes a corresponding depletion in the intensity profile of the fluorescence, called a "Lamb dip".

Intermodulated fluorescence (IMF) is a technique which enables relatively small Lamb dips to be detected against the large Doppler-broadened profile so that they are directly measured as spectral

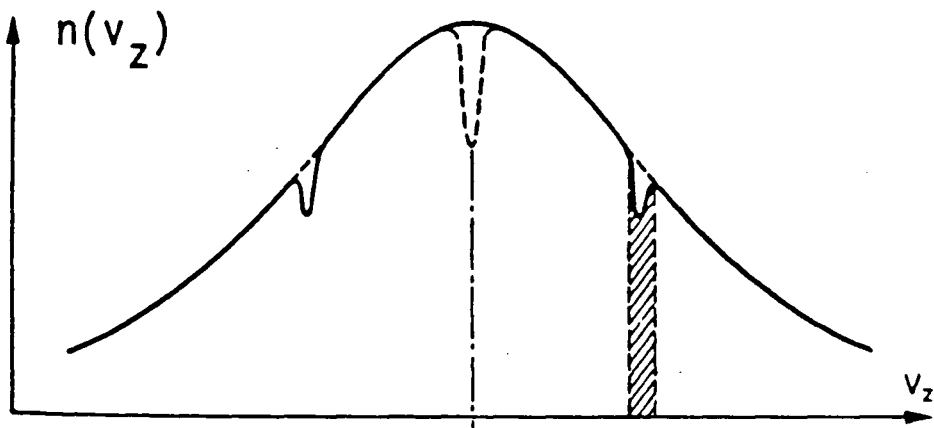


Fig. 2.1. Gaussian inhomogeneously Doppler-broadened velocity (v_z) population (n) profile, showing two Bennett holes (solid lines) which converge at zero velocity (dotted line) to form a Lamb dip in the profile of intensity versus laser tuning frequency.⁶⁶

peaks. The two laser beams are modulated (i.e., chopped to produce certain phase trains) with frequencies f_1 and f_2 . The lock-in amplifier, with the phase sensitive detector referenced to a frequency of $f_1 + f_2$, passes only $(f_1 + f_2)$ -modulated input signals, such as those occurring when two Bennet holes meet⁶⁶. A schematic diagram of the IMF experiment used to obtain the niobium nitride sub-Doppler spectra is illustrated in Fig. 2.2. In practice, the two counterpropagating laser beams must be slightly misaligned from one another to avoid feedback into the laser.

A LIF signal normally arises from Bennet holes caused by allowed $\Delta F = \Delta J$ transitions meeting at the velocity profile center. However, Lamb dips also originate from holes burned by "forbidden" $\Delta F \neq \Delta J$ transitions meeting at the center. Since the selection rules²⁴ on F and J are $\Delta F = 0, \pm 1$ and $\Delta J = 0, \pm 1$, transitions with $\Delta F = \Delta J \pm 1$ and ± 2 are also possible. For a Q transition, with $\Delta J = 0$, the F selection rule requiring that $\Delta F = 0, \pm 1$ allows the transitions rQ ($\Delta F = \Delta J + 1$), qQ ($\Delta F = \Delta J$) and pQ ($\Delta F = \Delta J - 1$). If $\Delta J = +1$, $\Delta F = +1, 0$ and -1 corresponds to the transitions rR, qR and pR (or $\Delta F = \Delta J, \Delta J - 1$ and $\Delta J - 2$). The same occurs for P branches where $\Delta F = \Delta J, \Delta J + 1$ and $\Delta J + 2$ lines (pP, qP and rP) occur. These satellite branches are observed only at low values of J because the intensity of the transitions is proportional to the angle between the vectors \mathbf{J} and \mathbf{F} .⁶⁷ When \mathbf{J} and \mathbf{F} are large with respect to \mathbf{I} this angle approaches zero, and only $\Delta F = \Delta J$ transitions are observed. The large value of $9/2$ for the nuclear spin of Nb allows $\Delta F \neq \Delta J$ transitions to be seen at higher values of J than is normally possible.

Accompanying a pair of $\Delta F = \Delta J$ and $\Delta F = \Delta J \pm 1$ transitions, or a

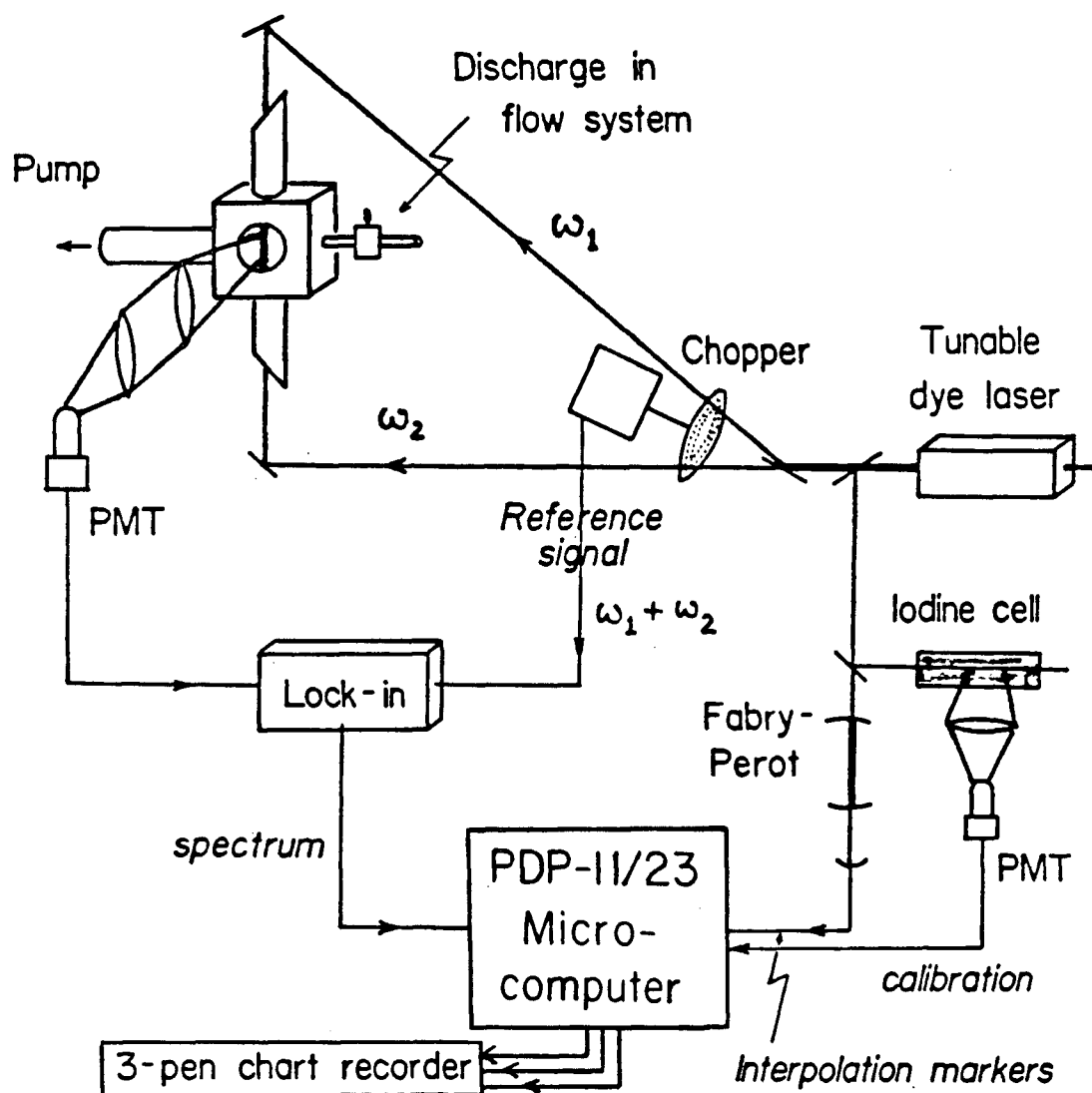


Fig. 2.2. Schematic drawing of the intermodulated fluorescence experiment used in this laboratory. The discharge cube where the sample and laser light are combined is shown in the top left corner.

$\Delta F = \Delta J \pm 1$ and $\Delta F = \Delta J \pm 2$ pair, may be a "crossover resonance" occurring exactly mid-way between the two. Such a phenomenon requires that the two transitions sharing a common level lie within the same Doppler profile. Crossover resonances occur in the IMF spectra of the nearly coincident transitions of closely spaced hyperfine components. The means by which crossover resonances are generated is depicted in Fig. 2.3, with a schematic stick drawing of the resulting spectrum.

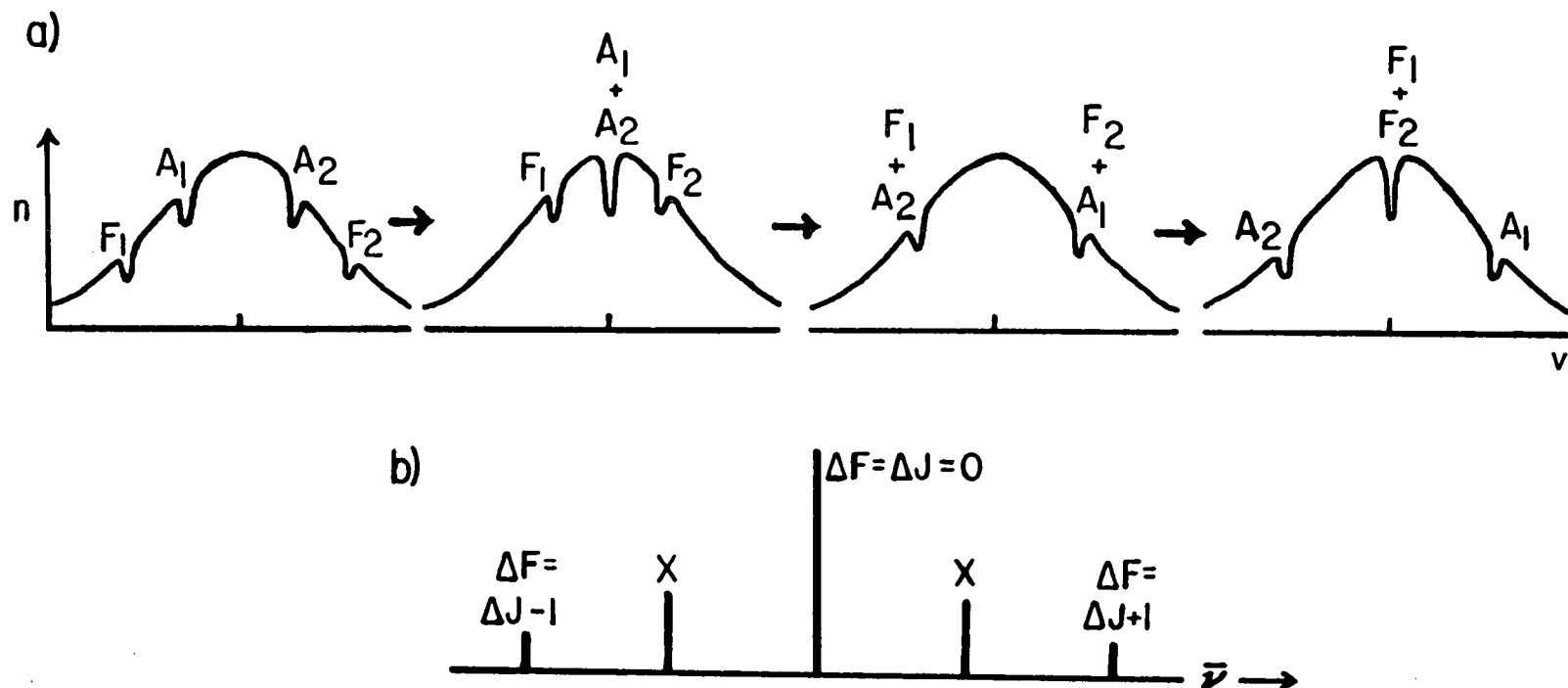


Fig. 2.3. a) The formation of crossover resonances ($F_1 + A_2$ and $F_2 + A_1$) as the result of allowed $\Delta J = \Delta F$ transitions (A_1 and A_2) occurring within the same Doppler-broadened velocity profile as forbidden $\Delta J \neq \Delta F$ transitions (F_1 and F_2). The diagram shows the laser scanning toward the non-Doppler-shifted $\Delta F = \Delta J$ transition (occurring at $A_1 + A_2$) and beyond toward higher frequency to the $\Delta F = \Delta J + 1$ transition ($F_1 + F_2$). If the F 's and A 's are exchanged, the first central Lamb dip is the $\Delta F = \Delta J - 1$ transition. b) Stick diagram of the spectrum of the four forbidden transitions that can accompany a $\Delta F = \Delta J = 0$ Q transition (X denotes a crossover). With an R line, the $\Delta F = 0$ and $\Delta F = -1$ transitions and the associated crossovers occur to the red of the $\Delta F = \Delta J + 1$ transition, while with a P line the forbidden transitions lie to the blue to the $\Delta F = \Delta J - 1$ transition.

II.C. Computerization.

Part of the work for this thesis involved computerizing all stages of the Doppler-limited and intermodulated fluorescence (sub-Doppler) LIF experiments on a PDP-11/23 microcomputer with an RSX-11M operating system. These stages included: 1) laser scanning, and data acquisition and storage; 2) peak finding; and 3) frequency calibration. Each stage comprises a separate program. All of the software was written with FORTRAN-77 except for the laser scanning and data acquisition, programmed in MACRO. The PDP-11 computer is structured such that space for executable code is quite limited. This constraint required that the three programs be overlaid. Overlaying is a method of memory management which allows the sum of the individual subroutines to far exceed the memory limitations of the computer. When an overlaid program is executed, only a portion of the subroutines are sent into memory, while the remainder resides in the relatively limitless disk space. A set of overlay directives is written which describes the program in terms of a calling "root" segment and any number of subprogram "branch" segments; the branches may themselves call "subbranches". The computer uses these directives to build the task file such that during program execution the memory space at any given time is occupied only by the root segment and the branch being called at that time. Since the main responsibility of the root is to call subroutines in the branches, the root is made as short as possible to allow most of the software to remain disk-resident throughout program execution.

The heart of the first program is the MACRO routine which orchestrates laser scanning and data acquisition via its control of the following hardware peripheral devices:

- The 16-bit digital-to-analog converter (D/A), which sends a voltage ramp to the laser so that it scans a range of up to 1.4 cm^{-1} .

- The 4-channel, 12-bit analog-to-digital converter (A/D), containing two registers to process incoming data. The control status register (CSR) receives the voltages (data points) from the sample, iodine and interferometer detectors. The buffer preset register receives the point from the CSR, stores it temporarily, then delivers it both to the 12-bit output D/A and to the appropriate storage buffer for transfer to disk. The sample spectrum is signal averaged over four points prior to transfer to the buffer.

- Three 12-bit D/A's, which send the three data points to the chart recorder for a hardcopy of the spectra.

- The real-time (crystal-oscillator) clock, by which the above peripheral devices are interrupt-driven to operate at a user-chosen rate producing a resolution compatible with the lock-in time constant and the frequency range scanned by the laser. The use of interrupts ensures that the task will be serviced by the computer's central processing unit exactly as dictated by the clock.

The interfacing of computer and experiment is illustrated schematically in Fig. 2.4. Upon return from the MACRO routine after scanning is complete, the three spectral vectors are stored in unformatted files with the first record of the sample file serving as a housekeeping record containing spectral identification and experimental parameters.

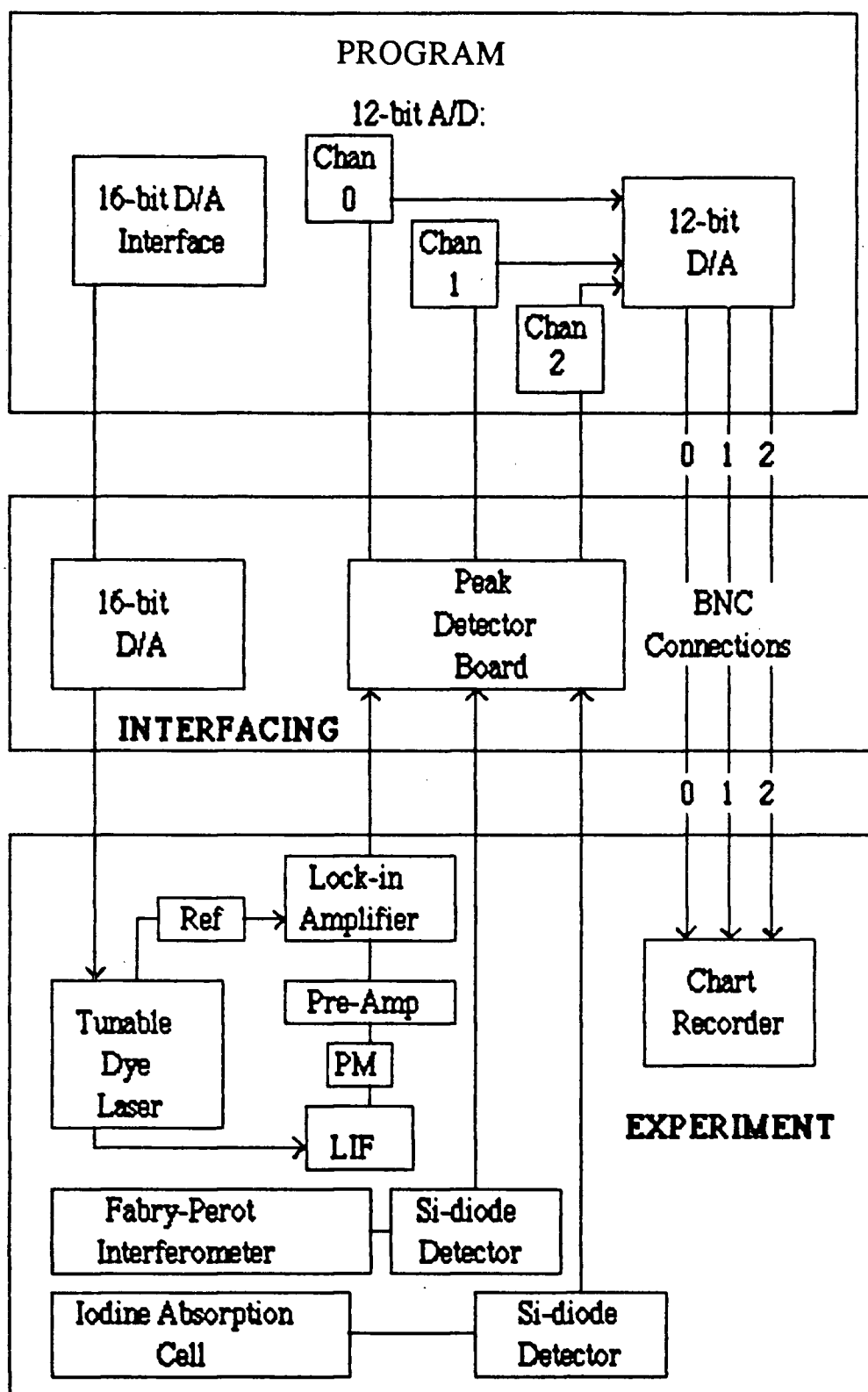


Fig. 2.4. Schematic diagram of the laser-induced fluorescence experiment and how it is interfaced to the PDP-11/23 micro-computer.

CHAPTER III

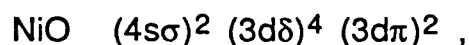
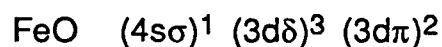
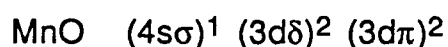
ROTATIONAL ANALYSIS OF THE RED SYSTEM OF COBALT OXIDE

III.A. Introduction.

In German-occupied Belgium during World War II, Malet and Rosen observed a number of electronic bands of gaseous cobalt oxide (CoO) between 5000 and 10000 Å using the exploding wire technique.⁶⁹ The lower state vibrational frequency (i.e., the separation of the $v''=0$ and $v''=1$ vibrational states) was found to be 840 cm^{-1} , and this state was assumed to be the ground electronic state. The next spectroscopic experiments on CoO came years later, in 1979. The first was a low resolution infrared spectrum of CoO (with $\pm 0.2\text{ cm}^{-1}$ line precision) obtained with a microwave discharge source, giving a vibrational frequency of 842.2 cm^{-1} , an equilibrium rotational constant (B_e) of 0.522, and an equilibrium bond length (r_e) of 1.60 Å.⁷⁰ The absence of a Q branch in the spectrum led to the tentative assignment of a Σ ground state²⁴, though the possibility was not ruled out that the spectrum was that of a low-lying excited state.⁷⁰ A matrix isolation infrared study followed shortly afterwards⁷¹, in which cobalt from a cobalt cathode sputtering source and oxygen were codeposited at low temperature (14 K) into a solid matrix of argon. The ground state vibrational frequency was measured in this work to be 846.4 cm^{-1} . In the next year, matrix isolation electron spin resonance (ESR) studies of a large group of transition metal-containing molecules with high spin multiplicities were reported, including CoO.⁷² In spite of high concentrations of CoO within the matrices and the expertise of the laboratory in conducting

experiments of this type, no CoO ESR signal was observed. CoO was therefore concluded to possess an orbitally degenerate ground state, because orbital degeneracy in linear molecules (in matrices of low enough temperature that only the ground state is populated) causes a g tensor anisotropy so large that the spectrum is spread out over such a large magnetic field that it cannot be observed. The ESR spectrum of a paramagnetic Σ state, on the other hand, will possess little or no g anisotropy and will exhibit only a small deviation from the free electron value, $g_e = 2.0023$, due to the spherical symmetry of the overall orbital angular momentum.^{72,73} The value of g is deduced from the relation $h\nu = g\mu_B H$, where ν is the resonance frequency, μ_B the Bohr magneton, H the applied magnetic field, and h Planck's constant; the g anisotropy is taken as $g_{\perp} - g_{\parallel}$. No further work has been published on CoO since this ESR study, leaving the ground state of the molecule to be the only one of the first row transition metal oxides yet to be established.

Field-free atomic orbitals of a diatomic transition metal molecule are split by the axial field of the other atom, as shown in Fig. 3.1. From the electron configurations of manganese, iron and nickel monoxides,



it can be seen that there are two possible candidates for the ground electronic state of CoO. If the seventh valence electron occupies the $4s\sigma$ orbital, the spin multiplicity and direct products given by the resulting $\sigma^2\delta^3\pi^2$ configuration produce a $^4\Delta_i$ electronic state⁷⁴; if

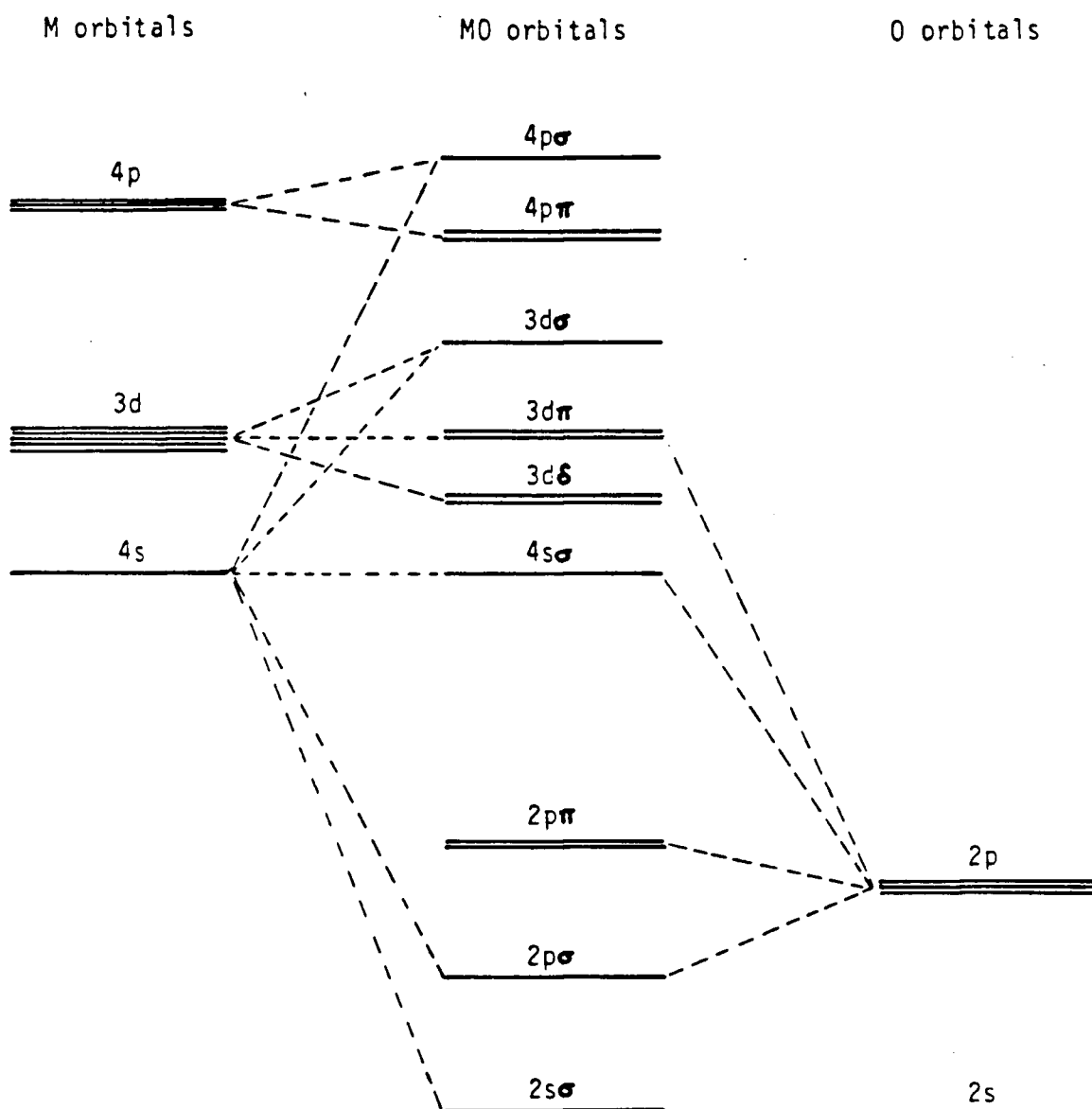


Fig. 3.1. Relative orbital energies of a diatomic 3d transition metal oxide.⁹² The ordering of the 3d δ and 4s σ molecular orbitals is variable.

instead it fills up the δ orbital, a $4\Sigma^-$ state results. However, the uncertain ordering of the $4s\sigma$ orbital with respect to the $3d\delta$ orbital⁷⁵ left the problem in the hands of the theoreticians. Multi-configuration self-consistent-field complete active space (CAS MCSCF) calculations on FeO were extrapolated to CoO to predict a $4\Sigma^-$ ground state.⁷⁶ Weltner, however, first predicted a state of Δ symmetry based on trends in the other TM oxides⁷⁷, then later predicted a 4Φ ground state based on ESR experiments⁷². It was from this stage of development that the current study proceeded.

III.B. Experimental

III.B.1. Synthesis of gaseous cobalt oxide.

Cobalt oxide was made in a Broida-type oven assembly⁷⁴ as follows: an alumina crucible containing cobalt metal powder (Fisher Scientific Co.; 0.14% Ni, 0.11% Fe) was heated resistively in a tungsten basket. The basket was enclosed in a radiation shield comprising an inner ceramic sleeve enveloped by an outer copper sleeve and fitted lid, with zirconia felt packed very tightly around the basket. To produce cobalt oxide (CoO) in quantities sufficient for measurable fluorescence, temperatures approaching the melting point of the alumina crucible (1920 °C) were required, well in excess of cobalt's melting point of 1495 °C. CoO was formed in the gaseous stream of vaporized cobalt atoms, argon carrier gas and molecular oxygen at a pressure of roughly 1 Torr, with a ratio of approximately 150(±15):1 argon to oxygen. Fluorescence, however, occurs only in the presence of laser excitation, which is as with NiO in which only the ground state is populated by the reaction of metal and O₂.⁷⁸ Unlike the production of CuO⁷⁹, which is more efficient with N₂O than O₂, no CoO fluorescence was observed using N₂O as the oxidant. The requirement of high temperature drastically hampered the efficiency of CoO synthesis in two ways. First, there was extensive formation of Thénard's Blue⁸⁰ (cobalt aluminate) deposits on the crucible and on the surface of the liquid cobalt; this phenomenon was also reported in 1966 by Grimely and coworkers who heated solid CoO in an alumina cell to high temperatures⁸¹. Second, the reaction of cobalt vapor with the tungsten basket produces an alloy that renders the basket very susceptible to

cracking, with breakage occurring after at most three heatings of a basket assembly.

III.B.2. The spectrum.

The laser excitation spectrum of gaseous CoO was investigated over the range of 7000 to 5800 Å at Doppler-limited resolution, as described in Section II.A. It is evident that the system extends further to both higher and lower energies. The bands observed by Malet and Rosen with the exploding wire technique⁶⁹ correspond in frequency to those we have measured, though the intensities sometimes varied dramatically between the two techniques. With the superior sensitivity provided by the LIF method, a number of additional bands were observed. The most prominent ones, as measured from a broadband laser spectrum (i.e., one obtained without the intracavity assembly), are listed in Table 3.1. The portion of the spectrum rotationally analyzed thus far covers the range from 15450 to 15790 cm⁻¹ (6470 to 6335 Å), which includes three red-degraded bands whose heads lie at 15778 cm⁻¹ (6338 Å), 15598 cm⁻¹ (6411 Å) and 15538 cm⁻¹ (6436 Å). The broadband spectrum of this region is shown in Fig. 3.2.

Table 3.1. The most prominent bandheads in the 7000 to 5800 Å broadband emission spectrum of gaseous CoO. Values are accurate to roughly ± 3 cm⁻¹, with band strength denoted by: s = strong, m = medium, w = weak.

| Wavelength group | 5920 Å | 6120 Å | 6320 Å | 6650 Å | 6900 Å |
|---------------------|---------|---------|---------|----------|---------|
| Wavenumber | 16916 m | 16366 w | 15832 w | 15296 vw | 14704 w |
| and intensity | 16846 s | 16322 s | 15778 s | 15228 w | 14477 m |
| | | 16256 m | 15597 w | 15036 m | 14469 s |
| | | 16088 w | 15538 m | 15004 s | |

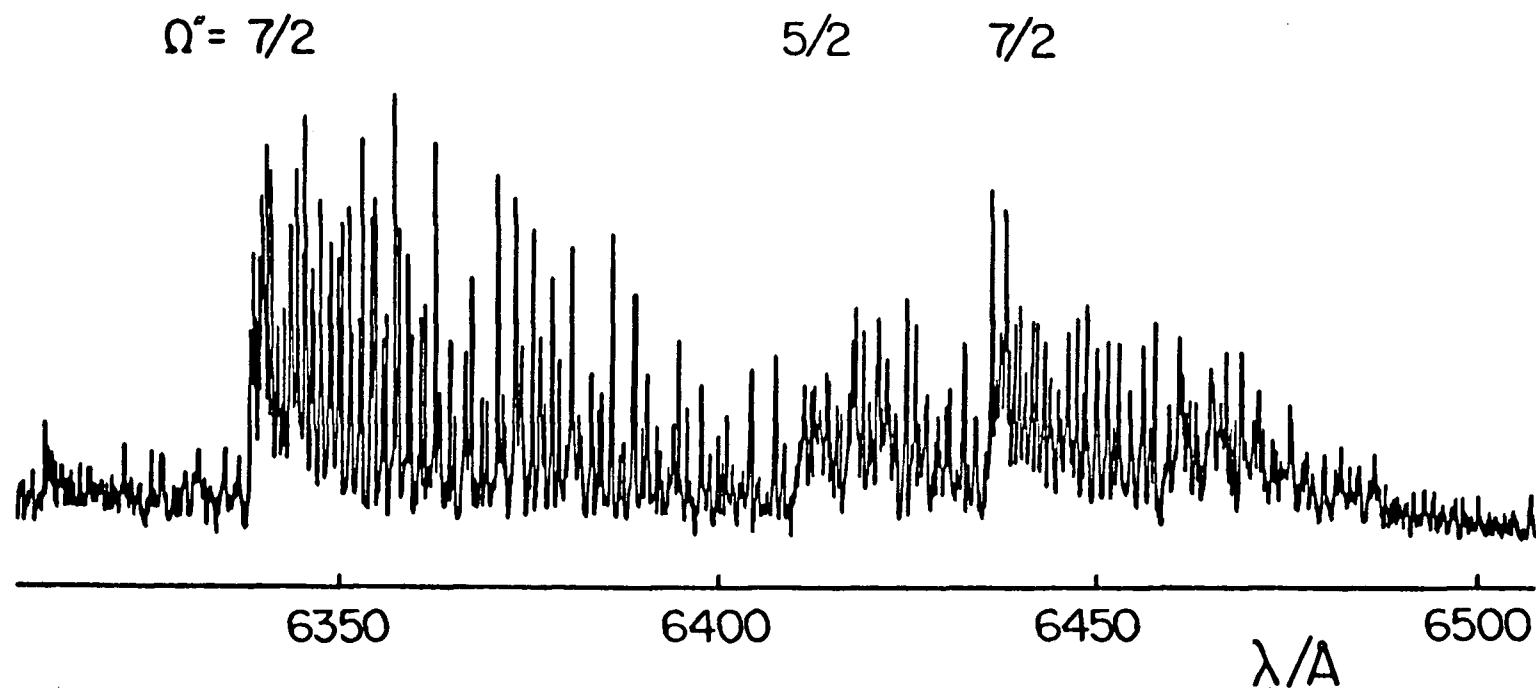


Fig. 3.2. Broadband laser excitation spectrum of the three bands of gaseous CoO analyzed in this work (linewidths are on the order of 1 cm^{-1}).

III.C. Analysis.

III.C.1. Rotational analysis of the 6338 Å subband.

III.C.1.a. Rotational constants and hyperfine structure.

The strongest band, at 6338 Å, was the only band of the three for which a complete analysis was possible, given the available data. The line assignments, listed in Table 3.II, were made using lower state combination differences. For added assurance, some wavelength-resolved fluorescence experiments were performed to verify that certain lines possessed common upper levels. For example, if a pair of lines with a common upper level, such as Q(J'') and R(J''-1), are excited, the fluorescence pattern produced as a result of the R line excitation will be identical to that obtained from the Q line, barring changes in the scattered laser light at the excitation wavelength.

Lower state combination differences measure differences between lines with a common upper state that differ in their J'' value, thereby providing information on the lower state energy structure:¹

$$\Delta_1 F''(J) = R(J) - Q(J + 1) = Q(J) - P(J + 1) \quad (3.1)$$

$$\Delta_2 F''(J) = R(J - 1) - P(J + 1) \quad (3.2)$$

From the definitions of R, Q and P, and from the energy level expressions, it can be shown that⁸³

$$\Delta_1 F''(J) = 2B''(J + 1) - 4D''(J + 1)^3 \quad (3.6)$$

$$\Delta_2 F''(J) = (4B'' - 6D'')(J + 1/2) - 8D''(J + 1/2)^3 \quad (3.7)$$

The lowest Q line of this band was assigned as J' = J'' = 7/2, using the average of the $\Delta_1 F''$ combination differences from the first R and P lines, and a rough estimate of 0.5 cm⁻¹ for the value of B. The

possible electronic states corresponding to a value of Ω of $7/2$ are 4Δ and 2Φ , but only the 4Δ state has an electronic configuration that can reasonably be expected to belong to the ground state. The three subbands analyzed in the current work demonstrate that the most intense CoO transitions are those with $\Omega'' = 7/2$. Presumably these must come from the lowest spin-orbit component of the ground state. Since the spin-orbit manifold must be inverted for its lowest energy component to be $7/2$, the electronic state is assigned as $4\Delta_i$. The relatively low intensity of the Q lines¹ (see Fig. 3.3), identifies the transition as parallel, or $\Omega' = \Omega'' = 7/2$. The lower state vibrational level can definitely be assigned as $v'' = 0$, based on resolved fluorescence experiments where the Q(3.5) line was excited: strong fluorescence was observed 851.7 cm^{-1} to the red of the Q(3.5) transition, but nothing to the blue. In the absence of isotopic labelling studies, such as with Co^{18}O , no information is available on the upper state quantum number.⁸³ Extensive structure to the red of the 6338 \AA band indicates that there are lower lying vibrational levels; on this basis, the upper state vibrational quantum number is suggested to be at least two.

The lower state rotational constants B and D were calculated by least squares from the $\Delta_2 F''$ combination difference formula in equation (3.7). The $\Delta_2 F''(J)$ combination differences are given in Table 3.II along with the assigned lines of the 6338 \AA band. Using these B'' and D'' values to calculate the lower state energy levels, the upper state energy levels were calculated; then a least squares fit to the expression

$$E(J) = T_0 + BJ(J + 1) - DJ^2(J + 1)^2 \quad (3.8)$$

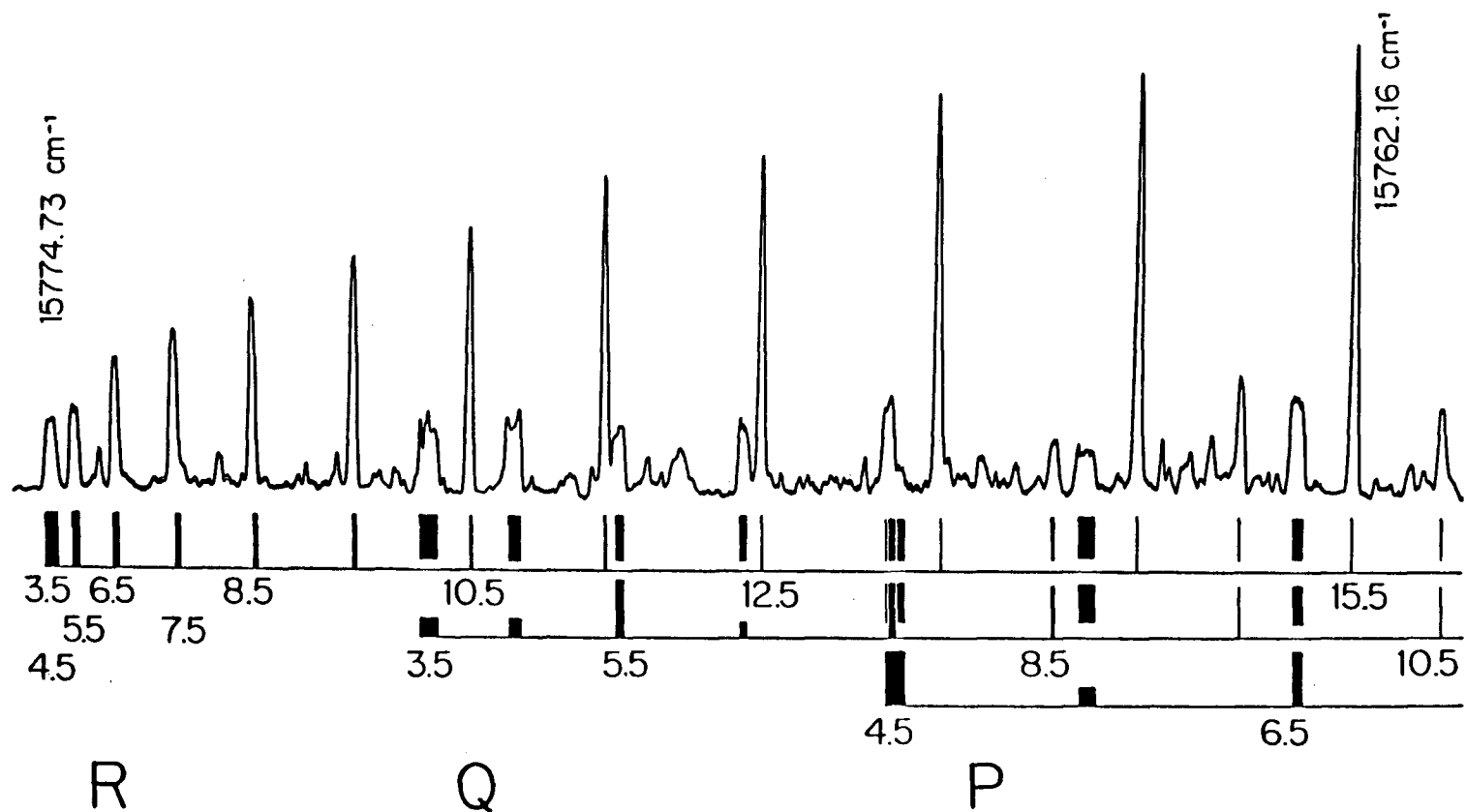


Fig. 3.3. Bandhead of the $\Omega' = \Omega'' = 7/2$ transition at 6338 Å, exhibiting the broadening due to hyperfine interactions and the weak Q branch signifying a parallel transition. The weak background is reproducible.

Table 3.II. Assigned lines from the 6338 Å band (${}^4\Delta_{7/2} - {}^4\Delta_{7/2}$) of CoO with the lower state combination differences, $\Delta_2 F''$, in cm^{-1} . An asterisk denotes a blended line.

| J'' | R | | Q | P | $\Delta_2 F''$ | ¹⁰³ O-C |
|------|-----------|-----------|-----------|-----------|----------------|-----------------------|
| 3.5 | 15774.7* | | 15771.060 | | | |
| 4.5 | 15774.7* | | 15770.2* | 15766.64* | | |
| 5.5 | 15774.509 | | 15769.2* | 15764.737 | | |
| 6.5 | 15774.110 | | 15768.002 | 15762.704 | 14.015 | 1 |
| 7.5 | 15773.526 | | 15766.64* | 15760.494 | 16.014 | -2 |
| 8.5 | 15772.760 | | 15765.024 | 15758.096 | 18.011 | -6 |
| 9.5 | 15771.810 | | 15763.259 | 15775.515 | 20.013 | -5 |
| 10.5 | 15770.668 | | 15761.291 | 15752.747 | 22.015 | -3 |
| 11.5 | 15769.343 | | 15759.158 | 15749.791 | 24.021 | 2 |
| 12.5 | 15767.828 | | 15756.829 | 15746.647 | 26.024 | 6 |
| 13.5 | 15766.126 | | 15754.316 | 15743.319 | 28.017 | -1 |
| 14.5 | 15764.236 | | 15751.615 | 15739.811 | 30.019 | 2 |
| 15.5 | 15762.159 | | 15748.715 | 15736.107 | 32.018 | 2 |
| 16.5 | 15759.892 | | | 15732.219 | 34.011 | -3 |
| 17.5 | 15757.445 | | | 15728.147 | 36.012 | 1 |
| 18.5 | 15754.806 | | | 15723.880 | 38.006 | -2 |
| 19.5 | 15751.994 | | | 15719.439 | 40.005 | 1 |
| 20.5 | 15749.350 | 15747.947 | | 15714.801 | 42.000 | 0 |
| | 15748.821 | 15749.039 | | | | |
| 21.5 | 15745.600 | 15745.906 | | 15709.994 | 43.995 | 0 |
| | | 15745.720 | | | | |
| 22.5 | 15742.273 | 15742.345 | 15705.347 | 15703.946 | 45.987 | -3 |
| | | | 15704.829 | 15705.045 | | |
| 23.5 | 15738.696 | 15738.769 | 15699.615 | 15699.914 | 47.984 | 1 |
| | | | | 15699.735 | | |
| 24.5 | 15734.923 | 15735.005 | 15694.290 | 15694.360 | 49.980 | 4 |
| 25.5 | 15730.951 | 15731.051 | 15688.720 | 15688.786 | 51.975 | 6 |
| 26.5 | 15726.783 | 15726.911 | 15682.948 | 15683.030 | 53.968 | 8 |
| 27.5 | 15722.428 | 15722.592 | 15767.986 | 15677.080 | 55.956 | 6 |
| 28.5 | 15717.883 | 15718.106 | 15670.826 | 15670.954 | 57.938 | -2 |

Table 3.II. continued.

| J" | R | | P | | $\Delta_2 F''$ | $\begin{matrix} 10^3 \\ \text{O-C} \end{matrix}$ |
|------|------------|-----------|-----------|------------|----------------|--|
| 29.5 | 15713.130 | 15713.500 | 15664.491 | 15664.654 | 59.929 | 0 |
| 30.5 | 15709.131 | 15708.185 | 15657.951 | 15658.178 | 61.908 | -9 |
| | 15707.960 | | | | | |
| 31.5 | 15703.047 | 15703.110 | 15651.226 | 15651.589 | 63.903 | 0 |
| 32.5 | 15697.705 | 15697.888 | 15645.226 | 15644.282 | 65.890 | 1 |
| | | | 15644.057 | | | |
| 33.5 | 15692.171 | 15692.441 | 15637.158 | 15637.220 | 67.870 | -4 |
| 34.5 | 15686.424 | 15686.786 | 15629.837 | 15630.015 | 69.861 | 3 |
| 35.5 | 15680.487 | 15680.945 | 15622.311 | 15622.580 | 71.836 | -5 |
| 36.5 | 15674.251 | 15674.893 | 15614.591 | 15614.950 | 73.820 | -2 |
| 37.5 | 15667.933 | 15668.678 | 15606.670 | 15607.122 | 75.787 | -15 ^a |
| 38.5 | 15661.347 | 15662.251 | 15598.464 | 15599.106 | 77.783 | 1 |
| 39.5 | 15654.547 | 15665.638 | 15590.150 | 15590.896 | 79.752 | -8 |
| 40.5 | 15647.498 | 15648.844 | 15581.594 | 15582.500 | 81.738 | 2 |
| 41.5 | 15640.453* | 15641.831 | 15572.810 | 15573.900 | 83.713 | 1 |
| 42.5 | | 15634.643 | 15563.785 | 15565.131 | 85.684 | -2 |
| 43.5 | | 15627.272 | 15554.769 | 15556.159 | 87.641 | -18 ^a |
| 44.5 | | 15619.712 | | 15547.002 | 89.615 | -15 ^a |
| 45.5 | | 15611.954 | | 15537.657 | 91.591 | -9 ^a |
| 46.5 | | 15604.010 | | 15528.121 | | |
| 47.5 | | | | 15518.405* | | |

^aNot included in the least squares fit.

was used to obtain B' and D' from the unperturbed levels with $J' = 5.5$ to 19.5. The results appear in Table 3.III. Note that since the upper state B value is only 81% of the lower state, by the relation $r''/r' = (B'/B'')^{1/2}$ the CoO bond length increases by a full 10% upon electronic excitation.

The hyperfine structure in CoO arising from the ^{59}Co nuclear spin of $7/2$ follows the case ($a\beta$) pattern where the hyperfine widths decrease with increasing rotation, described to a first approximation by equation (1.90).⁸⁵

$$E_{\text{Hfs}} \approx \Omega[a\Lambda + (b + c)\Sigma](1/J)\{[F(F+1) - J(J+1) - I(I+1)]/2(J+1)\} \quad (3.9)$$

(In case ($b\beta_J$) coupling the hyperfine widths are independent of N for each of the spin components.) The hyperfine splitting in the P lines is found to be wider than that in R lines of the same J'' , while P and R lines possessing the same upper state J are of comparable widths. Since a comparison of P and R lines of the same J'' demonstrate upper state properties, while those with equal J' represent the lower state, it can be seen that the hyperfine interactions produce larger splittings in the upper state than in the lower state. From equation (3.9) it can also be seen that the eight hyperfine components of a rotational line will be more widely spaced at higher values of F . Partially resolved hyperfine splittings in some low J lines, for instance P(5.5), show that the highest F value component is on the high frequency side. This ordering of the hyperfine components shows that the change in the Fermi contact parameter, $b' - b''$, is positive.⁸⁴

Table 3.III. Rotational constants for the analyzed bands of the red system of CoO.^a

| | T_0 | B | $10^7 D$ | σ |
|---------------------------------|-----------------------|-------------------|---------------|----------|
| Upper Levels: | | | | |
| 6338 Å, $\Omega = 7/2$ | 15772.513 ± 3 | 0.40531 ± 9 | 6.4 ± 19 | 0.0038 |
| 6411 Å, $\Omega = 5/2$ | $a + 15594.974 \pm 2$ | $0.4250_3 \pm 24$ | 27 ± 7 | 0.0049 |
| 6436 Å, $\Omega = 7/2$ | 15535.77 | 0.422_4^b | ... | ... |
| Lower Levels ($X^4\Delta_i$): | | | | |
| $\Omega = 5/2$ | a | $0.5026_6 \pm 9$ | 3.6 ± 14 | 0.0024 |
| $\Omega = 7/2$ | 0 | 0.50058 ± 4 | 6.50 ± 15 | 0.0031 |

^aValues in cm^{-1} , with error limits of three standard deviations in units of the last significant figure. $a = A\Lambda \approx 244 \text{ cm}^{-1}$.

^bNo least squares fit; see text.

III.C.1.b. Perturbations.

A plot of the upper state energy levels as a function of $J(J + 1)$ illustrates the perturbations in the upper states. The lower state appears to be free of Λ -doubling (cf. Section 1.B.6) and other perturbations, since the lower state combination differences are entirely regular: the two $\Delta_2 F''(J)$ values, given by the two Λ -doubling components, are equal to within experimental error. Figure 3.4 shows that upper state Λ -doublings begin at $J' = 21.5$, and that in some places extra transitions occur; the section of spectrum in Fig. 3.5 illustrates these perturbations. The extra lines could be securely identified because they give exactly the same $\Delta_2 F''(J)$ combination differences as the main lines and their relative intensities are in the same ratio.

Two avoided crossings can be seen in Fig. 3.4: a strong one, where both of the Λ components are perturbed, at $J' = 30.5 - 31.5$, and a weaker one where the lower Λ component is mildly perturbed at $J' = 37.5$. Since the avoided crossings affect the Λ -components differently, the perturbing state is orbitally non-degenerate, or alternatively has a very large Λ -doubling of its own. The state perturbing the $J' = 22.5$ level appears to have a relatively small Λ - or Ω -doubling. (Λ -doubling exhibited by a Σ state is referred to here as Ω -doubling⁸⁵.)

The state responsible for all of the above perturbations could conceivably be a single case (a) 4Σ state. The small Ω -doubling occurring near $J' = 22.5$ could arise from the $4\Sigma_{3/2}$ component, while the considerably larger Ω -type splitting associated with the $4\Sigma_{1/2}$ component⁸⁵ is capable of affecting upper state levels that are

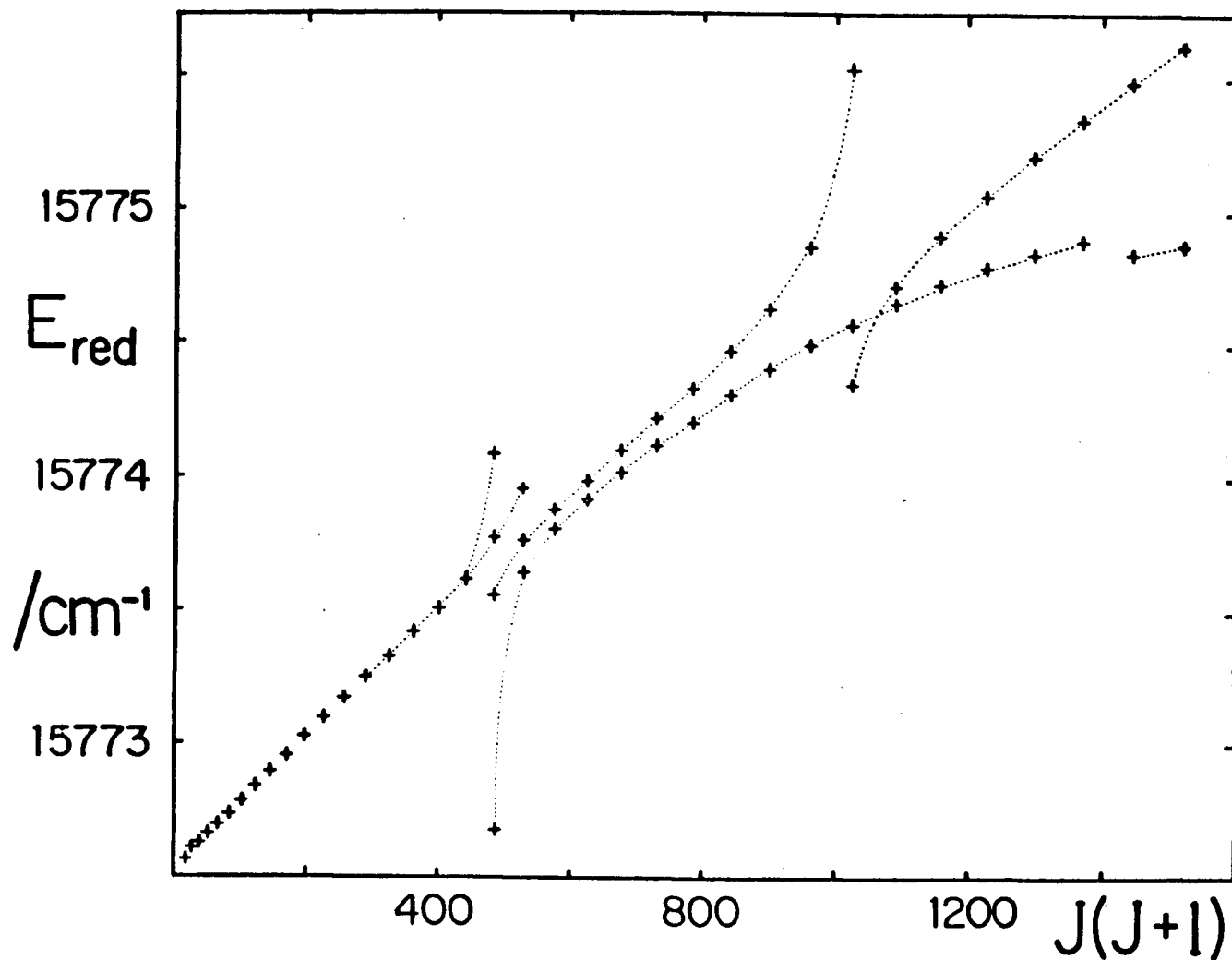


Fig. 3.4. Upper state energy levels of the ${}^4\Delta_{7/2} - {}^4\Delta_{7/2}$ 6338 Å band, scaled by subtracting the quantity $0.405J(J + 1) - 6.4 \times 10^{-7}J^2(J + 1)^2$, plotted against $J(J + 1)$.

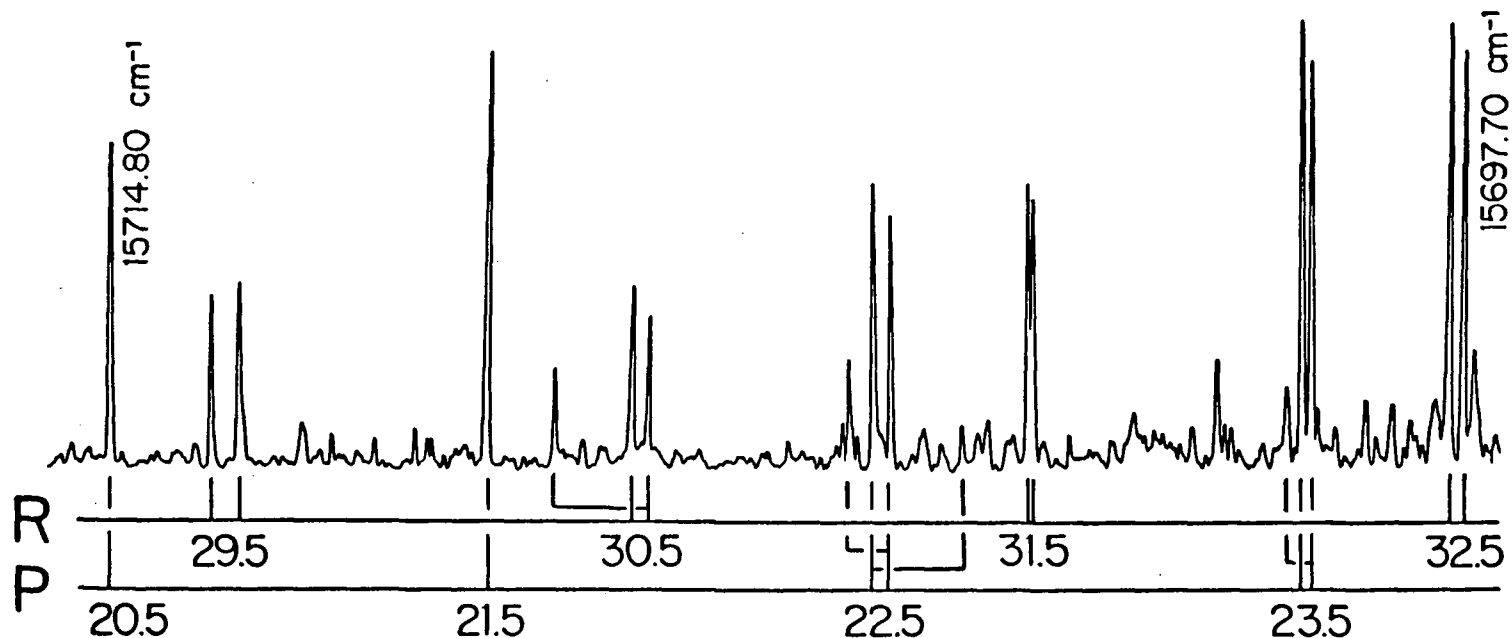


Fig. 3.5. A section of the spectrum of the 6338 Å band containing Λ -doubling, two avoided crossings, and extra lines. The extra R(30.5) line to the blue of the Λ -doubled R(30.5) lines corresponds to the anomalous point in Fig. 3.4 near $J(J + 1) = 1000$. All lines, down to the weakest, are reproducible, though relative intensities between lines at either end of the spectrum may not be accurate since the spectrum is compiled from several laser scans.

widely spaced in J , analogous to the situation observed in Fig. 3.4.

III.C.2. Rotational analysis of the 6436 Å subband.

The fairly intense 6436 Å band is another $\Omega' = \Omega'' = 7/2$ parallel transition whose lower state is the same as that of the 6338 Å band, as the lower state combination differences of the two bands are equal to within experimental error. Because the upper level lies only 237 cm^{-1} below that of the 6338 Å upper state, and the frequency separating the strong groups of subbands (cf. Table 3.1) is on the order of 600 cm^{-1} , it cannot belong to the same upper electronic state as the 6338 Å band. Also, the hyperfine structure is considerably wider than in the 6338 Å subband, which also points to a different upper electronic state. There is not enough information available to say what this other electronic state is. Although its high intensity suggests that it is another $^4\Delta_{7/2} - ^4\Delta_{7/2}$ transition, there are other channels through which intensity can be derived. In the very dense, perturbed "orange" system of FeO, for example, transitions to the high vibrational levels of various lower electronic states acquire considerable intensity by interacting with the upper state of the system.⁸⁶

The upper state energy levels are plotted as a function of $J(J + 1)$ in Fig. 3.6, up to the limit of our analysis thus far at $J' = 26.5$. Λ -doubling is first observed at $J' = 20.5$, very much like the 6338 Å band upper levels which are first seen to split at $J' = 21.5$. Perturbations in the upper state have scattered the levels to such a degree that a good least squares fit to the upper state constants was not possible, though a value of B' could be estimated (see Table

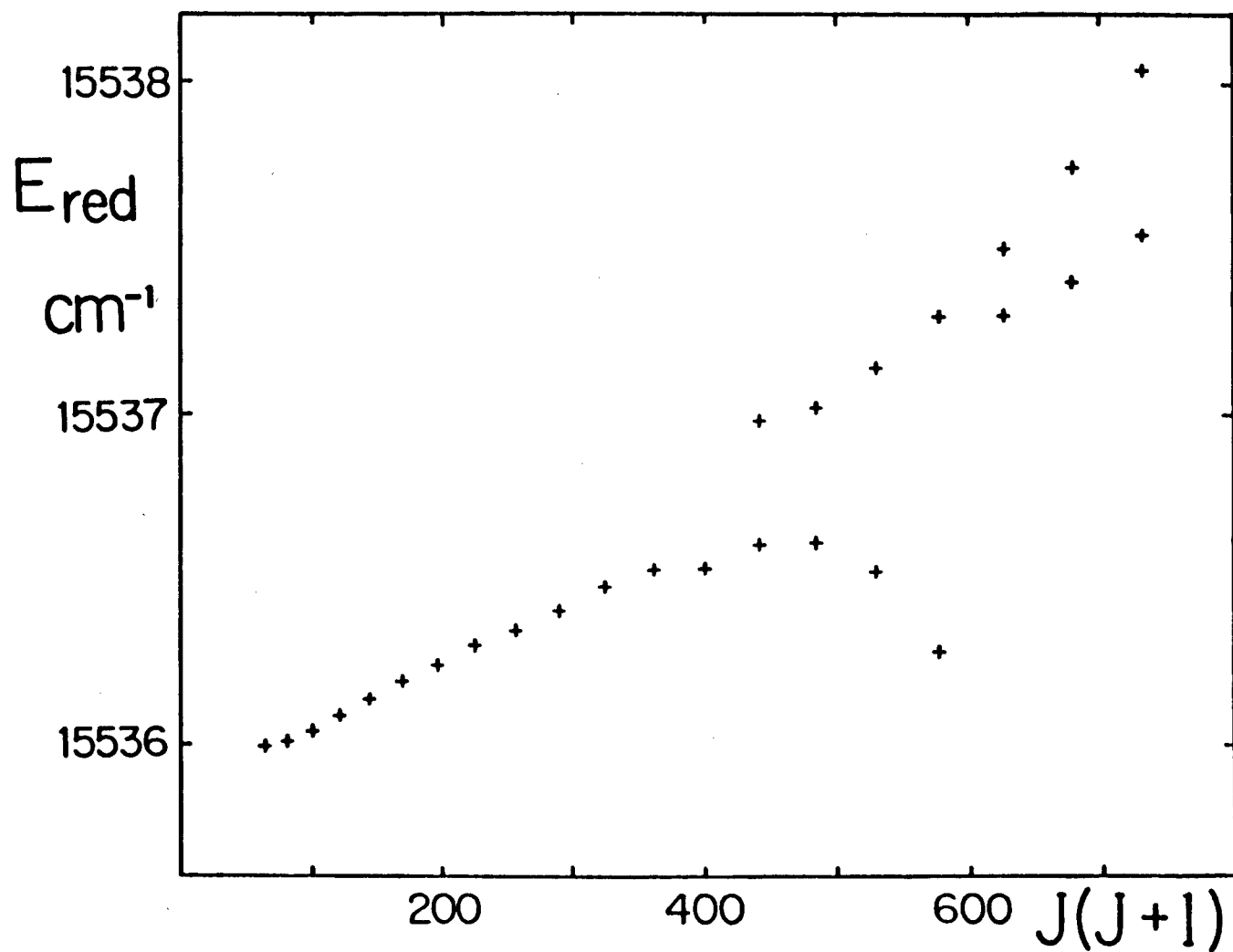


Fig. 3.6. Upper state energy levels of the $4\Delta_{7/2} - 4\Delta_{7/2}$ 6436 Å band, scaled by subtracting the quantity $0.42J(J + 1)$, plotted against $J(J + 1)$.

3.III). The lines assigned in the 6436 Å band are compiled in Table 3.IV.

III.C.3. Rotational analysis of the 6411 Å subband.

The $\Omega' = \Omega'' = 5/2$ subband whose head lies at 6411 Å is much weaker than the other two subbands, and is also badly perturbed, which has precluded analysis beyond $J' = 20.5$. All the lines assigned so far are listed in Table 3.V. The transition was assigned as $\Omega' = \Omega'' = 5/2$ by the methods used previously for the 6338 Å subband, and it appears that the lower state is the $\Omega = 5/2$ spin-orbit component of the ground electronic state. The crowded head region of the band is shown in Fig. 3.7.

The perturbations in the $\Omega' = 5/2$ upper state are illustrated by the plot of the scaled upper state energy levels as a function of $J(J + 1)$ in Fig. 3.8. The Λ -doubling is much larger than in the upper levels of the $\Omega = 7/2$ bands, with the splitting first discernible at Doppler-limited resolution at $J' = 10.5$. At $J' = 16.5$ one of the Λ -components is drastically pushed to lower energy, and no further J' levels could be assigned. The other component also disappears abruptly at $J' = 20.5$. The suddenness with which the branches break off is surprising, because there is no appreciable loss of intensity before the rotational structure ceases. This fragmentary behavior has been observed before, for example in the 5866 Å band of FeO where the structure disappears suddenly at $J' = 15$, and then reappears 12 cm^{-1} to the blue.⁸⁶ The 6411 Å upper level in CoO has obviously suffered a massive perturbation near $J' = 20.5$. To find where the branches resume will require extensive wavelength resolved

Table 3.IV. Assigned lines from the 6436 Å ($4\Delta_{7/2}-4\Delta_{7/2}$) band of CoO, in cm^{-1} .

| J" | R | | P | |
|------|-----------|-----------|-----------|-----------|
| 7.5 | 15537.998 | | 15524.45 | |
| 8.5 | 15537.505 | | 15522.347 | |
| 9.5 | 15536.866 | | 15519.996 | |
| 10.5 | 15536.061 | | 15517.490 | |
| 11.5 | 15535.096 | | 15514.839 | |
| 12.5 | 15533.976 | | 15512.039 | |
| 13.5 | 15532.692 | | 15509.082 | |
| 14.5 | 15531.241 | | 15505.950 | |
| 15.5 | 15529.644 | | 15502.682 | |
| 16.5 | 15527.897 | | 15499.226 | |
| 17.5 | 15525.955 | | 15495.625 | |
| 18.5 | 15523.820 | | 15491.877 | |
| 19.5 | 15521.589 | 15521.967 | 15487.959 | |
| 20.5 | 15519.589 | 15519.536 | 15483.815 | |
| 21.5 | 15516.412 | 15517.029 | 15479.586 | 15479.959 |
| 22.5 | 15513.383 | 15514.393 | 15475.130 | 15475.539 |
| 23.5 | 15511.448 | 15511.650 | 15470.420 | 15471.035 |
| 24.5 | 15508.438 | 15508.784 | 15465.395 | 15466.408 |
| 25.5 | | | 15461.468 | 15461.670 |
| 26.5 | | | 15456.463 | 15456.809 |
| 27.5 | | | 15451.345 | 15451.840 |

Table 3.V. Assigned lines from the 6411 Å band ($^4\Delta_{5/2}$ - $^4\Delta_{5/2}$) of CoO, in cm^{-1} . An asterisk denotes a blended line.

| J" | R | | Q | P |
|------|------------|-----------|------------|----------------------|
| 2.5 | 15597.270* | | 15594.293 | |
| 3.5 | 15597.577* | | 15593.751 | |
| 4.5 | 15597.730* | | 15593.067 | 15589.2* |
| 5.5 | 15597.730* | | 15592.23* | 15587.557 |
| 6.5 | 15597.577* | | 15591.183 | 15585.670 |
| 7.5 | 15597.270* | | 15590.039* | 15583.654 |
| 8.5 | 15596.194 | | 15588.739 | 15581.492 |
| 9.5 | 15596.194 | 15596.240 | | 15579.076 |
| 10.5 | 15595.432 | 15595.512 | | 15576.718 |
| 11.5 | 15594.523 | 15594.647 | | 15574.076* 15574.125 |
| 12.5 | 15593.461 | 15593.618 | | 15571.307 15571.389 |
| 13.5 | 15592.254 | 15592.708 | | 15568.389 15568.512 |
| 14.5 | 15590.896 | 15591.441 | | 15565.323 15565.493 |
| 15.5 | 15589.390 | 15588.739 | | 15562.106 15562.559 |
| 16.5 | 15587.729 | | | 15582.734 15559.270 |
| 17.5 | 15585.958 | | | 15555.222 15554.561 |
| 18.5 | 15583.958 | | | 15551.558 |
| 19.5 | 15581.845 | | | 15547.736 |
| 20.5 | | | | 15543.770 |
| 21.5 | | | | 15539.646 |

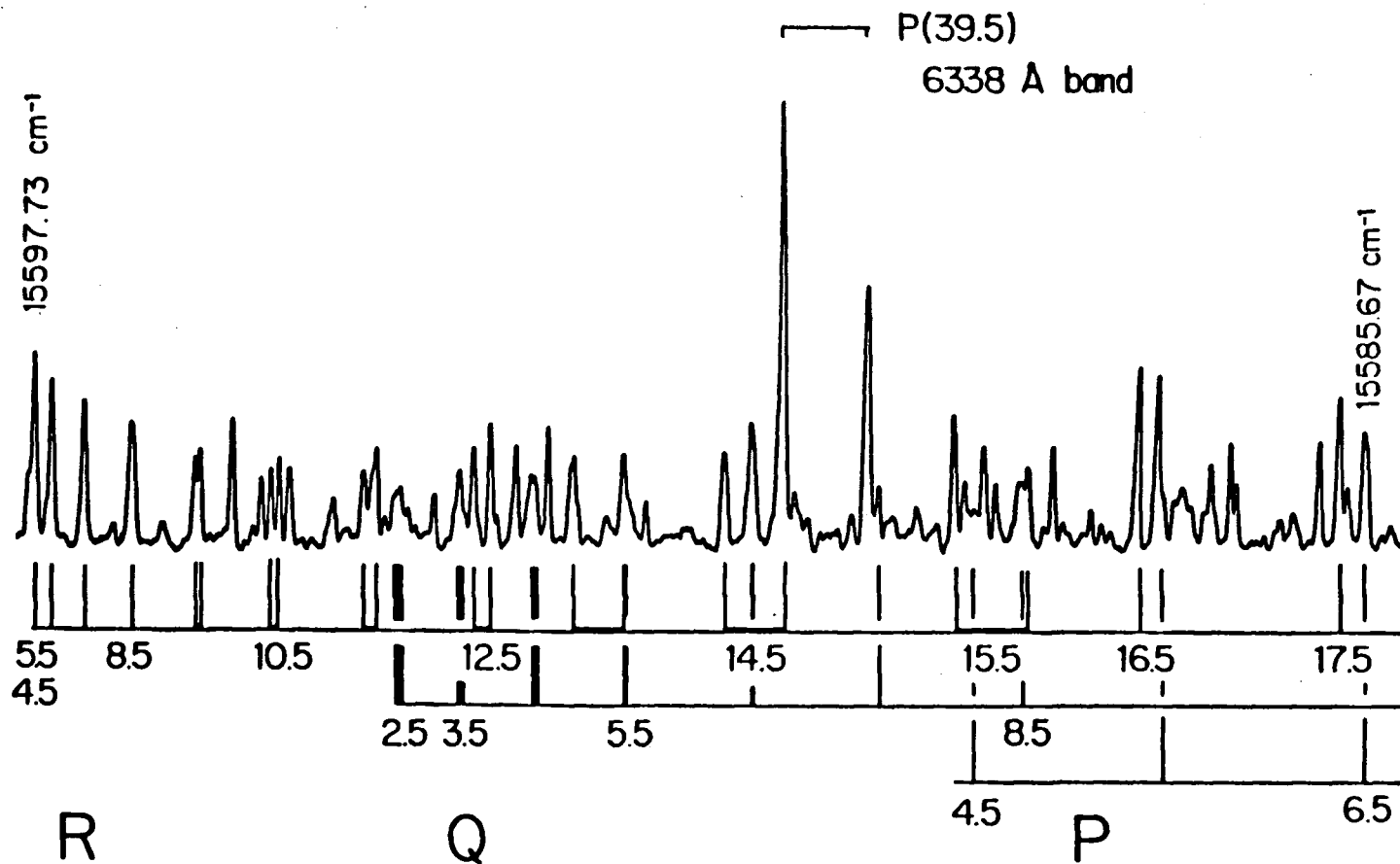


Fig. 3.7. Bandhead of the $\Omega' = \Omega'' = 5/2$ transition at 6411 Å. The band is extensively overlapped by other bands, as evidenced by the dense collection of unassigned lines.

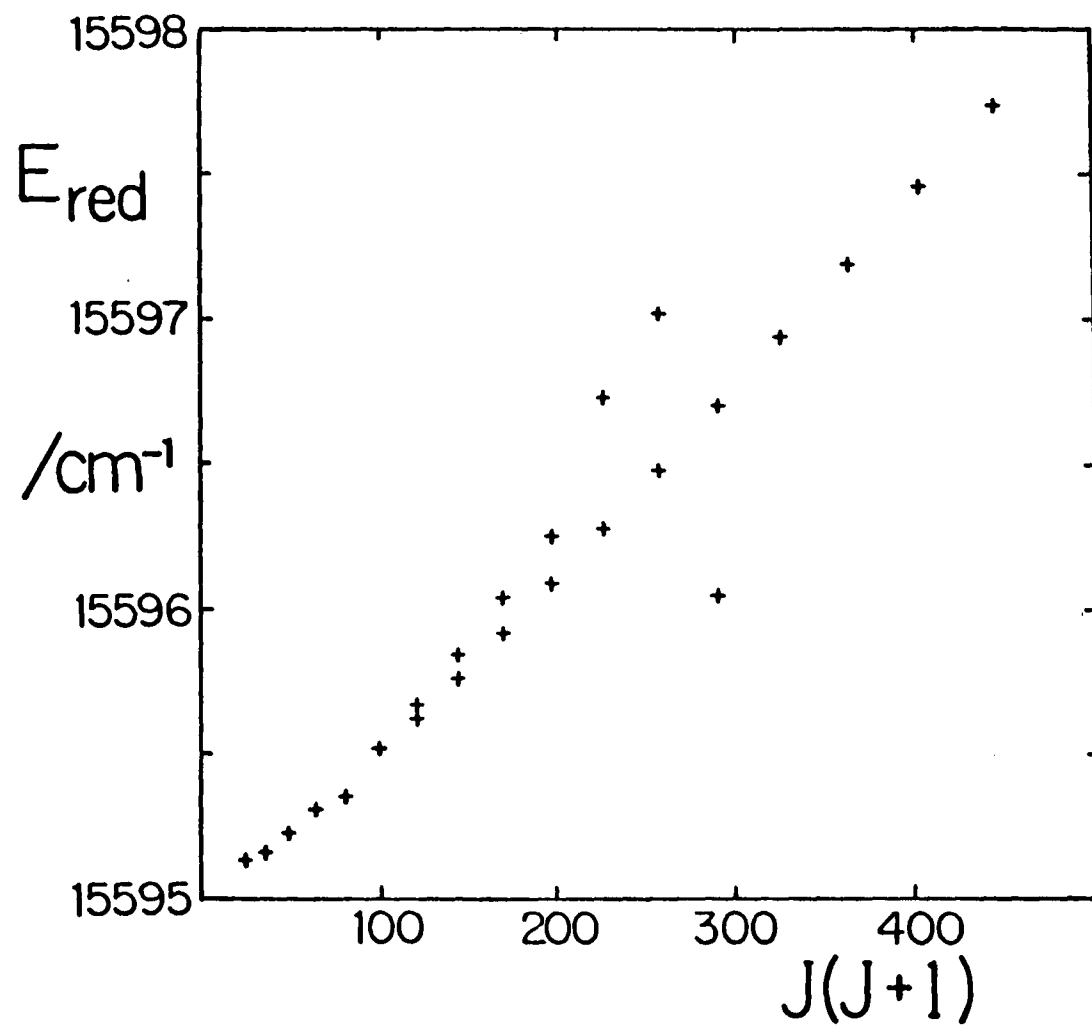


Fig. 3.8. Upper state energy levels of the $4\Delta_{5/2} - 4\Delta_{5/2}$ 6411 Å band, scaled by subtracting the quantity $0.42J(J + 1)$, plotted against $J(J + 1)$.

fluorescence measurements in the surrounding region. Such studies must be postponed until we develop a less cumbersome method by which to synthesize gaseous CoO.

The upper and lower state B and D rotational constants, calculated in the same manner as for the 6338 Å band, are given in Table 3.III. Kratzer's relationship⁸³,

$$D_e = 4B_e^3/\omega_e^2 \quad (3.10)$$

for the equilibrium values of the rotational constants and the vibrational frequency (ω_e) can be approximated for the $v = 0$ level by

$$D_0 = 4B_0^3/\Delta G_{1/2}^2 \quad (3.11)$$

Using equation (3.11) to calculate an approximate value for D'' , it is found to be about 60% larger than the observed value.

III.D. Discussion.

Of the two possible ground electronic state configurations for CoO, $4\Sigma^- (\sigma\pi^2\delta^4)$ or $4\Delta(\sigma^2\pi^2\delta^3)$, evidence has been presented in the rotational analysis of the excitation spectrum of gaseous CoO which strongly supports that the ground state is $4\Delta_i$. The fundamental vibrational frequency of 846.4 cm^{-1} measured by infrared spectroscopy in low-temperature (14 K) matrix isolation⁷¹ closely matches the value of 851.7 cm^{-1} obtained from this laser induced fluorescence work. Since the ground electronic state should be the only one populated at 14 K, and a 5.3 cm^{-1} shift from the solid to gas phase is not unreasonable, this suggests that the lower electronic state of the three bands studied here is the ground state. The matrix isolation electron spin resonance study⁷² which could not produce a signal from CoO eliminates the possibility for $4\Sigma^-$ as the ground state, taking this absence of a result as valid. The only condition under which an orbitally non-degenerate electronic state with case (a) coupling can produce no ESR signal when isolated in a low-temperature matrix is if it possesses an odd spin multiplicity with the $\Omega = 0$ level the only one populated. The band intensities support an inverted order for the spin-orbit manifold since the $\Omega' = \Omega'' = 7/2$ bands are strongest, followed by $\Omega' = \Omega'' = 5/2$.

The rotational analysis of two Ω spin-orbit components of the same electronic state provides the information required to determine the true B value and an estimate for the spin-orbit interval, $A\lambda$. For molecules in which spin uncoupling is small because the spin-orbit interaction is very large, the effective B value for a given spin-orbit component differs from the true B value

by an amount that depends on the spin-uncoupling operator, $-2B\hat{J}\cdot\hat{S}$. A second order perturbation treatment of two Ω substates separated by $A\Lambda$ and connected by this operator produces the relation:²⁴

$$B_{\text{eff},\Omega} = B(1 + 2B\Sigma/A\Lambda) \quad (3.12)$$

Solving equation (3.12) simultaneously for both $A\Lambda$ and the true B value for the $v'' = 0$ level, using the effective $B_{\Omega=7/2}$ and $B_{\Omega=5/2}$ values in Table 3.III, gives

$$B = 0.5037 ; \quad A\Lambda \approx -244 \text{ cm}^{-1} \quad (3.13)$$

The spin-orbit coupling interval $A\Lambda$ is not expected to be accurate to better than 10%, as equation (3.12) does not take into account the centrifugal distortion corrections to A and λ , called A_D and λ_D (cf. Section I.B.3). For example, the initial estimate of $|A\Lambda|$ made for FeO^{75} was 180 cm^{-1} , based on the approximation in equation (3.12), yet the value was later found⁸⁷ to be 190 cm^{-1} . The definition of B , as a function of the mean value of the bond length r during the vibration, is⁸³

$$B = (h/8\pi^2c\mu)\langle r^{-2} \rangle \quad (3.14)$$

where μ is the reduced mass of the molecule. With the B value in equation (3.13), the bond length in the zero point vibrational level is calculated from equation (3.14) to be:

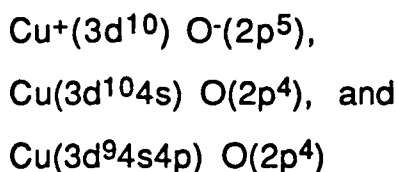
$$r_0(X^4\Delta_i) = 1.631 (\pm 0.001) \text{ \AA} \quad (3.15)$$

The 10% increase in bond length to 1.80 \AA upon electronic excitation to the upper $^4\Delta_i$ state is quite large compared to transitions in the other first row diatomic transition metal oxides. The $A^4\Pi \leftarrow X^4\Sigma^-$ transition of VO produces a 7% increase⁴⁵; $A^5\Sigma \leftarrow X^5\Pi_r$ and $B^5\Pi_r \leftarrow X^5\Pi_r$ in CrO give 2-1/2 and 5-1/2% increases⁹⁰; the $^6\Sigma^+ \leftarrow ^6\Sigma^+$ parallel transition of MnO at 6500 \AA shows a 4% increase⁹¹; but

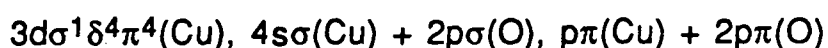
various subbands of the orange system of FeO do show bond length increases of up to as much as 11%⁸⁷, and a state perturbing the MnO $A^6\Sigma^+$ state has a bond 10% longer than that of the ground state⁹¹.

The magnetic hyperfine structure and spin-orbit coupling constant can be used to give information about the excited states as well as the ground state. The insignificant hyperfine structure in the ground state is consistent with the lack of unpaired s electron density in the $4\Delta \sigma^2\pi^2\delta^3$ configuration. The upper state configuration can be assigned as $\sigma\pi^2\delta^3\sigma^*$ for three reasons:

1) the large, positive hyperfine splittings in the upper state indicate a strong Fermi contact interaction due to open shell s electrons (cf. Section I.B.3). When an unpaired s electron is present in a diatomic transition metal oxide it usually shows up clearly in the Fermi contact parameter. Most states with unpaired s electrons have positive values for a_F : a_F for $\text{ScO}^{73} \sigma^2\Sigma^+ = +0.0667 \text{ cm}^{-1}$; a_F for $\text{VO}^{45} \sigma\delta^2 4\Sigma^- = +0.02593 \text{ cm}^{-1}$; a_F for $\text{MnO}^{90} \sigma\delta^2\pi^2 6\Sigma^+ = +0.0151 \text{ cm}^{-1}$. An exception is the ground state of CuO, which has a large, negative Fermi contact parameter in spite of the presence of open shell s σ electrons.⁷⁹ Three configurations are believed to make significant contributions to the $^2\Pi_i$ ground state:



Only the last one has open shell metal-centered orbitals which will participate significantly in the hyperfine interactions. In terms of molecular orbitals, this configuration is proposed to be:⁷⁹



The wavefunction can therefore be expressed as a linear combination of Slater determinants (showing only the unpaired electrons for clarity):

$$\begin{aligned} \psi(^2\Pi_i) = (1/\sqrt{6})\{ & 2|d\sigma(\alpha) p\sigma(\alpha) p\pi(\beta)| - |d\sigma(\alpha) p\sigma(\beta) p\pi(\alpha)| \\ & - |d\sigma(\beta) p\sigma(\alpha) p\pi(\alpha)|\} \end{aligned} \quad (3.16)$$

The authors propose that the negative terms in the wavefunction are responsible for the negative value for a_F of -0.0139 cm^{-1} . The $C^4\Sigma^-$ state of VO, with a $3d\delta^2\sigma^*$ configuration, is an example where the promotion of an electron from $s\sigma$ to a non-s type σ orbital produces a negative value for the $I\cdot S$ interaction constant of -0.00881 cm^{-1} , as a result of spin polarization.⁴⁵ The σ^* orbital is believed to be a linear combination of $3d\sigma$, $4s\sigma$ and $O(2p\sigma)$.

2) the fact that the $\Omega = 7/2$ and $\Omega = 5/2$ subbands lie very close in the spectrum shows that the spin-orbit intervals $A\Lambda''$ and $A\Lambda'$ are nearly equal. The $^4\Delta$ states of the configurations $\sigma^2\pi^2\delta^3$ and $\sigma\pi^2\delta^3\sigma^*$ will have orbital angular momentum coming only from the ' δ ' hole, so that they should have roughly the same spin-orbit couplings.

3) Following from 2), the negative sign of A also suggests a δ hole, or δ^3 configuration.

The $\sigma\pi^2\delta^3\sigma^*$ configuration can give rise to 19 electronic states from the different arrangements of the electrons within the orbitals.⁷⁴ The result will be a dense collection of states ranging up to $S = 5/2$ and $\Lambda = 4$, among which are, for example, a $^4\Gamma$ state with the configuration $\sigma(\uparrow)\pi(\uparrow\downarrow)\delta(\uparrow\downarrow\uparrow)\sigma^*(\uparrow)$, and a $\sigma(\uparrow)\pi(\uparrow\uparrow)\delta(\uparrow\downarrow\uparrow)\sigma^*(\uparrow)$ $^6\Delta$ state. As the states comprising such a melange are expected to interact strongly with one another, this

could explain the extensive perturbations experienced by the upper states of CoO investigated here. As discussed in Section III.C.1.c, the only perturbing state for which we have clear evidence appears to be a $^4\Sigma$ state, arising possibly from a $\sigma\pi^2\delta^3\sigma^*$ configuration, or $2\Sigma \times 1\Delta \times 2\Delta \times 2\Sigma = ^4\Sigma$.

Now that the ground state configuration of CoO has been determined in this work, the entire series of first row diatomic transition metal oxide ground states is now established. The ground states and some major molecular constants of the 3d transition metal monoxides appear in Table 3.V. Although many more excited states of cobalt oxide remain to be discovered, the most interesting results for the immediate future would be the direct measurements of the spin-orbit coupling intervals, and sub-Doppler measurements of the hyperfine structure. However, the experiments would require a more efficient means of generating CoO than has been used so far.

Table 3.VI. Ground states and configurations of the first row diatomic transition metal oxides, with the fundamental vibrational frequency $\Delta G_{1/2}$, B and r for the $v'' = 0$ state, and the spin-orbit interval $A\Lambda$ for the orbitally degenerate electronic states. The $A\Lambda$ value for CoO has not been established with certainty.

| Ground state | Electron configuration | $\Delta G_{1/2}$ (cm ⁻¹) | B_0 (cm ⁻¹) | r_0 (Å) | $A\Lambda$ | Ref |
|------------------|-------------------------|---|------------------------------|--------------|------------|-----------|
| ScO $^2\Sigma^+$ | σ | 964.65 | 0.51343 | 1.668 | - | 29,30 |
| TiO $^3\Delta_r$ | $\sigma\delta$ | 1000.02 | 0.53384 | 1.623 | 101.30 | 89 |
| VO $^4\Sigma^-$ | $\sigma\delta^2$ | 1001.81 | 0.54638 | 1.592 | - | 45,88 |
| CrO $^5\Pi_r$ | $\sigma\delta^2\pi$ | 884.98 | 0.52443 | 1.621 | 63.22 | 90 |
| MnO $^6\Sigma^+$ | $\sigma\delta^2\pi^2$ | 832.41 | 0.50122 | 1.648 | - | 91 |
| FeO $^5\Delta_i$ | $\sigma\delta^3\pi^2$ | 871.15 | 0.51681 | 1.619 | -189.89 | 87 |
| CoO $^4\Delta_i$ | $\sigma^2\delta^3\pi^2$ | 851.7 | 0.5037 ₀ | 1.631 | (-240) | this work |
| NiO $^3\Sigma^-$ | $\sigma^2\delta^4\pi^2$ | 825.4 | 0.505 ₈ | 1.631 | - | 78 |
| CuO $^2\Pi_i$ | $\sigma^2\delta^4\pi^3$ | 629.39 | 0.44208 | 1.729 | -277.04 | 92,93 |

CHAPTER IV

HYPERFINE ANALYSIS OF NIOBIUM NITRIDE

IV.A. Introduction.

Niobium nitride (NbN) is an exemplary molecule in which to study hyperfine interactions in diatomic molecules, because the nuclear magnetic moment (μ_N) of ^{93}Nb exceeds that of any other non-radioactive atom. The magnetic hyperfine structure which results is proportionately large and well-resolved, allowing precise, informative analysis. Following the initial observation of NbN in 1969 by Dunn and Rao⁹⁴, the first low resolution hyperfine analysis of the $^3\Phi$ - $^3\Delta$ system was performed in 1975 by Féménias *et al*⁹⁵ with a grating spectrograph. The study produced values for the magnetic hyperfine constants a , b and c which suggested that the excited $^3\Phi$ state makes a non-negligible contribution to the hyperfine structure. The spectra also exhibited line broadening at very high J values, indicating either Λ -doubling in the $^3\Delta$ state or a transition from case (a_β) to ($b_\beta J$) coupling with increasing rotation. In the meantime, the fundamental frequencies of the ground states of Nb^{14}N and Nb^{15}N were measured to be 1002.5 cm^{-1} and 974 cm^{-1} by IR spectroscopy in a 14 K argon matrix.⁹⁶ A Russian group published a number of papers on the $^3\Phi$ - $^3\Delta$ system^{97,98,99}, culminating in the 1986 publication by Pazyuk *et al*¹⁰⁰, in which they proposed a set of rotational, centrifugal distortion and spin-orbit coupling constants (B , D and A), and an energy level scheme for the system. However, the spin-orbit splittings for both states were drastically miscalculated, and the ordering of the spin-orbit

manifolds was inverted, due to their interpretation of bands they observed near 5600 Å as ${}^3\Phi_3 - {}^3\Delta_3$ and ${}^3\Phi_2 - {}^3\Delta_2$ spin-orbit satellites, rather than as parts of the $\Pi - \Delta$ system to which they actually belong. In 1979, an optical emission study measured eight subbands belonging to five systems, including ${}^3\Phi - {}^3\Delta$, and determined the upper and lower state B values for each.¹⁰¹ Most recent was a grating spectrograph analysis of the ${}^3\Phi - {}^3\Delta$ system performed by the same investigators involved in the preliminary 1975 study, but at a higher resolution (± 0.01 cm⁻¹ line position), and up to $J'' = 88$.¹⁰² Their work produced the following set of molecular constants for the (0,0) band, in units of cm⁻¹ with the uncertainty in the last digit given in parentheses:

| | T_0 | A | δ | B | $10^7 D$ | $10^5 A_D$ |
|-------------|--------------|----------|----------|------------|----------|--------------|
| $X^3\Delta$ | fixed to 0 | 183.0(2) | -33.1(2) | 0.50144(4) | 4.56(6) | ≈ -4 |
| $A^3\Phi$ | 16504.938(3) | 241.6(1) | 7.39(2) | 0.49578(4) | 4.88(6) | ≈ -4 |

The central shift parameter δ accounts for the shift in the ${}^3\Phi_3 - {}^3\Delta$ subband because of second order spin-orbit effects. The investigations described in the current work mark the first high resolution laser spectroscopy performed on NbN.

IV.B. Experimental.

IV.B.1. Synthesis of gaseous niobium nitride.

Niobium nitride was formed in a flow system by reacting the vapor from a sample of warmed niobium (V) chloride ($\approx 80^\circ\text{C}$) with nitrogen. The nitrogen was entrained with argon in a ratio of approximately 1:18 (v/v) at 1 Torr pressure. A few centimeters upstream from the fluorescence cell, the vapor was passed through a 2450 MHz microwave discharge (powered by a Microtron model 200 microwave generator). To obtain intermodulated fluorescence spectra, two nearly coincident laser beams were passed in opposite directions across the lavender-colored flame of the discharge, with the fluorescence detected at right angles to the beams through a deep red low pass filter to the photomultiplier tube, as described in Section II.A.

IV.B.2. Description of the $^3\Phi$ - $^3\Delta$ spectrum.

Broadband spectra of the three subbands of the $^3\Phi$ - $^3\Delta$ system of NbN are illustrated in Fig. 4.1. The middle spin-orbit component, $^3\Phi_3$ - $^3\Delta_2$, is shifted to higher energy rather than being equidistant between the outer subbands, and is also considerably weaker, presumably due to intensity stealing by an unseen state. The vibrational sequences are plainly visible, up to $(v',v'') = (5,5)$ in the $^3\Phi_4$ - $^3\Delta_3$ subband.

At sub-Doppler resolution, the variation in hyperfine structure between the three subbands is apparent from the Q head regions shown in Fig. 4.2. The hyperfine interaction in the $^3\Phi_3$ - $^3\Delta_2$ subband is much less pronounced than that in the other two because

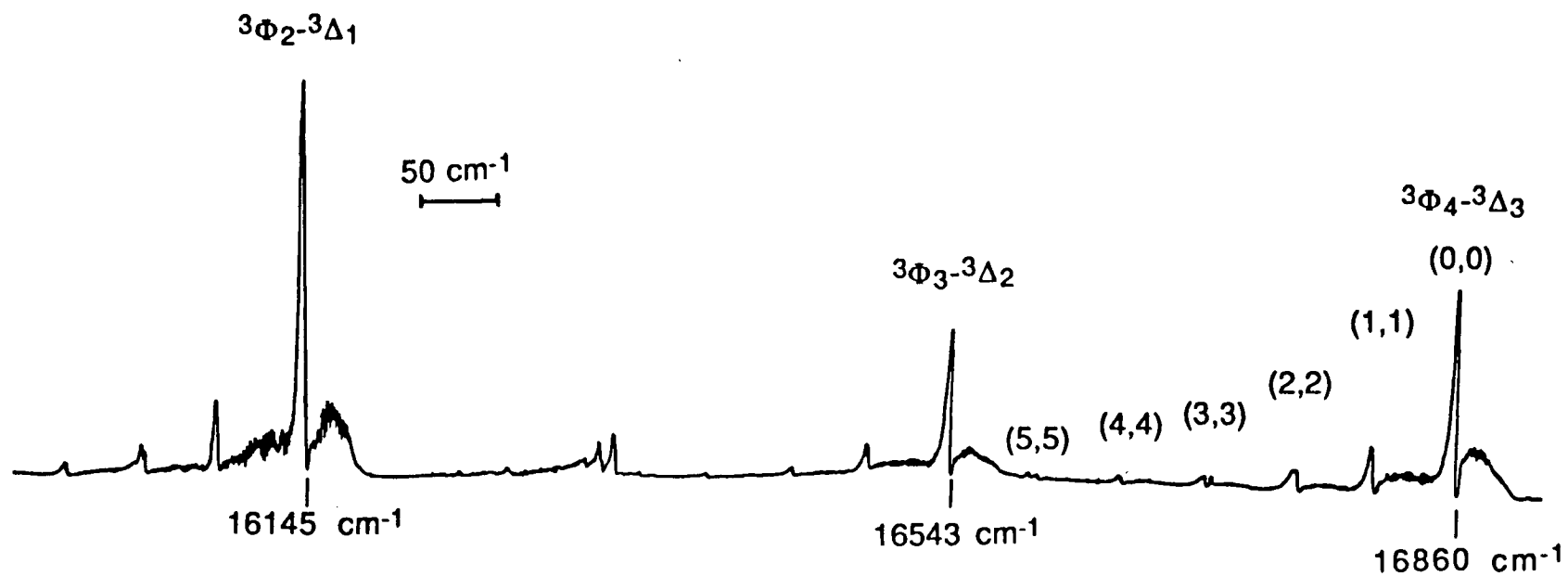


Fig. 4.1. Broadband spectrum of the ${}^3\Phi$ - ${}^3\Delta$ system of NbN, obtained with the intracavity assembly removed, using the dye rhodamine 6G. Note that the vibrational sequence of the ${}^3\Phi_4$ - ${}^3\Delta_3$ subband is visible up to $(v',v'') = (5,5)$.

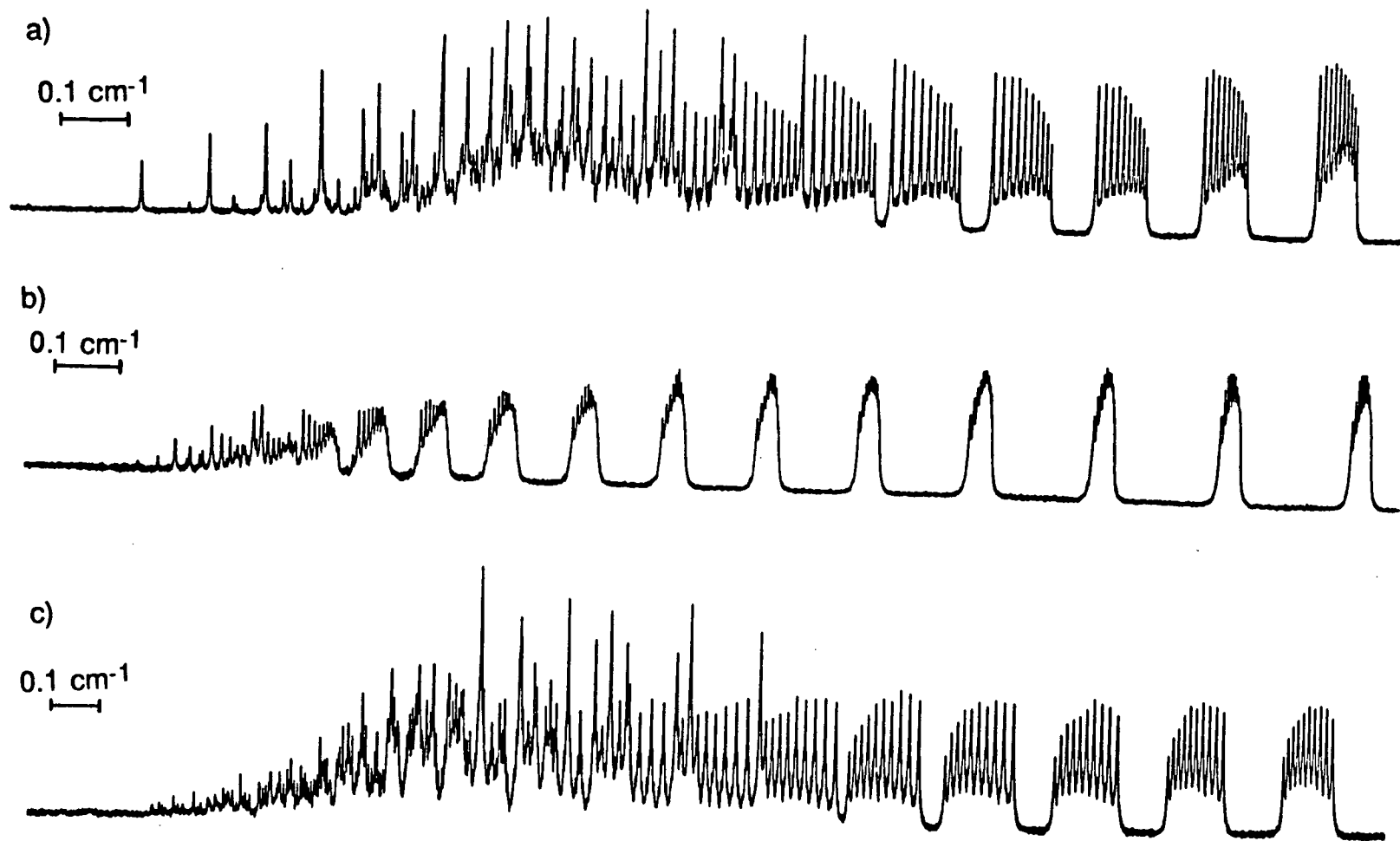


Fig. 4.2. The Q heads of the a) $^3\Phi_2-^3\Delta_1$, b) $^3\Phi_3-^3\Delta_2$, and c) $^3\Phi_4-^3\Delta_3$ subbands of NbN.

the value of Σ in both states is zero. In the ${}^3\Phi_4$ - ${}^3\Delta_3$ subband the hyperfine splitting is considerably larger than that in ${}^3\Phi_2$ - ${}^3\Delta_1$, since Ω is three times as large in the former subband (cf. equations 1.90 and 1.98). The assignment of the densely overlapped ${}^3\Phi_2$ - ${}^3\Delta_1$ Q head is shown in Figs. 4.3 and Fig. 4.4. The low-J R branches of the ${}^3\Phi_2$ - ${}^3\Delta_1$ subband, illustrated in Fig. 4.5, are exemplary for their completely resolved $\Delta F \neq \Delta J$ transitions and crossover resonances (cf. Section II.B for a discussion of these transitions). The hyperfine pattern is quite different in the central subband: at $J'' = 2$ the high F component is on the low frequency side, but at $J'' = 3$ the hyperfine structure reverses order and continues on at higher J values with the highest F component at high frequency. The development of this ${}^3\Phi_3$ - ${}^3\Delta_2$ R branch hyperfine structure is shown in Fig. 4.6.

As the rotation of the molecule increases, spin-uncoupling is observed in the Q branches of the outer two subbands as a reversal in the hyperfine structure: the hyperfine splitting narrows with increasing J until the components collapse into a spike; then they reverse their order and widen with increasing rotation (see Fig. 4.7). Therefore hyperfine structure which begins with its components increasing in F toward increasing frequency reverse to an order in which the F values decrease with frequency. The reversal in the Q branches occurs at $J = 27$ and $J = 38$ in the ${}^3\Phi_2$ - ${}^3\Delta_1$ and ${}^3\Phi_4$ - ${}^3\Delta_3$ subbands, respectively. The hyperfine structure in the ${}^3\Phi_3$ - ${}^3\Delta_2$ transition is less sensitive to the effects of rotation, since its diagonal matrix elements are independent of b and c. The Q branch of

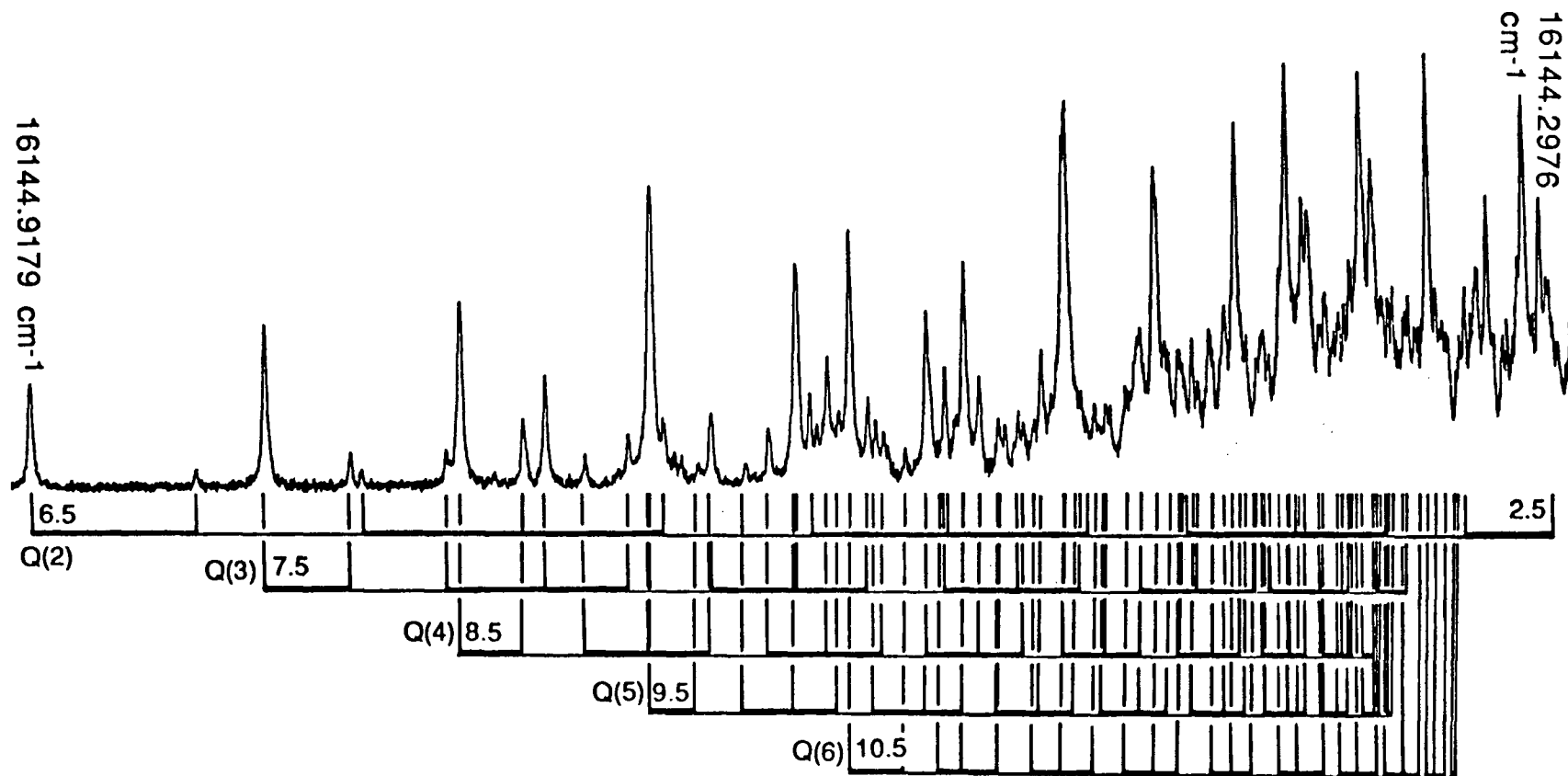


Fig. 4.3. The beginning of the Q head of the ${}^3\Phi_2$ - ${}^3\Delta_1$ subband. Each $\Delta F = 0$ line is connected to the $\Delta F = \pm 1$ lines with the same F'' value by a thick horizontal line. Components of the Q(7) and Q(8) lines are also present in this region, but are not labelled.

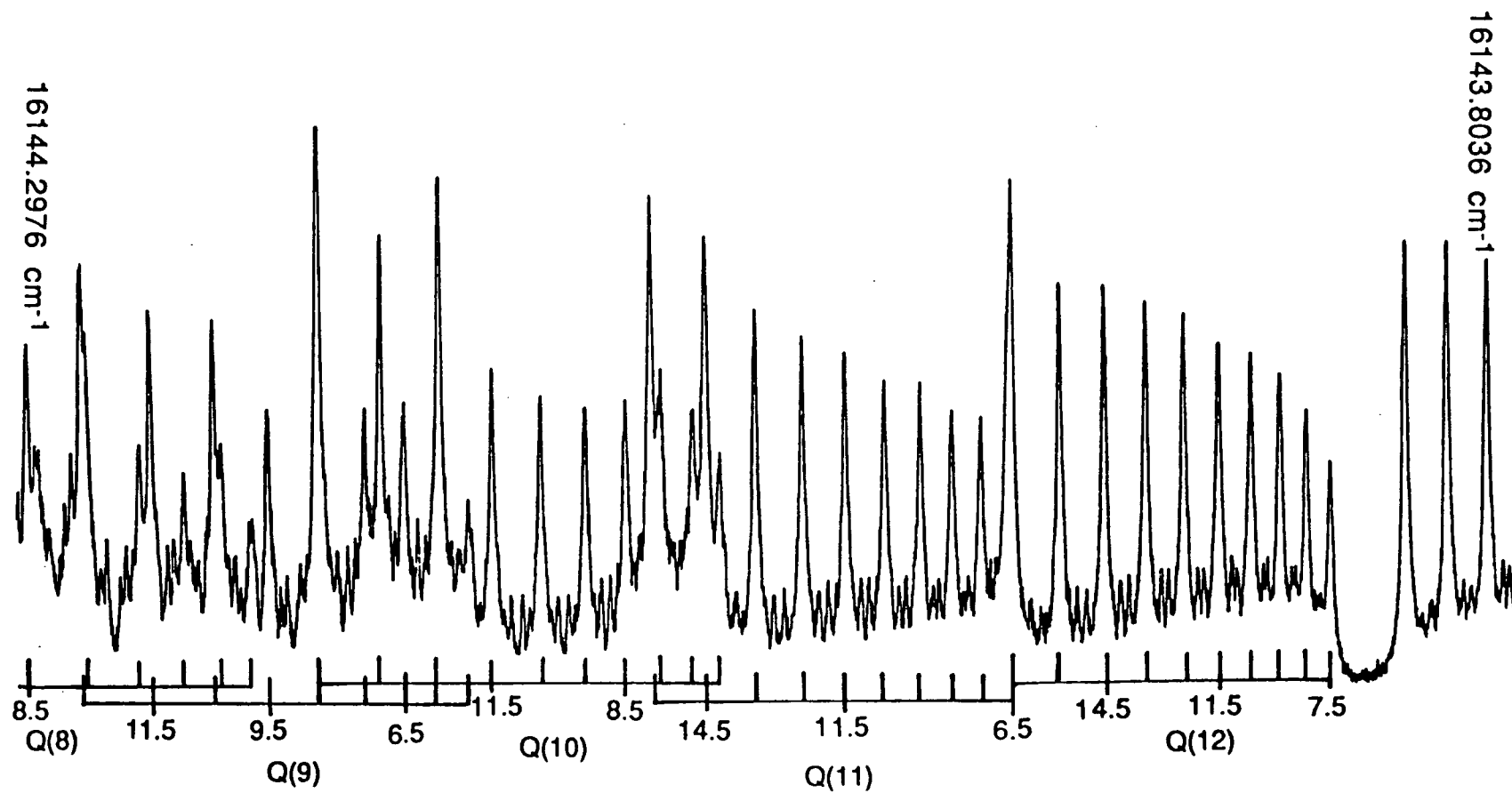


Fig. 4.4. The higher J portion of the ${}^3\Phi_2$ - ${}^3\Delta_1$ Q head, and the first resolved Q lines. The crossover resonances are not labelled.

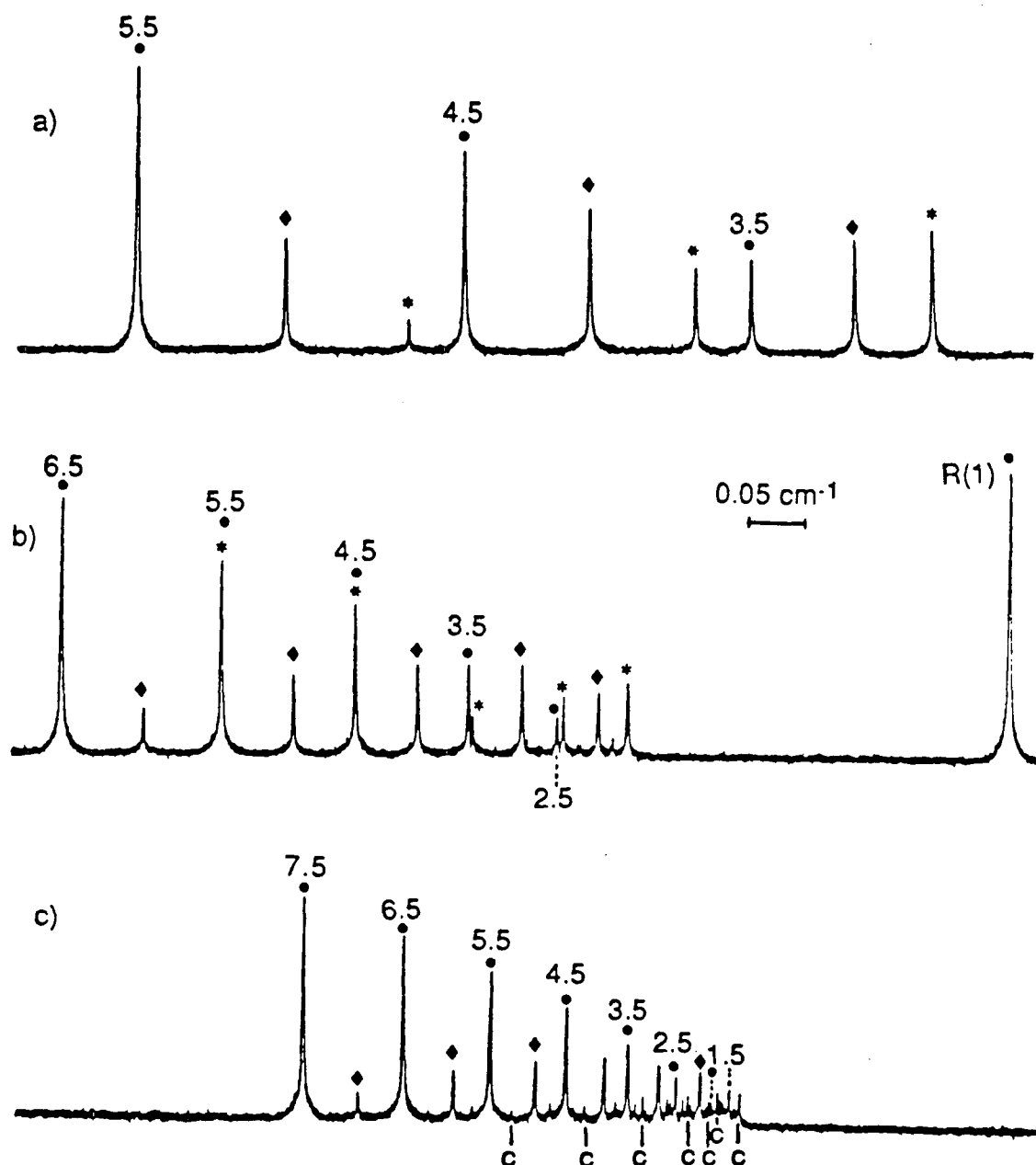


Fig. 4.5. a) R1, b) R2, and c) R3 lines of the $3\Phi_2-3\Delta_1$ subband, illustrating the "forbidden" $\Delta F \neq \Delta J$ transitions (♦ for qR, * for pR) and the crossover resonances (c) between the rR and qR lines. Each $\Delta F = \Delta J$ transition (•) is labelled with the lower state F value, with the corresponding satellite transitions following it to the red (right) in the order: c (if seen), ♦, * (if seen). The scale shown in (b) is the same for all spectra.

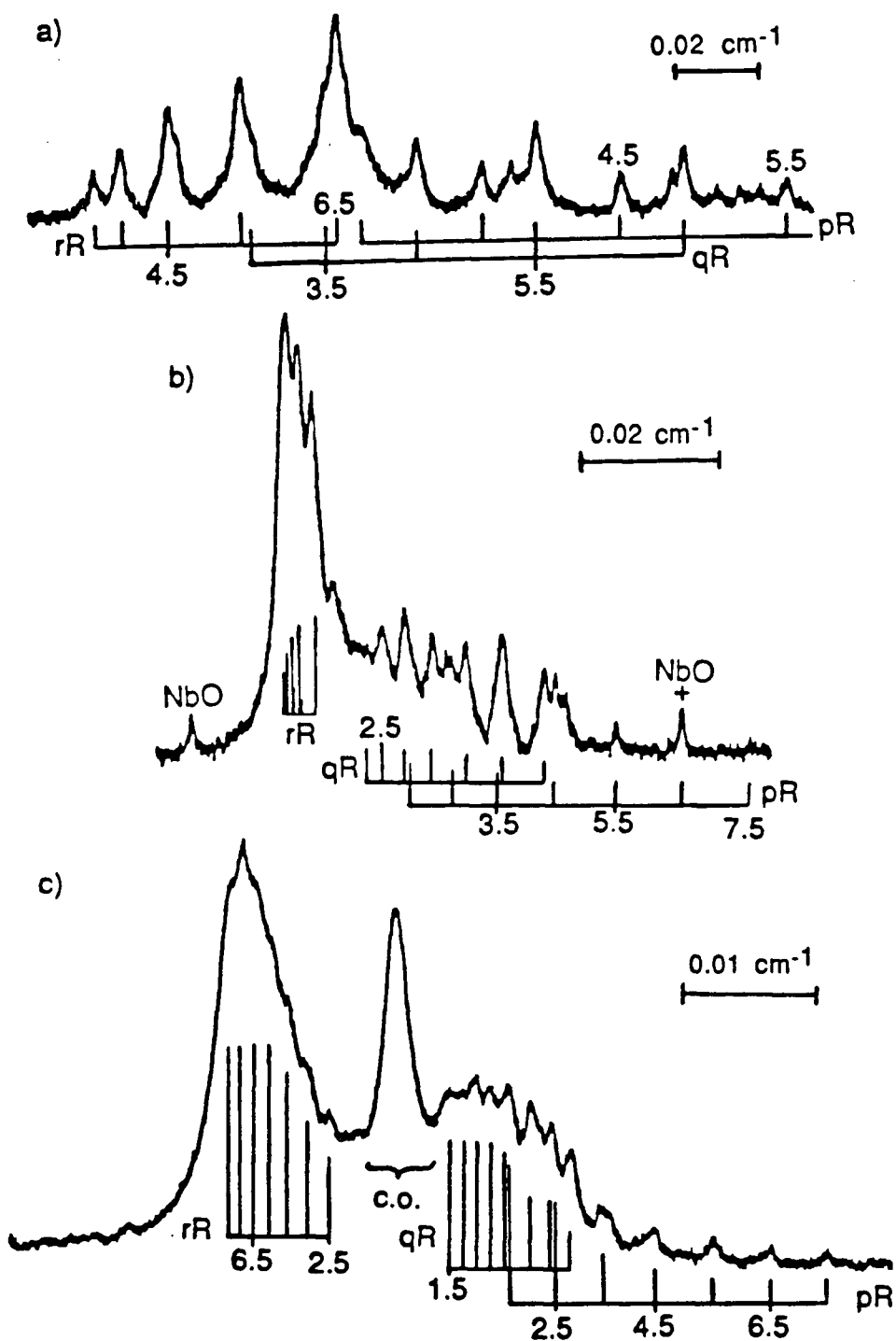


Fig. 4.6. a) R2, b) R3 and c) R4 lines of the $3\Phi_3-3\Delta_2$ subband of NbN, showing the rR, qR and pR transitions and the crossover resonances associated with the rR and qR lines (denoted by c.o.).

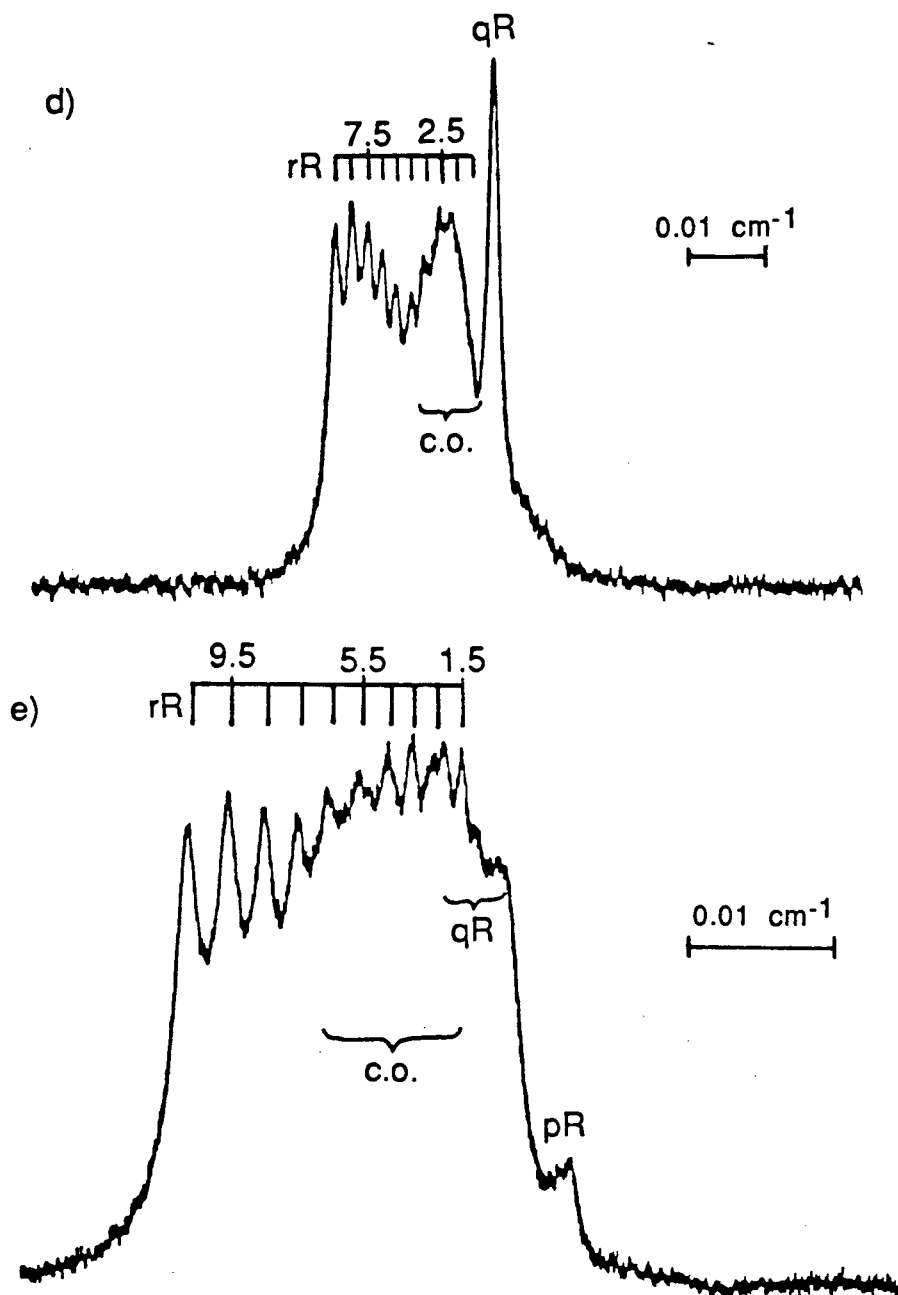


Fig. 4.6. d) R5 and e) R6 lines of the $3\Phi_3-3\Delta_2$ subband of NbN; the labelling follows that of Fig. 4.6 a, b and c.

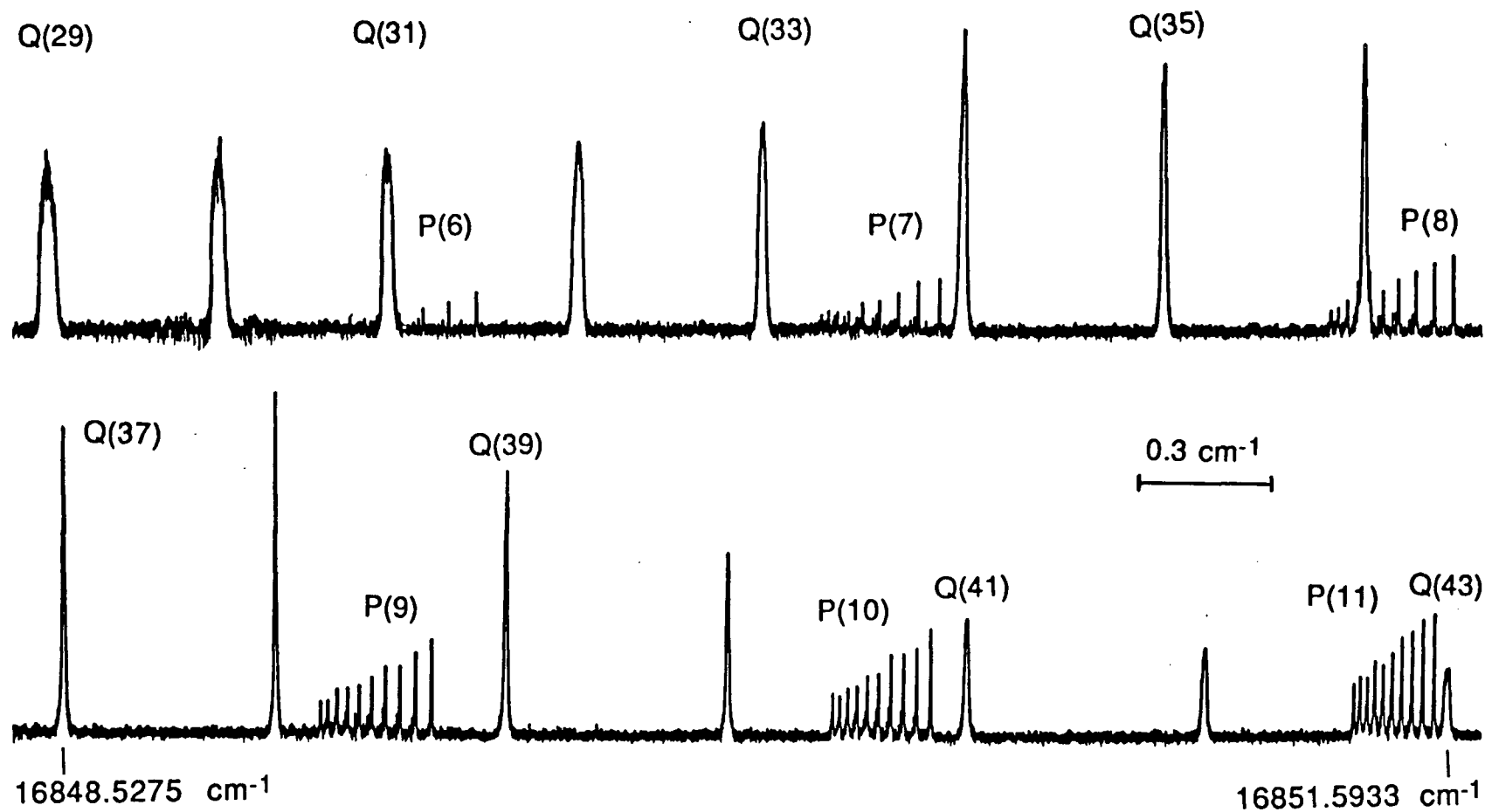


Fig. 4.7. The reversal of hyperfine structure at high J in the ${}^3\Phi_4$ - ${}^3\Delta_3$ Q branch, caused by the effects of spin-uncoupling. Actual reversal occurs in the line of maximum intensity, Q(38).

this subband therefore narrows up to about $J = 12$, and then remains nearly constant in width up to the limit of our data at $J = 27$.

IV. C. Non-Linear Least Squares Fitting of Spectroscopic Data.

In order to acquire the best set of molecular constants in a Hamiltonian, one must iteratively improve an estimated set of constants until a satisfactory fit of the observed data is obtained. In approaching the non-linear type of Hamiltonian typically describing a spectroscopic problem, the Hamiltonian is divided into its two constituents: the coefficients containing the quantum number dependence, and the molecular constants, or¹⁰³

$$\hat{H} = \sum_{m=1}^p X_m H_m \quad (4.1)$$

X_m is the m th parameter (or molecular constant) out of a total of p parameters, and H_m is the "skeleton matrix" containing the quantum number dependence of the m th parameter. For example, a simple 2Π Hamiltonian may be expressed as:¹⁰³

$$\hat{H} = T_0 \cdot \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + A \cdot \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix} + B \cdot \begin{bmatrix} (J + 1/2)^2 - 2 & -[(J + 1/2)^2 - 1]^{1/2} \\ -[(J + 1/2)^2 - 1]^{1/2} & (J + 1/2)^2 \end{bmatrix}$$

The matrix of eigenvalues (or energy levels) E of the Hamiltonian is obtained by diagonalization with the eigenvectors U :

$$U^\dagger \hat{H} U = E \quad (4.2)$$

U is a unitary matrix such that the adjoint of U (U^\dagger , or the conjugate of the transpose U^T) equals the inverse of U (U^{-1}).

The combination of equations (4.1) and (4.2) allows the Hellmann-Feynman theorem to be employed, which states:¹⁰⁴

$$\partial E_m / \partial X = \int \Psi_m^* (\partial H / \partial X) \Psi_m d\tau \quad (4.3)$$

For a single matrix element ii of parameter m , the Hellmann-Feynman theorem becomes:¹⁰³

$$[\mathbf{U}^T(\partial\hat{H}/\partial X_m)\mathbf{U}]_{ii} = \partial E_i/\partial X_m = B_i \quad (4.4)$$

Using equation (4.1), equation (4.4) can also be written as:

$$B_{im} = [\mathbf{U}^T\hat{H}_m\mathbf{U}]_{ii} \quad (4.5)$$

The Hellmann-Feynman derivatives B_{im} form the derivatives matrix, \mathbf{B} , which give the dependence of the energy on variations in the parameters.

To apply this relation to an iterative solution of unknown molecular parameters, equation (4.2) is expressed in terms of a single energy level, E_i^{calc} :

$$E_i^{\text{calc}} = (\mathbf{U}^T\hat{H}\mathbf{U})_{ii} \quad (4.6)$$

Substituting equation (4.1) into equation (4.6) gives

$$E_i^{\text{calc}} = \sum_{m=1}^p X_m (\mathbf{U}^T\hat{H}_m\mathbf{U})_{ii} \quad (4.7)$$

With the relations in equations (4.4) and (4.5), the energy can be written:

$$E_i^{\text{calc}} = \sum_{m=1}^p X_m B_{im} \quad (4.8)$$

To express equation (4.8) in terms of transitions rather than energy levels, the upper and lower state eigenvalue vectors (\mathbf{E}' and \mathbf{E}'') are subtracted to give \mathbf{y} , and \mathbf{B}' and $-\mathbf{B}''$ are combined into one derivatives matrix \mathbf{B} . Equation (4.8) therefore transforms to:¹⁰⁵

$$\mathbf{y} = \mathbf{B}\mathbf{X} \quad (4.9)$$

where \mathbf{y} is the vector of calculated transitions, \mathbf{B} is the matrix of known derivatives, and \mathbf{X} is the vector of estimated parameters. If

there are N transitions and p parameters to be determined, \mathbf{y} has length N , \mathbf{B} is a matrix of size N by p , and \mathbf{X} has length p . To obtain \mathbf{X} , both sides of equation (4.9) are multiplied by $(\mathbf{B}^T \mathbf{B})^{-1} \mathbf{B}^T$:

$$\begin{aligned} (\mathbf{B}^T \mathbf{B})^{-1} (\mathbf{B}^T \mathbf{B}) \mathbf{X} &= (\mathbf{B}^T \mathbf{B})^{-1} \mathbf{B}^T \mathbf{y} \\ \mathbf{X} &= (\mathbf{B}^T \mathbf{B})^{-1} \mathbf{B}^T \mathbf{y} \end{aligned} \quad (4.10)$$

In a problem where the estimated parameters \mathbf{X} are iteratively improved, we calculate parameter changes $\Delta \mathbf{X}$, rather than \mathbf{X} itself. Equation (4.10) is therefore expressed as:¹⁰⁶

$$\Delta \mathbf{X} = (\mathbf{B}^T \mathbf{B})^{-1} \mathbf{B}^T \Delta \mathbf{y} \quad (4.11)$$

where $\Delta \mathbf{y}$ is the vector of residuals (i.e., the observed transitions minus the calculated). The fitting process begins with a set of estimates for the molecular constants, which are used to generate calculated transitions (y^{calc}) and their residuals (Δy). The set of corrections to the constants, given by equation (4.11), is added to the initial estimates to provide improved constants for the next iteration. The process is repeated, iteratively producing improved sets of calculated transitions, residuals and constants until the magnitude of the residuals is reduced to a satisfactory level, for example, to the vicinity of the experimental precision.

The least squares program for the $^3\Phi - ^3\Delta$ system of NbN was written in FORTRAN 77 by the author, except for UBC Amdahl library routines for diagonalizing and inverting matrices, and calculating parameter changes from the Hellman-Feynman derivatives. The Hamiltonian matrices for the $^3\Phi$ and $^3\Delta$ states have a maximum dimension of $(2I + 1)(2S + 1)$, or 30. The 30 x 30 matrices (one for each F) were diagonalized in two steps. In the first step, only the rotational part of the Hamiltonian was diagonalized, in ten separate

J submatrices. In the second step, the entire matrix (rotational and hyperfine) was diagonalized. Two steps were employed because the ordering of eigenvalues from step one was used in the second diagonalization to preserve the matching of eigenvalues with the original basis functions. This is possible because the separation of the spin-orbit components is large compared to the perturbation made by the hyperfine interactions.

Analogous to the common formula for the standard deviation,

$$s = [\sum (x^{\text{obs}} - x^{\text{calc}})^2/n]^{1/2} \quad (4.12)$$

the weighted least squares standard deviation is obtained from:¹⁰⁵

$$\sigma = \left[\sum_{i=1}^n (y_i^{\text{obs}} - y_i^{\text{calc}})^2 W_{ii}/(n-m) \right]^{1/2} \quad (4.13)$$

where n is the number of independent measurements, m the number of unknowns to be estimated, $n-m$ the degrees of freedom, and W_{ii} the diagonal element of the weight matrix for point i .¹⁰⁵ To determine estimates of the precision of the estimated constants, a variance-covariance matrix Θ is calculated by:¹⁰⁵

$$\Theta = \sigma^2 (\mathbf{B}^T \mathbf{B})^{-1} \quad (4.14)$$

A diagonal element Θ_{ii} is called the variance (not to be confused with the variance that is the square of the standard deviation, σ^2). The square root of Θ_{ii} gives the standard error, or precision, of estimated molecular constant i . The off-diagonal elements Θ_{ij} are covariances. Both the variances and covariances are only estimated values, because they depend on the precision of the measurements, σ^2 . The goodness of the structure of the model lies in $(\mathbf{B}^T \mathbf{B})^{-1}$.

Normalization of the variance-covariance matrix gives the correlation matrix, **C**, with elements

$$c_{ij} = \Theta_{ij}/(\Theta_{ii}\Theta_{jj})^{1/2} \quad (4.15)$$

where $c_{ij} = 1$ for $i = j$, and $(-1 < c_{ij} < +1)$ for $i \neq j$. **C** is independent of the precision of the measurements since σ^2 has been cancelled out. Therefore the off-diagonal elements represent the interdependence of the molecular constants on one another, for a given data set. A value for c_{ij} that closely approaches unity indicates that constants i and j cannot be determined independently.

IV.D. Results and Discussion.

Initial line assignments were facilitated by the unpublished grating spectrograph work of Dunn *et al*¹⁰², who listed the positions of the P, Q and R rotational lines. Initial attempts to obtain a least squares fit to the hyperfine constants in a case (a) basis (i.e., as they were presented in Sections I.D.3 and I.D.4) did not succeed, because the hyperfine constants required to fit the three subbands are not consistent with one another. In the light of this observation, and the unequal first order spin-orbit spacings, it was concluded that the various substates are perturbed differently by second order spin-orbit interactions. According to the $\Delta\Omega = 0$ selection rule for this interaction¹⁰⁹, the electronic states perturbing the $^3\Phi$ substate include $^3\Gamma_{3,4}$, $^1\Gamma_4$, $^1\Phi_3$, $^3\Delta_{2,3}$ and $^1\Delta_2$. The $^3\Delta$ substates can interact with $^3\Phi_{2,3}$, $^1\Phi_3$, $^1\Delta_2$, $^3\Pi_{1,2}$ and $^1\Pi_1$. The $^1\Phi$ and $^1\Delta$ states isoconfigurational with $^3\Phi$ and $^3\Delta$ are expected to be the closest of these states to $^3\Phi$ and $^3\Delta$, and therefore the ones most responsible for the perturbations (see Fig. 4.8). The effect would be to shift the central spin-orbit components, $^3\Phi_3$ and $^3\Delta_2$, to lower energy. However, the hyperfine constants suggest that there could also be second order spin-orbit interactions occurring with the other members of the manifolds, though we can say nothing about their relative sizes. The $^3\Phi$ - $^3\Delta$ system of NbN is the first observed instance of a molecule represented by Hund's case (a) which requires modifications to the Hamiltonian because of extensive second order spin-orbit interactions. This phenomenon can be considered a slight tendency toward the case (c) coupling scheme.¹⁰⁹

The molecular constants obtained for the $^3\Phi$ - $^3\Delta$ system of NbN

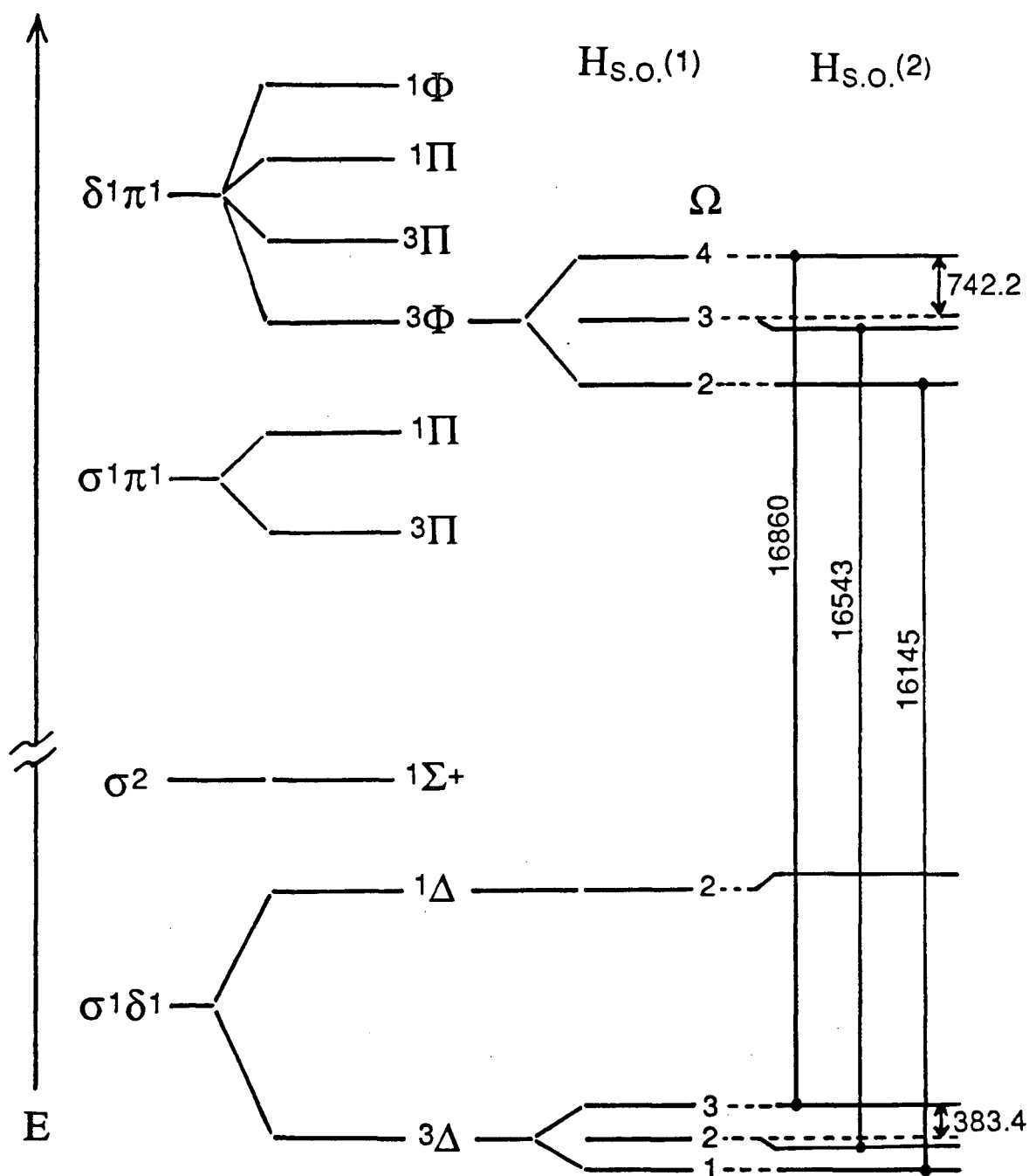


Fig. 4.8. Partial energy level diagram for NbN. The figure is not to scale, but illustrates the relative ordering of states, except in the case of the low-lying configurations σ^2 and $\sigma\delta$ where the ordering is uncertain.

are given in Table 4.1. The unequal perturbations in the $^3\Phi$ and $^3\Delta$ spin-orbit manifolds means that, in the magnetic hyperfine structure, only the h constants in the matrix elements diagonal in Ω and Σ can be determined, rather than individual a , b and c constants (cf. equations 1.90 and 1.98). The h constants, subscripted by their Σ values, are as follows:

$$h_{-1} = a\Lambda - b - c = a\Lambda - (b + c)_{-1} \quad (4.16)$$

$$h_0 = a\Lambda \quad (4.17)$$

$$h_{+1} = a\Lambda + b + c = a\Lambda + (b + c)_{+1} \quad (4.18)$$

In an unperturbed system, the average of h_{-1} and h_{+1} equals h_0 ; that is, $(b + c)_{-1}$ and $(b + c)_{+1}$ in equations (4.16) and (4.18) are equal. This is far from the case in the $^3\Phi$ - $^3\Delta$ system of NbN, where $(b + c)_{+1}$ is 39% smaller than $(b + c)_{-1}$ in the $^3\Delta$ state, and 10% larger in $^3\Phi$. It was also found, in the $^3\Delta$ state, that two distinct b constants are required in the $\langle \Sigma = -1 | \Sigma = 0 \rangle$ and $\langle \Sigma = 0 | \Sigma = +1 \rangle$ matrix elements (referred to here as $b_{-1/0}$ and $b_{0/+1}$, respectively). Therefore, a total of five magnetic hyperfine constants are required to fit the data, rather than the usual three: h_{-1} , h_0 , h_{+1} , $b_{-1/0}$ and $b_{0/+1}$ replace a , b and c .

It is clear that the perturbations in the $^3\Delta$ state are much more pronounced than those in $^3\Phi$. The $^3\Delta$ $b_{+1/0}$ value is 34% smaller than $b_{0/-1}$, comparable to the 39% difference between the $^3\Delta$ $(b + c)_{-1}$ and $(b + c)_{+1}$ constants. In the upper state, however, two distinct b values off-diagonal in Σ are not necessary: attempts to distinguish two $^3\Phi$ b constants produced values that were very highly correlated (-0.998) and with standard errors so high that the constants were indeterminable. It is evident, then, that the $^1\Delta$ state lies closer to

Table 4.1. Molecular constants for the $^3\Phi$ - $^3\Delta$ system of NbN.^a

| | Φ | Δ |
|--------------------|----------------------------|-----------------------------|
| T_0 | 16518.509(1) | 0 |
| A | 247.4116(5) | 191.7038(8) |
| B | 0.495814(4) | 0.501465(4) |
| D | $0.4943(4) \times 10^{-6}$ | $0.4622(2) \times 10^{-6}$ |
| λ | -16.817(2) | 3.430(2) |
| γ | 0.011(2) | -0.0217(6) |
| A_D | $-0.58(2) \times 10^{-4}$ | $-0.105(3) \times 10^{-3}$ |
| λ_D | $-0.150(6) \times 10^{-4}$ | $-0.1314(6) \times 10^{-3}$ |
| h_{-1} | 0.0633(2) | -0.0616(3) |
| h_0 | 0.0411(4) | 0.0458(5) |
| h_{+1} | 0.0168(2) | 0.1112(3) |
| b | -0.02(1) | - |
| $b_{-1/0}$ | - | 0.085(5) |
| $b_{0/+1}$ | - | 0.056(5) |
| e^2Qq_0 | $-0.39(8) \times 10^{-2}$ | fixed to zero |
| Derived constants: | | |
| $(b+c)_{-1}$ | -0.0222(4) | 0.1074(6) |
| $(b+c)_{+1}$ | -0.0246(5) | 0.0654(6) |
| σ | 0.000547 | |

^a Values are in cm^{-1} . The numbers in parentheses are three times the standard errors of the constants, in units of the last significant figure. The standard deviation of the transition measurements is given by σ . The magnetic hyperfine constants, h , $(b + c)$ and b , are explained in the text.

the $^3\Delta$ state than $^1\Phi$ does to $^3\Phi$. Note from Fig. 4.8 that the ordering of states in the $\delta\pi$ manifold is contrary to that dictated by Hund's rule¹¹⁰, which would place the higher multiplicity $^1\Phi$ state below $^1\Pi$ (and therefore closer to the $^3\Phi$ state). The dipolar hyperfine constant c cannot be extracted since separate b constants are required for the three substates.

The $(b + c)$ and b constants clearly support the $5s\sigma^1 4d\delta^1$ and $4d\pi^1 \delta^1$ configurations for the $^3\Delta$ and $^3\Phi$ states, respectively. The $^3\Delta$ $(b + c)$ and b values are large and positive, indicating that the dominant mechanism for the coupling of electronic and nuclear spins is the Fermi contact interaction. This is consistent with the presence of an unpaired σ electron, as in the $s\sigma^1 d\delta^1$ configuration of $^3\Delta$. The $^3\Phi$ $(b + c)$ and b constants are negative, and small compared to those in $^3\Delta$. This is characteristic of a hyperfine interaction which occurs because of spin polarization by electrons in orbitals having nodes at the nucleus, such as $\pi^1 \delta^1$. The difference between the Fermi contact and spin polarization hyperfine constants in NbN is similar to that found in the VO states⁴⁵ $4s\sigma^1 3d\delta^2 X^4\Sigma^-$ and $4p\sigma^1 3d\delta^2 C^4\Sigma^-$. The ratio of $^3\Delta(b + c)_{ave}/^3\Phi(b + c)_{ave} = -3.7$, while $b(X^4\Sigma^-)/b(C^4\Sigma^-) = -3.1$.

The quadrupole coupling constant for the lower state is $-3.9 (\pm 0.8) \times 10^{-3} \text{ cm}^{-1}$, while that of the upper state was fixed to zero after it was found to be too small to be determined. The sign of the $^3\Phi$ state e^2Qq_0 is consistent with the quadrupole moment for ^{93}Nb of $-2 \times 10^{-24} \text{ e}\cdot\text{cm}^2$. The upper and lower state constants for the interaction of nuclear spin and rotation (c_l) were fixed to zero, as they were found to be on the order of -10^{-5} to -10^{-6} cm^{-1} , almost completely

correlated (.999), and with standard errors as large as the values themselves. It is the usual case for diatomics containing a transition metal for c_1 to be too small to be determined (see for example references 31, 45, 79 and 91).

In the rotational part of the Hamiltonian, the A , B and D constants are very well determined in spite of the high correlations between A' and A'' (.9985) and B' and B'' (.995). The high rotational lines carrying information about the spin-uncoupling operator, $-2\mathbf{BJ} \cdot \mathbf{S}$, allow B and D to be determined individually, rather than simply determining their differences, $B' - B''$ and $D' - D''$. Since all three subbands were fitted simultaneously, and B was extracted with good precision, A could also be determined. This is possible since A , B and the effective B values for each subband are related by:²⁴

$$B_{\text{eff},\Omega} = B(1 + 2B\Sigma/A\Lambda) \quad (4.19)$$

From the B values, the bond lengths are calculated to be:

$$r_0(^3\Delta) = 1.6618 \text{ \AA}$$

$$r_0(^3\Phi) = 1.6712 \text{ \AA}$$

There have been very few rotational studies of transition metal mononitrides. Aside from the current work, the known bond lengths (r_0 , in \AA) are:

| | | |
|--------------------|---------------------------|-------|
| TiN ¹¹¹ | X ² Σ | 1.583 |
| | A ² Π_r | 1.597 |
| | B ² Σ | 1.646 |
| ZrN ¹¹² | X ² Σ | 1.696 |
| | B ² Σ | 1.740 |
| | A ² Π | 1.702 |
| MoN ¹¹³ | X ⁴ Σ^- | 1.634 |

A⁴Π 1.654

The 3d transition metal monoxide series isovalent with ZrN (and TiN), NbN, MoN is ScO, TiO, VO, whose ground state bond lengths go as 1.668 Å³⁰, 1.623 Å⁸⁹ and 1.592 Å⁴⁵. Here the bond length decreases with each addition of a bonding δ electron. The ³Δ and ³Φ NbN bond lengths show that the nitrides are consistent with this trend, with values intermediate between those of ZrN and MoN.

The very large spin-spin interaction constants λ (equations 1.72 and 1.73) are caused by contributions from the second order spin-orbit interactions which induce the substantial shift of the ³Φ₃-³Δ₂ subband. The centrifugal distortion correction to λ , however, is considerably larger than its expected value of $\lambda_D \approx \lambda(A_D/A)$. The reason for this probably lies in the fact that we have not yet made direct measurements of the spin-orbit intervals. In this context, then, the centrifugal distortion correction constants A_D and λ_D are essentially fudge factors which enable the least squares fit to converge to a minimum lying within a broad minimum which contains the true molecular constants. So although this set of constants is an internally consistent one which fits the data, once the derived A values are replaced by direct measurements the constants may change slightly to enable the fit to converge to the true, nearby minimum. With the data we now possess, however, the A_D and λ_D values given in Table 4.1 are necessary to obtain a fit.

To demonstrate this fact, a fit of the rotational constants was made in which λ_D and γ were fixed to zero, and all hyperfine constants were fixed at the values determined in this work. The initial values for the floated constants were taken from the grating

spectrograph work of Dunn *et al*¹⁰² (see p. 85), with the exception of A_D which was given an initial value of zero; the parameter δ in their work is equal to -2λ . The fit converged to a standard deviation of 0.00138 cm^{-1} , which is about 2.5 times higher than the fit which incorporates λ_D and γ . As expected, the final set of constants (Table 4.II) is very similar to those determined by the grating spectrograph analysis, with the exception of T_0 , which was found from LIF data to be 13.5 cm^{-1} higher than that from the grating work. The residuals contain systematic errors in the positions of the rotational lines, as compared to the random residuals generated by the full set of constants. The systematic errors and higher standard deviation reflect the inability of the model to fit the data without λ_D , A_D and γ . However, as stated above, the resulting rotational constants, other than B and D, are only effective ones. Another important feature of this fit is that the first order spin-orbit coupling constants A' and A'' are 100% correlated, as are the second order spin-orbit parameters λ' and λ'' (see the correlation matrix in Table 4.II). This is a direct reflection of the fact that the spin-orbit coupling constants are derived rather than measured. As a result, only the difference $\Delta\lambda$ can be determined, rather than separate λ' and λ'' values. For these reasons, a fit excluding λ_D and γ may produce a set of rotational constants that more accurately represents the real situation, though the addition of λ_D and γ creates a model which is able to fit the data. It is worth noting that in a purely case (a) basis, γ , A_D and λ_D are correlated such that only two of the three can be determined.⁴¹ In the $3\Phi-3\Delta$ system of NbN this correlation is broken

Table 4.II. Rotational constants obtained for the 3Φ - 3Δ system of NbN with the λ_D and γ parameters fixed to zero, and the hyperfine constants fixed to the values in Table 4.I.^a The correlation matrix follows the constants.

| | Φ | Δ |
|-----------|----------------------------|----------------------------|
| T_0 | 16518.4653(2) | 0 |
| A | 242.59(8) | 184.5(1) |
| B | 0.495796(8) | 0.501447(8) |
| D | $0.5005(7) \times 10^{-6}$ | $0.4685(4) \times 10^{-6}$ |
| λ | -3.70(8) | 16.53(8) |
| A_D | $-0.484(5) \times 10^{-4}$ | $-0.793(8) \times 10^{-4}$ |
| σ | 0.00138 | |

^aThe format of the table follows that of Table 4.I.

| Correlation Matrix | | | | | | |
|--------------------|--------|--------|---------|---------|-----------|---------|
| | T_0 | A' | B' | D' | λ | A_D |
| T_0 | 1.0000 | 0.0996 | 0.0820 | -0.4333 | 0.3401 | 0.1538 |
| A' | | 1.0000 | -0.0473 | 0.1235 | 0.5124 | -0.0645 |
| B' | | | 1.0000 | -0.0973 | 0.0934 | -0.3204 |
| D' | | | | 1.0000 | 0.0366 | -0.4503 |
| λ' | | | | | 1.0000 | -0.0664 |
| A_D' | | | | | | 1.0000 |

| | A'' | B'' | D'' | λ'' | A_D'' |
|-------------|---------|---------|---------|-------------|---------|
| T_0 | 0.0995 | 0.1580 | -0.2227 | 0.3408 | 0.1715 |
| A' | 1.0000 | -0.0335 | 0.3977 | 0.5115 | 0.3233 |
| B' | -0.0474 | 0.9936 | -0.0789 | 0.0928 | -0.3322 |
| D' | 0.1233 | -0.1874 | 0.4224 | 0.0360 | -0.2099 |
| λ' | 0.5124 | 0.1025 | -0.2270 | 1.0000 | 0.0874 |
| A_D' | -0.0643 | -0.2737 | -0.0883 | -0.0659 | 0.8660 |
| A'' | 1.0000 | -0.0336 | 0.3976 | 0.5116 | 0.3233 |
| B'' | | 1.0000 | -0.0839 | 0.1020 | -0.2929 |
| D'' | | | 1.0000 | -0.2275 | 0.0982 |
| λ'' | | | | 1.0000 | 0.0875 |
| A_D'' | | | | | 1.0000 |

to some extent by the high J data where there is a distinct tendency towards case (b) (see the correlation matrices in Appendix I and Table 4.II).

For the future, a direct measurement of the spin-orbit intervals must be made. The most likely method for doing this is to locate forbidden "spin-orbit satellite" transitions which disobey the case (a) selection rule $\Delta\Sigma = 0$ (equation 1.57). Since these transitions are very weak, resolved fluorescence experiments can be performed to enhance the signal. To record the spectrum of a ${}^3\Phi_2$ - ${}^3\Delta_2$ line, for example, an allowed ${}^3\Phi_2$ - ${}^3\Delta_1$ transition is excited. The resulting emission spectrum of the satellite transition is recorded over a long exposure time using the microchannel-plate intensified array detector. The lines which hold the most promise for producing spin-orbit satellites are high J lines affected by spin-uncoupling, since the $\Delta\Sigma = 0$ selection rule weakens with increasing rotation. However, it is also important that the excited line be strong, so a compromise must be made between high J and line strength when choosing lines for excitation.

Other important tasks are to locate the singlet states which interact with the ${}^3\Delta_2$ and ${}^3\Phi_3$ spin-orbit components, and to search for the expected $\sigma^2 {}^1\Sigma^+$ state to determine if the ground state is ${}^3\Delta$ or ${}^1\Sigma^+$. The ordering of the $\sigma\delta$ states (${}^3\Delta$ and ${}^1\Delta$) and the σ^2 state (${}^1\Sigma^+$) depends on the relative ordering of the $4s\sigma$ and $3d\delta$ metal-centered molecular orbitals (see Fig. 3.1). Diatomic transition metal oxides and fluorides isoelectronic with NbN demonstrate that these orbitals lie very close to one another. Therefore one cannot readily predict in NbN whether the ${}^3\Delta_r$ or ${}^1\Sigma^+$ state will be lower in energy.

For example, the d²-transition metal monoxide series, consisting of titanium oxide (TiO), zirconium oxide (ZrO) and hafnium oxide (HfO), is variable in this respect. TiO has a $^3\Delta_r$ ground state¹¹⁴, with the $^1\Delta$ state lying 3500 cm⁻¹ above that¹¹⁵. However, ZrO has a $^1\Sigma^+$ ground state¹¹³ which lies 1650 cm⁻¹ below the $^3\Delta_r$ state¹¹⁶. HfO is believed to have a $^1\Sigma^+$ ground state also, but with the $\sigma\delta$ states further removed from the ground state than those in ZrO due to the greater ligand field splitting between the σ and δ orbitals in HfO.¹¹⁴ In the d¹-transition metal monofluoride series, comprising scandium fluoride (ScF), yttrium fluoride (YF) and lanthanum fluoride (LaF), ScF¹¹⁵ and YF have $^1\Sigma^+$ ground states, while the ordering of $^1\Sigma^+$ and $^3\Delta_r$ in LaF is not known¹¹⁸. Tantalum nitride (TaN), the 5d counterpart of NbN, is predicted from matrix isolation studies to have a $^1\Sigma$ ground state, though the possibility of $^3\Delta$ has not been entirely ruled out.¹¹⁹ To identify the ground state of NbN securely, then, the relative position of the $^1\Sigma^+$ and $^3\Delta_r$ states must be determined experimentally.

CHAPTER V
ROTATIONAL ANALYSIS OF THE ν_7 -FUNDAMENTAL
OF AMINOBORANE, NH_2BH_2

V.A. Background.

This work examines the BH_2 out-of-plane wagging fundamental of aminoborane (NH_2BH_2), the simplest alkene in the $\text{B}=\text{N}$ homologues of the hydrocarbons. Long before NH_2BH_2 was studied experimentally, its small size and the interest in B-N compounds led to extensive theoretical studies of it. In particular, the donor-acceptor nature of the B-N bond attracted attention, as Hückel theory calculations¹²⁰ done in 1964 predicted that the bond moment was in the direction B to N rather than the reverse, as required by formal valence theory. These preliminary calculations, covering charge distributions, electronic structures and geometries for a number of B-N compounds, were followed by CNDO (complete neglect of differential overlap)¹²¹ and ab initio^{122,123,124} calculations predicting these and other properties such as the dipole moment, force constants, barriers to rotation and stabilities. Aminoborane's extreme instability at room temperature, however, imposed practical difficulties for experimentalists to verify or refute the theoreticians' predictions. Its first synthesis was in 1966 from the symmetrical cleavage of vacuum sublimed cycloborazine pyrolyzed at 135°C, where NH_2BH_2 and other decomposition products could be trapped in a liquid nitrogen cold trap, and then identified by mass spectroscopy¹²⁵. The aminoborane was found to have decomposed spontaneously after warming to room temperature. In

1968, gaseous aminoborane and diborane (B_2H_6) were observed by molecular beam mass spectroscopy as products of the spontaneous decomposition of solid ammonia borane (NH_3BH_3) at room temperature.¹²⁶ When Kwon and McGee performed both pyrolysis and radiofrequency discharge experiments on borazine (the BN analog of benzene), NH_2BH_2 and B_2H_6 were again the products.¹²⁷ They were recovered in a $-168\text{ }^{\circ}C$ trap, then separated by vacuum distillation of diborane from aminoborane at $-155\text{ }^{\circ}C$. At this temperature, small amounts of both evaporation and polymerization of NH_2BH_2 were observed. Polymerization becomes the dominant process at temperatures above this, and is fairly significant at $-130\text{ }^{\circ}C$.¹²⁷ The pronounced instability of monomeric aminoborane led Pusatcioglu *et al*¹²⁸ in 1977 to investigate the possibility of using NH_2BH_2 to build thermally stable inorganic polymers. They pyrolyzed gaseous ammonia borane, condensed the monomeric NH_2BH_2 product at 77 K, then allowed it to polymerize as it warmed. In 1979 a microwave spectrum of NH_2BH_2 was obtained, using a sample formed from the reaction of 5-10 mTorr each of ammonia and diborane at $500\text{ }^{\circ}C$.¹²⁹ Molecular constants calculated by a least-squares fit were consistent with a planar configuration, thereby establishing the symmetrical structure $NH_2=BH_2$ for aminoborane, rather than the asymmetrical NH_3BH . Perhaps the most important outcome of this work was the determination of the dipole moment to be 1.844 D in the direction from N to B, as opposed to the theoretical predictions of B to N.^{120,121} The assumption of an $N \rightarrow B$ direction for the dipole moment was based on the observation that the dipole moment of NH_2BH_2 is 0.751 D smaller than that in BH_2BF_2 .

The same group recently reported microwave spectra of five isotopic species of NH_2BH_2 , improving the constants and geometric parameters obtained in the previous study.¹³⁰

Recently, at the University of British Columbia, the first gas phase Fourier transform infrared spectrum of aminoborane was measured.¹³¹ The synthesis combined the solid-state and vapor-phase ammonia borane pyrolysis techniques. Solid NH_3BH_3 was heated to about 70 °C in a flow system maintained at approximately 200 microns, and the vapors produced were passed through a furnace at about 400 °C, to pyrolyze unreacted sublimed sample. Nine of aminoborane's eleven infrared (IR) active fundamental vibrations were recorded at medium resolution (0.05 cm^{-1}), with the ν_4 A-type band at 1337 cm^{-1} being also recorded at very high resolution (0.004 cm^{-1}). Since that time the bands of all of the IR active fundamentals have been recorded at UBC at 0.004 cm^{-1} resolution (see Table 5.1), though ν_5 is vanishingly weak because its dipole derivative appears to be very small. Some analysis has been completed^{132,133,134}, with the remainder currently underway. The present work is a contribution to the high resolution Fourier transform IR study of aminoborane, being the rotational analysis of the C-type ν_7 fundamental whose origin is at 1004.7 cm^{-1} .

Table 5.I. Vibrational fundamentals of gaseous $\text{NH}_2^{11}\text{BH}_2$.

| Symmetry | | cm^{-1} | Type of motion |
|----------|------------|-----------------------|------------------------------|
| A_1 | ν_1 | 3451 | NH symmetric stretch |
| | ν_2 | 2495 | BH symmetric stretch |
| | ν_3 | 1617 | NH_2 symmetric bend |
| | ν_4 | 1337.474 ¹ | BN stretch |
| | ν_5 | 1145 | BH_2 symmetric bend |
| A_2 | ν_6 | 837 | Torsion (twist) |
| B_1 | ν_7 | 1004.6842 | BH_2 wag |
| | ν_8 | 612.1987 ² | NH_2 wag |
| B_2 | ν_9 | 3533.8 | NH asymmetric stretch |
| | ν_{10} | 2564 ³ | BH asymmetric stretch |
| | ν_{11} | 1122.2 | NH_2 rock |
| | ν_{12} | 742 | BH_2 rock |

¹Reference (131)²Reference (133): ν_8 (1,0) band; reference (132): ν_8 (2,0) band³Reference (134)

V.B. The Michelson Interferometer and Fourier Transform Spectroscopy.

The infrared interferogram was recorded and Fourier transformed with a BOMEM DA3.002 Michelson interferometer and associated software (version 3.1). Three sources of infrared light are available depending on the wavelength region desired: a quartz-halogen lamp for the near IR and visible regions, a globar for the mid-IR, and a mercury-xenon lamp for the far IR. After first being filtered and focused at an aperture, the infrared light passes to a collimating mirror and is reflected as a parallel beam to a beamsplitter, where it is divided in two. One beam continues through to a fixed mirror, while the other is reflected onto a mirror moving at constant velocity. As one of the beams has a fixed path length and the other a constantly varying one, the recombination of the beams at the beamsplitter produces a resultant of sinusoidal waves that are out of phase.¹³⁵ The portion of the resultant not absorbed by the sample is measured at the detector as the interferogram. The point along the moving mirror's travel at which the fixed and moving mirrors are exactly equidistant--called the zero path difference (ZPD)--should in principle bring all the sinusoidal waves into phase, with constructive interference producing a maximum in the amplitude.¹³⁵

Because the interference patterns producing the infrared interferogram result from the optical path difference between the two light beams, it is essential that signal sampling occur at constant intervals of mirror displacement. This is achieved in the BOMEM DA3 spectrophotometer by a He-Ne laser. Operating at 632.8

nm, or 15796 cm^{-1} , the laser provides an extremely precise time base of 31,592 cycles per cm of mirror travel.¹³⁶ The cycles, called fringes, trigger spectral sampling at a frequency normally equal to one sample/laser fringe, though the rate can be increased to up to eight times the laser fringe frequency. The phase coherence provided by this laser is excellent: its single-mode operation prevents destructive interference by two other closely lying transition frequencies, and its thermal stabilization removes temperature dependent fluctuations in the laser optics. The resulting uncertainty in the mirror's position is 0.0025 fringes per cm of mirror travel, which even at the maximum translation of 125 cm amounts to a variation of only 0.3 fringes over the length of the mirror's scan.¹³⁶

The interferogram not only requires that its points be sampled at precise intervals, but also that one of these points occurs at an origin that is exactly reproducible from scan to scan. The BOMEM DA3 spectrophotometer achieves this by triggering the commencement of each scan at the ZPD of an interferogram of white light. The beams from the white light source follow the same optical path as that of the radiation of interest, with the incoherent nature of the white light producing an interferogram characterized by an intense pulse at ZPD (the WLZPD), and low intensity amplitudes at non-zero mirror translations. The occurrence of the pulse is precise to well within one laser fringe, so the actual WLZPD trigger is marked as the laser fringe immediately following the pulse. The result is a synchronization signal which references the points in the

IR interferogram to a constant position along the scanning mirror's path.^{136,137}

A Fourier transform infrared experiment is therefore the process of obtaining the infrared interferogram in conjunction with the white light reference interferogram and the time base generated by the He-Ne laser. These data are processed by Fourier transformation from the IR interferogram time domain to an IR spectrum in the frequency domain. The integrals of the Fourier transformation can be understood in terms of the phase differences between the IR beams split by the beamsplitter. When a wave with angular frequency ω reflects off a mirror moving with velocity v , the frequency is Doppler shifted by an amount¹³⁸

$$\Delta\omega = 4\pi v/\lambda \quad (5.1)$$

Expressed as a function of the speed of light and the incident frequency, using the relation $\lambda = 2\pi c/\omega$, the phase shift becomes¹³⁸

$$\Delta\omega = (v/c)2\omega \quad (5.2)$$

The magnitude of $\Delta\omega$ is on the order of 1 kHz to 100 kHz, a frequency that can be processed easily as compared to the 10^{13} to 10^{15} Hz frequencies of IR radiation itself.

The time-averaged beat intensity, I , produced by the combination of two waves out of phase by $\Delta\omega$ is¹³⁸

$$I = I_0(1 + \cos\Delta\omega t)\cos^2[(\omega + \omega')t/2] = (I_0/2)(1 + \cos\Delta\omega t) \quad (5.3)$$

where I_0 is the signal intensity when $\Delta\omega = 0$. Represented in terms of amplitude or electric field strength $[E_0(\omega)]$, phase difference $[\delta(\omega) = \Delta\omega t]$, and the reflectivity (R) and transmittance (T) of the beamsplitter, equation (5.3) becomes¹³⁸:

$$I(\omega, \delta) = c\epsilon_0 RT |E_0(\omega)|^2 [1 + \cos\delta(\omega)] \quad (5.4)$$

where c is the speed of light and ϵ_0 is the vacuum permittivity¹³⁹, equal to $8.85 \times 10^{-12} \text{ C}^2\text{J}^{-1}\text{m}^{-1}$. Integrating over all frequencies of the spectral components,

$$I(\delta) = \int I(\omega, \delta) d\omega = c\epsilon_0 RT \left[\int |E_0(\omega)|^2 d\omega + \int |E_0(\omega)|^2 \cos \delta d\omega \right] \quad (5.5)$$

At zero path difference, or $\delta = 0$, the two terms in brackets in equation (5.5) are equal, so the ZPD intensity is given by:

$$I_0 = 2c\epsilon_0 RT \int |E_0(\omega)|^2 d\omega \quad (5.6)$$

The time-averaged signal intensity as a function of phase difference, $I(\delta)$, is the quantity measured at the detector. The interferogram points themselves are taken to be the oscillations of these intensities about $I_0/2$:¹³⁸

$$|I(\delta) - I_0/2| = c\epsilon_0 RT \int |E_0(\omega)|^2 \cos \delta d\omega \quad (5.7)$$

The cosine Fourier transform of an interferogram of the form of equation (5.7) yields a spectral intensity distribution function $I(\omega)$ in which intensity is a function of discrete frequencies:

$$I(\omega) = (1/\pi RT) \int [I(\delta) - I_0/2] \cos \delta d\delta \quad (5.8)$$

However, since imperfections in manufacture do not produce equivalent reflectivities in the fixed and moving mirrors, sine components as well as cosine are introduced into the interferogram. The actual Fourier transform therefore employs the complex form of the expression^{138,140,141}

$$I(v) = C \int [I(\delta) - I_0/2] e^{-i2\pi v \delta} d\delta \quad (5.9)$$

In general form, the Fourier transform of function $f(x)$ is¹⁴²

$$\mathfrak{F}\{f(x)\} = F(\alpha) = \int f(x) e^{-i\alpha x} dx \quad (5.10)$$

The inverse Fourier transform of $F(\alpha)$ is therefore

$$\mathfrak{F}^{-1}\{F(\alpha)\} = f(x) = (1/2\pi) \int F(\alpha) e^{i\alpha x} d\alpha \quad (5.11)$$

Likewise, the spectrum expressed in equation (5.9) is one member of a Fourier pair, which consists of two non-periodic functions related by the Fourier integral transforms¹⁴¹:

$$g(v) = \int f(\delta) e^{i2\pi v \delta} d\delta \quad (5.12)$$

$$f(\delta) = \int g(v) e^{-i2\pi v \delta} dv \quad (5.13)$$

A Fourier pair is illustrated graphically in Fig. 5.1.

Fourier transform spectroscopy is able to exploit the Fourier pair relationship between the time domain (phase, δ) and the frequency domain (ω or v), because frequency can be obtained with greater accuracy, resolution and speed by measuring and transforming phase differences rather than by directly measuring relative frequency. With the Michelson interferometer the integration cannot be performed over all space ($-\infty$ to $+\infty$) but is limited to the range $0 - L$ where L is the total mirror displacement. As the distance travelled by the mirror increases, the number of terms included in the integration increases, extending the amount of information available for extraction into the spectrum $I(v)$.¹⁴¹ The theoretical maximum spectral resolution of an interferometer is therefore inversely proportional to the maximum optical path difference between the fixed and moving mirrors.¹⁴² Defining resolution as the full width at half height, the maximum unapodized resolution is:¹⁴⁴

$$\Delta v_{1/2} = 1/(2L) \quad (5.14)$$

Imposing the 0 to L limits on an interferogram is known as a "boxcar" truncation (see Fig. 5.2).¹⁴⁴ When a boxcar-truncated interferogram is Fourier transformed, the spectral line shape contains the sinc function [$\text{sinc } z = (\sin z)/z$]:^{146,147}

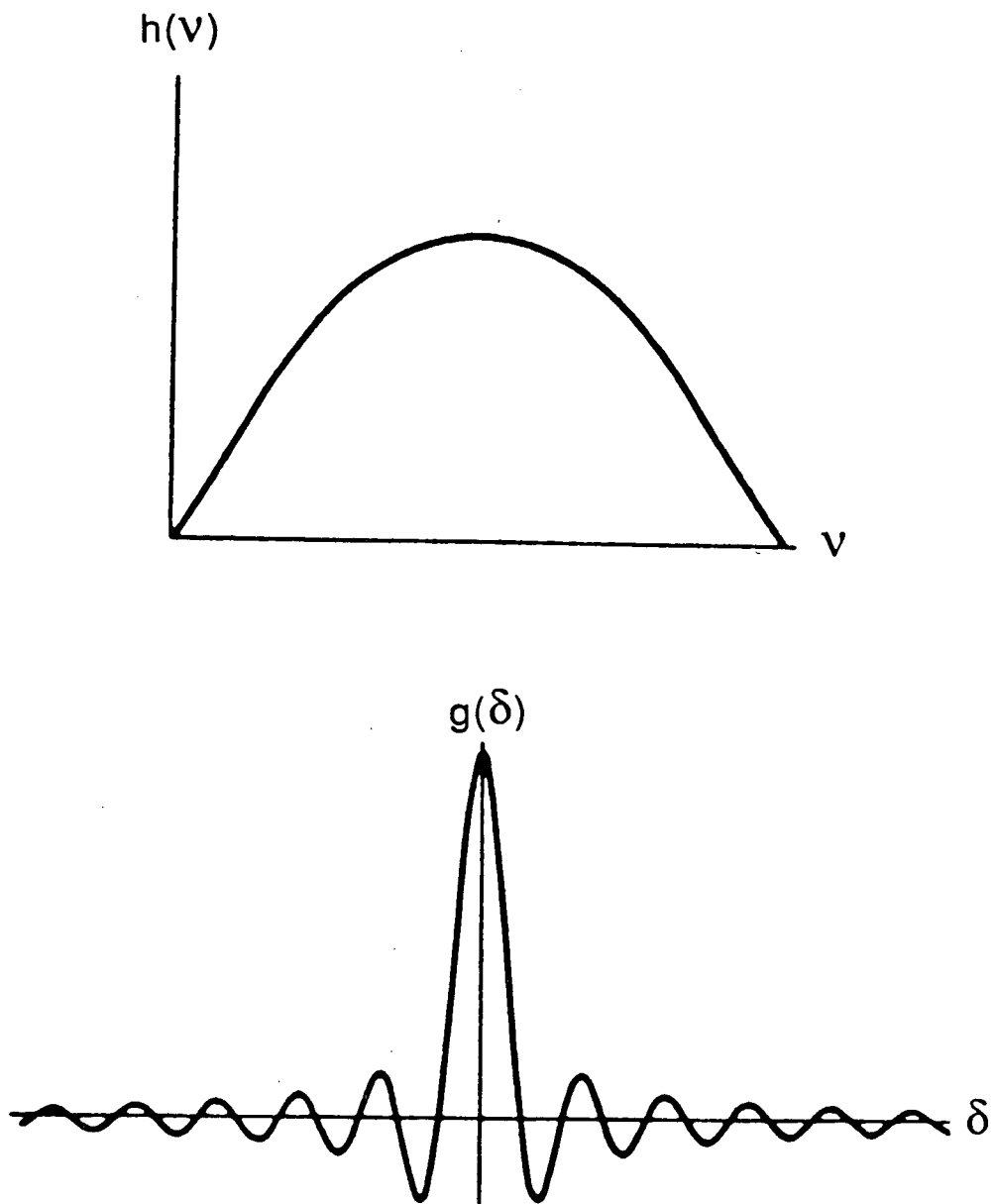


Fig. 5.1. A polychromatic signal in the frequency domain (above) Fourier transformed into the time domain (below).¹⁴¹

$$F\{D(x)\} = 2L(\text{sinc } z) \quad (5.15)$$

where $z = 2\pi(\sigma - \sigma_0)L$. The half-width of the center spike of this form is very narrow: $\Delta\sigma = 1.207/2L$, or about 20% wider than the theoretical resolution of $1/2L$. However, the sidelobes next to the central peak have about 21% of its intensity, and the amplitudes of subsequent lobes are slow to die away.¹⁴⁵ In order to approximate more closely the true frequency domain spectrum, an apodization function is often included in the data processing. This process dampens the effects caused by truncating the interferogram at a definite mirror displacement of L . Though there are many forms of apodization functions, the effect is to give decreasing weight to the data points recorded at large mirror displacements.^{145,146} One of the simplest is the triangular function in Fig. 5.3, in which all sidelobes are positive and the largest is only about 4.5% that of the center spike; the linewidth is increased by almost 50% over the boxcar case.^{146,147} The apodization applied to the aminoborane experiment in this work was a cosine function referred to as "Hamming" or "Happ-Genzel". It produces spectral lines with negative sidelobes of only 0.0071 the height of the maximum peak, and lines about 2% broader than those from the triangular apodization.¹⁴⁵

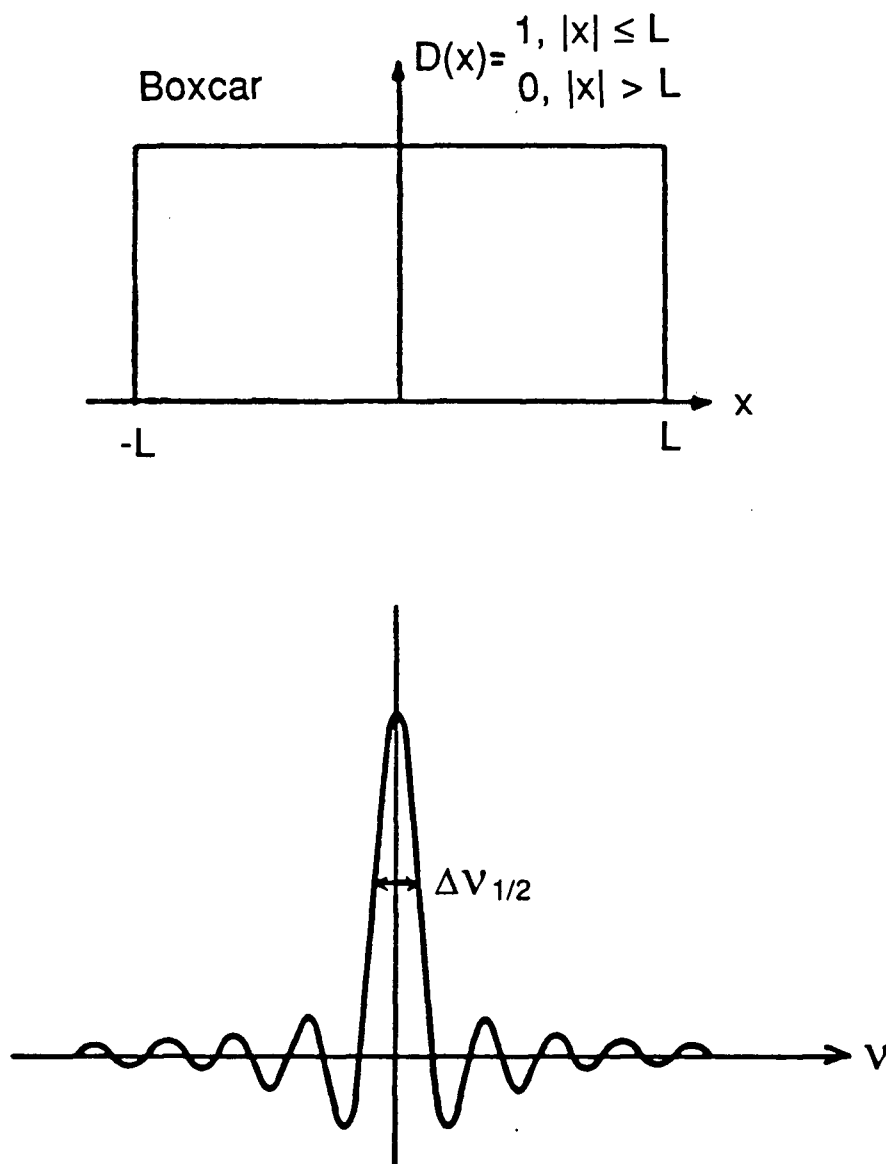


Fig. 5.2. A boxcar function $D(x)$ (above). The Fourier transform of a boxcar truncated interferogram is a spectrum with the line shape function $F\{D(x)\} = 2L\sin(2\pi\nu L)/2\pi\nu L$ (where L denotes the maximum mirror displacement.) The full width at half-height ($\Delta\nu_{1/2}$) is $1.207/2L$, and the strongest sidelobe has 21% the intensity of the maximum.¹⁴⁵

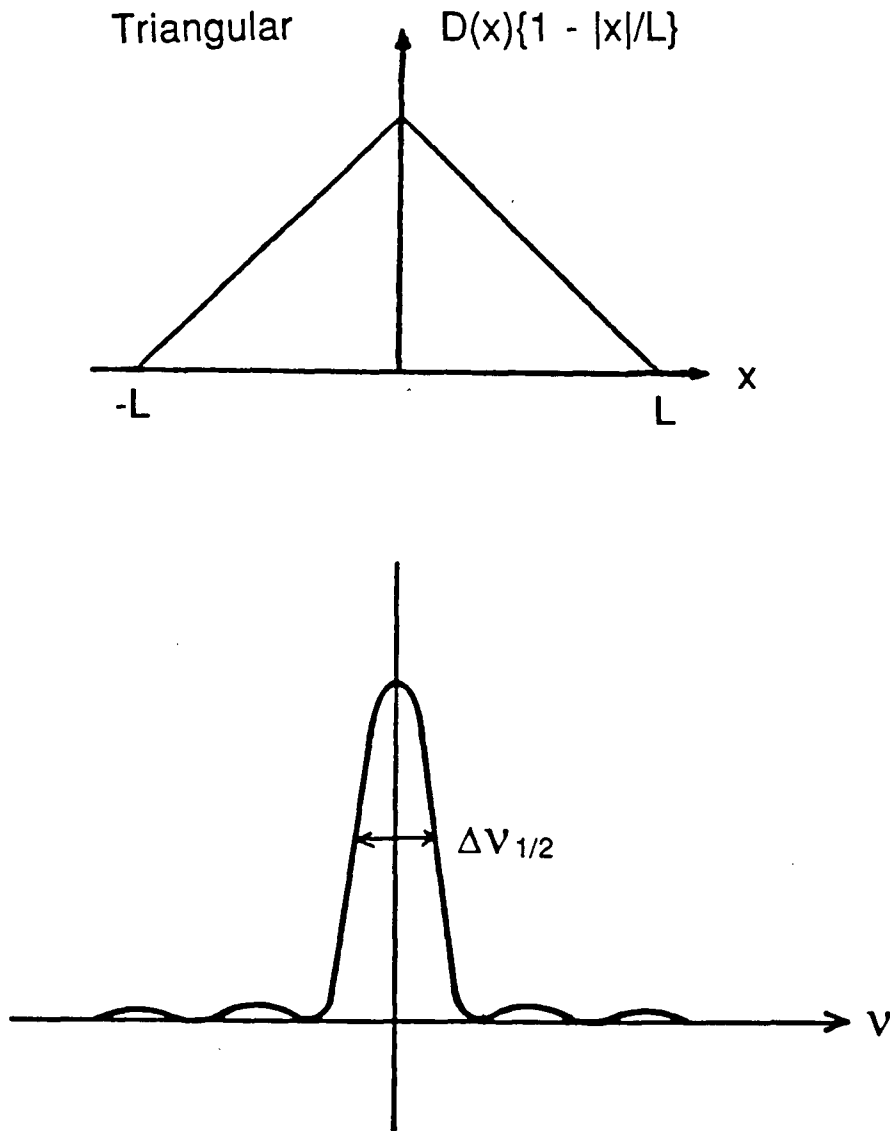


Fig. 5.3. The triangular apodization function $D(x)$ (above) produces a spectrum with the line shape function $F\{D(x)\} = 2L\sin(2\pi\nu L)/(2\pi\nu L)^2$ (below). The full width at half-height ($\Delta\nu_{1/2}$) is $1.772/2L$, with the strongest sidelobe only 4.5% of the maximum intensity.¹⁴⁵

V.C. Experimental.

The aminoborane was prepared by pyrolysis of borane ammonia (BH_3NH_3 , Alfa Products) according to the procedure of Gerry and coworkers¹³¹, except that in the present work the temperature of the solid NH_3BH_3 was raised to only 67 °C - 68 °C for the first several hours, then lowered to 63 °C - 65 °C for the remainder of the experiment. The 70 °C pyrolysis temperature employed in reference 131 was found to be unnecessarily close to the temperature of uncontrolled thermal decomposition, which initiates violently at approximately 71 °C. At the time the interferogram was measured, the temperature of the solid ammonia borane was 63.5 (± 0.5) °C. The sample absorption cell, set to an optical path of 9.75 m, was maintained at a pressure of 100 μ during data acquisition. The BOMEM DA3.002 interferometer was fitted with a potassium chloride beam splitter and a liquid nitrogen-cooled HgCdTe detector.

V.D. The Asymmetric Rotor.

A vibrational fundamental is infrared active if the dipole moment μ changes as a result of motion along the normal coordinate Q_k , or in other words if the derivative $(\partial\mu/\partial Q_k)_0$ in the Taylor series expansion of the dipole moment

$$\mu = \mu^0 + \sum (\partial\mu/\partial Q_k)_0 Q_k \quad (5.16)$$

is non-zero.¹⁴⁸ The linear character of the dipole operator means that its components transform as translations along the principal axes, and therefore so do the various $(\partial\mu/\partial Q_k)_0 Q_k$'s.

Aminoborane is a prolate asymmetric top molecule belonging to the point group C_{2v} , whose character table is given in Table 5.II. The irreducible representations of the normal vibrations are: $5A_1 + A_2 + 2B_1 + 2B_2$, for a total of twelve fundamental vibrations. The BH_2 out-of-plane wagging vibration is antisymmetric with respect to reflection in the yz plane, and therefore transforms as the B_1 representation (see Fig. 5.4). Thus the ν_7 vibration represents translation along the c inertial axis and generates a C-type infrared band.

Accompanying any molecular vibration are the rotational transitions involving changes in the total angular momentum, J . In order to understand the rotational selection rules for an asymmetric top molecule, one must write down asymmetric top rotational wave functions which are eigenfunctions of the symmetry operations of the molecular point group, in this case C_{2v} . We begin by examining the effects of the C_{2v} symmetry operations on the symmetric top wave functions, $Y_{JK}(\theta, \phi)$. From equation (1.23) we know that:

$$Y_{JK}(\theta, \phi) = NP_J^K(\cos \theta) e^{iK\phi} \quad (5.17)$$

Table 5.II. Character table for the C_{2v} point group, and the correlation of the axes of translation to infrared band type. The molecule-fixed axes x , y , z given here are related to the inertial axes a , b , c by the I' representation.

| C_{2v} | E | C_2 | $\sigma_v(xz)$ | $\sigma_v'(yz)$ | Rotation (R) and Translation (T) axes |
|----------|---|-------|----------------|-----------------|--|
| A_1 | 1 | 1 | 1 | 1 | T_a |
| A_2 | 1 | 1 | -1 | -1 | R_a (R_z) |
| B_1 | 1 | -1 | 1 | -1 | T_c, R_b (R_y) |
| B_2 | 1 | -1 | -1 | 1 | T_b, R_c (R_x) |

where N is a normalization factor, $P_J^K(\cos \theta)$ is an associated Legendre polynomial, and the spherical polar angles θ and ϕ are shown in Fig. 5.4.

A C_2 rotation about the a inertial axis ($C_2^{(a)}$) adds an amount π to ϕ , but does not change the θ coordinate:

$$C_2^{(a)}Y_{JK}(\theta, \phi) = NP_J^K(\cos \theta)e^{iK(\phi+\pi)} \quad (5.18a)$$

$$= NP_J^K(\cos \theta)e^{iK\phi}e^{iK\pi} \quad (5.18b)$$

$$= e^{iK\pi}Y_{JK}(\theta, \phi) \quad (5.18c)$$

where

$$e^{iK\pi} \begin{cases} = 1 & \text{for even } K \\ = -1 & \text{for odd } K \end{cases} \quad (5.19)$$

Note that the operation of C_2 on $Y_{JK}(\theta, \phi)$ gives a multiple of the original spherical harmonic, $Y_{JK}(\theta, \phi)$. C_2 rotations about the b and c inertial axes are not symmetry operations of the C_{2v} point group.

Unlike $C_2^{(a)}$, the σ_v^{ac} and σ_v^{ab} operators reverse the directions of the angles θ and ϕ . Both reflections change θ into $-\theta$, causing the associated Legendre polynomial to become $P_J^K(-\cos \theta)$. By the Rodrigues formula¹⁴⁹

$$P_J^K(-\cos \theta) = (-1)^{J+K}P_J^K(\cos \theta) \quad (5.20)$$

The operation of σ_v^{ac} changes ϕ to $-\phi$. σ_v^{ab} projects the c axis in the opposite direction and changes ϕ to $\pi - \phi$. The overall effects of the reflections are therefore:

$$\sigma_v^{ac}Y_{JK}(\theta, \phi) = (-1)^{J+K}NP_J^K(\cos \theta)e^{-iK\phi} \quad (5.21)$$

and

$$\sigma_v^{ab}Y_{JK}(\theta, \phi) = (-1)^{J+K}NP_J^K(\cos \theta)e^{iK\pi}e^{-iK\phi} \quad (5.22)$$

Clearly the spherical harmonics themselves are not eigenfunctions of the reflection operators, though the linear combinations obtained

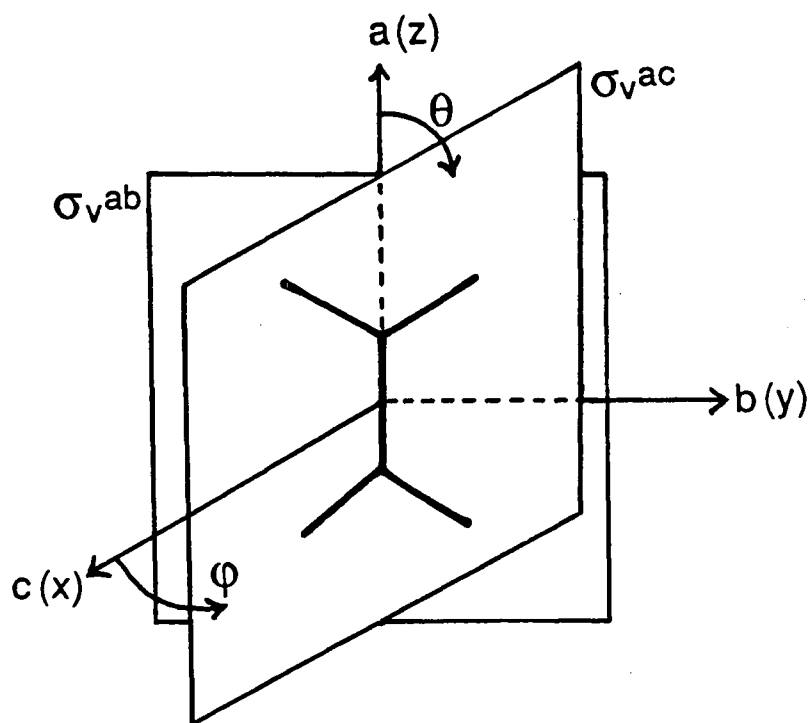


Fig. 5.4. Schematic drawing of the C_{2v} NH_2BH_2 molecule in the x , y , z principal axis system and the a , b , c inertial axis system, showing the $C_2 \sigma_v$ reflection planes.

by taking Wang sum and difference functions¹⁵⁰ are eigenfunctions of these operators:

$$\Psi_{JK\pm} = (1/\sqrt{2})(Y_{JK} \pm Y_{J,-K}) \quad (5.23)$$

In equation (5.23) the sums and differences (JK_+ and JK_- , respectively) correspond to the upper and lower asymmetry components of a JK level.

The effects of the C_{2v} symmetry operations, performed on asymmetric top rotational wavefunctions, follow from equations (5.18c), (5.19), (5.21), (5.22) and (5.23):

$$C_2(a) \Psi_{JK\pm} = (-1)^K \Psi_{JK\pm} \quad (5.24)$$

$$\begin{aligned} \sigma_v^{ac} \Psi_{JK\pm} &= (1/\sqrt{2})(-1)^{J-K} Y_{J,-K} \pm (1/\sqrt{2})(-1)^{J+K} Y_{JK} \\ &= \pm(-1)^{J+K}(1/\sqrt{2}) (Y_{JK} \pm Y_{J,-K}) \\ &= \pm(-1)^{J+K} \Psi_{JK\pm} \end{aligned} \quad (5.25)$$

$$\begin{aligned} \sigma_v^{ab} \Psi_{JK\pm} &= (-1)^K(-1)^{J+K} \Psi_{JK\pm} \\ &= \pm(-1)^J \Psi_{JK\pm} \end{aligned} \quad (5.26)$$

For even and odd values of K, and the + and - asymmetry components, the result of each operation can be tabulated using (5.24) through (5.26), as given in the first two sections of Table 5.III. The irreducible representations in the third section of Table 5.III are obtained by substituting even and odd values for J into section 2. The quantum numbers K_a and K_c in section 3 denote the projections of the angular momentum components J_a and J_c along the axes of lowest and highest inertia. The values of K_a and K_c corresponding to each irreducible representation are derived from the rule that $K_c = J - K_a$ and $K_c = J - K_a + 1$, for the + and - asymmetry components, respectively. For example, for even J, even K_a and the - asymmetry component, K_c must be odd, giving $K_a K_c = eo$. The eo notation

Table 5.III. Character sets for an asymmetric top rotational wavefunction in the C_{2v} point group.

| Wang sum & difference | | | | | | | Irred. represen- tations ($K_a K_c$) | | E^\pm/O^\pm notation |
|-----------------------|-------------------|-----------|---|-------|-------------------|-------------------|---|------------------|---------------------------|
| J | K_a | functions | E | C_2 | $\sigma_{v^{ac}}$ | $\sigma_{v^{ab}}$ | J_{even} | J_{odd} | |
| J | K_{even} | + | 1 | 1 | $(-1)^J$ | $(-1)^J$ | $A_1(ee)$ | $A_2(eo)$ | E^+ |
| J | K_{even} | - | 1 | 1 | $-(-1)^J$ | $-(-1)^J$ | $A_2(eo)$ | $A_1(ee)$ | E^- |
| J | K_{odd} | + | 1 | -1 | $-(-1)^J$ | $(-1)^J$ | $B_2(oe)$ | $B_1(oo)$ | O^+ |
| J | K_{odd} | - | 1 | -1 | $(-1)^J$ | $-(-1)^J$ | $B_1(oo)$ | $B_2(oe)$ | O^- |

indicates that the rotational wavefunction is symmetric with respect to rotation about the a inertial axis and antisymmetric with respect to rotation about the c inertial axis.¹⁵¹ The E^\pm/O^\pm notation given in the last column of Table 5.III is explained in Section V.E. From Table 5.III, the selection rules for a C-type band are:

$$A_1 \Leftrightarrow B_2 \text{ and } A_2 \Leftrightarrow B_1 \quad (5.27)$$

or in $K_a K_c$ notation:

$$ee \Leftrightarrow oe \text{ and } eo \Leftrightarrow oo \quad (5.28)$$

The restrictions on changes in K_a and K_c are therefore:

$$\Delta K_a = \pm 1, \pm 3, \pm 5, \dots \text{ and } \Delta K_c = 0, \pm 2, \pm 4, \dots \quad (5.29)$$

so that C-type bands consist of the following branches, in $\Delta K_a \Delta J$ notation:

| <u>Branch</u> | <u>ΔJ</u> | <u>ΔK_a</u> | <u>ΔK_c</u> | <u>Intensity</u> |
|---------------|------------------------------|--------------------------------|--------------------------------|------------------|
| rR | +1 | +1 | 0,0 | strong |
| pP | -1 | -1 | 0,0 | strong |
| rQ | 0 | +1 | 0,-2 | intermediate |
| pQ | 0 | -1 | 0,+2 | intermediate |
| rP | -1 | +1 | -2,-2 | weak |
| pR | +1 | -1 | +2,+2 | weak |

V.E. The Rotational Hamiltonian.

V.E.1. The Hamiltonian without vibration interaction.

The rotational Hamiltonian representing the purely kinetic energy, T , of a freely rotating rigid asymmetric top molecule is:

$$\hat{H}^{\text{rigid}} = (B_x + B_y) \hat{J}_+^2/2 + [B_z - (B_x + B_y)/2] \hat{J}_z^2/2 + (B_x - B_y)(\hat{J}_+^2 + \hat{J}_-^2)/4 \quad (5.20)$$

where $\hat{J}_+^2 + \hat{J}_-^2 = (\hat{J}_x + i\hat{J}_y)^2 + (\hat{J}_x - i\hat{J}_y)^2$, and the quantities $B_\alpha = h/8\pi^2 c I_\alpha$ (in cm^{-1}) are the rotational constants.¹⁵² B_x , B_y and B_z are to be identified with the rigid-rotor rotational constants B , C and A , respectively, for the I^r representation which is appropriate for a near-prolate asymmetric top molecule.

The third term of equation (5.20) (which vanishes in a symmetric top) produces a matrix representation for \hat{H}^{rigid} that contains off-diagonal matrix elements with $\Delta K \pm 2$:

$$\begin{aligned} \langle J, K \pm 2 | \hat{J}_\pm^2 | J, K \rangle &= (\hbar^2/4) [J(J+1) - K(K \pm 1)]^{1/2} \\ &\times [J(J+1) - (K \pm 1)(K \pm 2)]^{1/2} \quad (5.21) \end{aligned}$$

The matrix of \hat{H}^{rigid} can be factorized at once into blocks containing only odd or even values of K in the basis set (because no matrix elements of the type $\Delta K = \pm 1$ arise from (5.20)). These submatrices can be further factorized by taking sums and differences of the original symmetric top basis functions by means of a Wang similarity transformation¹⁵⁰:

$$\begin{aligned} |J, 0^+\rangle &= |J, 0\rangle \\ |J, K^\pm\rangle &= (1/\sqrt{2}) \{ |J, K\rangle \pm |J, -K\rangle \}, \quad (K > 0) \quad (5.22) \end{aligned}$$

The four submatrices constructed from the basis functions $|J, K^\pm\rangle$ are designated E^\pm and O^\pm for even and odd K , respectively.

To obtain a more accurate description of the rotational structure of an asymmetric top, centrifugal distortion must be considered. Centrifugal forces cause expansion (or stretching) and distortion in a rotating molecule, which lead to deviations from the rigid rotor Hamiltonian that increase with increasing angular momentum. The distortion Hamiltonian, H'_d , is therefore treated as a power series which adds higher degree angular momentum terms to the rigid rotor Hamiltonian:

$$\hat{H}'_d = (\hbar^4/4) \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} J_\alpha J_\beta J_\gamma J_\delta \quad (5.23)$$

where $\tau_{\alpha\beta\gamma\delta}$ is the centrifugal distortion constant and α, β, γ and $\delta = x, y$ or z .¹⁵³ The number of terms in the general power series of equation (5.23) is 81. However, symmetry constraints reduce the number to 6 for an orthorhombic molecule (i.e., one which possesses at least two perpendicular planes of symmetry), since all terms vanish which are antisymmetric with respect to one or more of the symmetry operations. All of the remaining terms have only even powers of J , since those with odd powers change sign under the operation of Hermitian conjugation and time reversal.^{152,154} Further reduction of the orthorhombic Hamiltonian follows one of two routes: the "asymmetric top reduction" for the general asymmetric top, or the "symmetric top reduction" for asymmetric tops that are nearly symmetric. In the A-reduction the $J_+^4 + J_-^4$ term is eliminated, leaving only terms of the type $\Delta K = 0, \pm 2$, whereas the "S" reduced Hamiltonian retains $\Delta K = \pm 4, \pm 6, \dots$ terms. Aminoborane was treated using Watson's "A" reduced

Hamiltonian.¹⁵² Written out completely up to terms in J^8 , this is:¹⁵⁴

$$\begin{aligned}
 \hat{H}_{\text{rot}}(A) = & B_x(A)\hat{J}_x^2 + B_y(A)\hat{J}_y^2 + B_z(A)\hat{J}_z^2 - \Delta_J\hat{J}^4 - \Delta_{JK}\hat{J}^2\hat{J}_z^2 - \Delta_K\hat{J}_z^4 \\
 & - 2\delta_J\hat{J}^2(\hat{J}_x^2 - \hat{J}_y^2) - \delta_K[\hat{J}_z^2(\hat{J}_x^2 - \hat{J}_y^2) + (\hat{J}_x^2 - \hat{J}_y^2)\hat{J}_z^2] + \Phi_J\hat{J}^6 \\
 & + \Phi_{JK}\hat{J}^4\hat{J}_z^2 + \Phi_{KJ}\hat{J}^2\hat{J}_z^4 + \Phi_K\hat{J}_z^6 + 2\phi_J\hat{J}^4(\hat{J}_x^2 - \hat{J}_y^2) \\
 & + \phi_{JK}\hat{J}^2[\hat{J}_z^2(\hat{J}_x^2 - \hat{J}_y^2) + (\hat{J}_x^2 - \hat{J}_y^2)\hat{J}_z^2] + \phi_K[\hat{J}_z^4(\hat{J}_x^2 - \hat{J}_y^2) \\
 & + (\hat{J}_x^2 - \hat{J}_y^2)\hat{J}_z^4] + L_J\hat{J}^8 + L_{JK}\hat{J}^6\hat{J}_z^2 + L_{JK}\hat{J}^4\hat{J}_z^4 + L_{KKJ}\hat{J}^2\hat{J}_z^6 \\
 & + L_K\hat{J}_z^8 + 2l_J\hat{J}^6(\hat{J}_x^2 - \hat{J}_y^2) + l_{JK}\hat{J}^4[\hat{J}_z^2(\hat{J}_x^2 - \hat{J}_y^2) + (\hat{J}_x^2 - \hat{J}_y^2)\hat{J}_z^2] \\
 & + l_{KJ}\hat{J}^2[\hat{J}_z^4(\hat{J}_x^2 - \hat{J}_y^2) + (\hat{J}_x^2 - \hat{J}_y^2)\hat{J}_z^4] + l_K[\hat{J}_z^6(\hat{J}_x^2 - \hat{J}_y^2) \\
 & + (\hat{J}_x^2 - \hat{J}_y^2)\hat{J}_z^6] \quad (5.24)
 \end{aligned}$$

The fitting program employed in this work to analyze the aminoborane ν_7 band included all matrix elements through to the off-diagonal sextic terms (J^6), plus the diagonal elements from the octic terms:

$$\begin{aligned}
 E_{K,K} = & \langle J,K | \hat{H}_{\text{rot}}(A) | J,K \rangle \\
 = & [B_x(A) + B_y(A)]J(J+1)/2 + \{B_z(A) + [B_x(A) + B_y(A)]/2\}K^2 \\
 & - \Delta_JJ^2(J+1)^2 - \Delta_{JK}J(J+1)K^2 - \Delta_KK^4 + \Phi_JJ^3(J+1)^3 \\
 & + \Phi_{JK}J^2(J+1)^2K^2 + \Phi_{KJ}J(J+1)K^4 + \Phi_KK^6 + L_JJ^4(J+1)^4 \\
 & + L_{JK}J^3(J+1)^3K^2 + L_{JK}J^2(J+1)^2K^4 + L_{KKJ}J(J+1)K^6 + L_KK^8 \quad (5.25)
 \end{aligned}$$

$$\begin{aligned}
 E_{K\pm 2,K} = & \langle J,K\pm 2 | \hat{H}_{\text{rot}}(A) | J,K \rangle \\
 = & \{[B_x(A) - B_y(A)]/4 - \delta_JJ(J+1) - \delta_K[(K\pm 2)^2 + K^2]/2 + \\
 & + \phi_JJ^2(J+1)^2 + \phi_{JK}J(J+1)[(K\pm 2)^2 + K^2]/2 + \phi_K[(K\pm 2)^4 + K^4]/2\} \\
 & \{[J(J+1 - K(K\pm 1))][J(J+1) - (K\pm 1)(K\pm 2)]\}^{1/2} \quad (5.26)
 \end{aligned}$$

V.E.2. Coriolis interaction.

The only perturbation present in the ν_7 fundamental, up to the limit of this analysis at $K_a' = 11$, is a Coriolis interaction globally affecting all levels to an extent which increases quadratically with the rotational quantum number K . A Coriolis interaction is the coupling of two vibrations by the rotation of the molecule. Put simply, certain combinations of vibrations generate an internal angular momentum which is part of the total angular momentum of the molecule.¹⁵⁵ In other words, rotational and vibrational motion are not separable. This internal, or vibrational, angular momentum is a vector, written Π , whose components are Π_x , Π_y and Π_z . To obtain the rotational Hamiltonian, the vibrational angular momentum must be subtracted from the total angular momentum, P , to give the rotational angular momentum. Instead of the simple form

$$\hat{H} = \hbar^2(\hat{J}_x^2/I_x + \hat{J}_y^2/I_y + \hat{J}_z^2/I_z)/2 + \hat{H}_{\text{vib}} \quad (5.27)$$

the rotation-vibration Hamiltonian (in joules) becomes^{155,156,157}:

$$\hat{H} = \hbar^2\{[(\hat{P}_x - \hat{\Pi}_x)]^2/I_x + [(\hat{P}_y - \hat{\Pi}_y)]^2/I_y + [(\hat{P}_z - \hat{\Pi}_z)]^2/I_z\}/2 + \hat{H}_{\text{vib}} \quad (5.28)$$

$$\begin{aligned} \hat{H} = & \hbar^2(\hat{P}_x^2/I_x + \hat{P}_y^2/I_y + \hat{P}_z^2/I_z)/2 - \hbar^2(\hat{\Pi}_x\hat{P}_x/I_x + \hat{\Pi}_y\hat{P}_y/I_y + \hat{\Pi}_z\hat{P}_z/I_z) \\ & + \hbar^2(\hat{\Pi}_x^2/I_y + \hat{\Pi}_y^2/I_y + \hat{\Pi}_z^2/I_z) + \hat{H}_{\text{vib}} \end{aligned} \quad (5.29)$$

The first term in equation (5.29), independent of the vibrational angular momentum, is the rigid rotor Hamiltonian, while the third term, independent of rotational angular momentum, affects only the vibrational energy. The second term, a function of both the vibrational and the total angular momenta, represents Coriolis coupling. The Coriolis interaction can therefore be considered as the scalar product of the rotational and vibrational angular momenta,

the magnitude of which increases the faster the molecule rotates and the nearer the vibrations approach degeneracy. According to Jahn's rule two normal coordinates Q_k and Q_l are coupled via an α -axis Coriolis interaction only if the product of their irreducible representations is of the same symmetry as P_α .¹⁵⁷ Thus the ν_7 (B_1) fundamental at 1005 cm^{-1} undergoes an a-axis Coriolis interaction with the nearby ν_{11} (B_2) fundamental at 1122 cm^{-1} , since $B_1 \times B_2$ gives the A_2 symmetry species (corresponding to rotation around the a-axis). The ν_{11} vibration in turn interacts with ν_5 (A_1) at 1145 cm^{-1} (the BH_2 symmetric bending vibration) by a c-axis Coriolis interaction, while the direct product of the ν_7 and ν_5 symmetries produces B_1 symmetry for a b-axis Coriolis interaction. Each of these three vibrations is therefore affected by the other two.

The vibrational angular momentum, in units of \hbar , is defined as¹⁵⁵:

$$\Pi_\alpha = \sum_{k,l} \zeta_{kl}^{(\alpha)} q_k p_l (\omega_l/\omega_k)^{1/2} \quad (5.30)$$

where the normal coordinate Q and its momentum conjugate, $P = -i\hbar\partial/\partial Q$, are expressed in the dimensionless forms, q and p :

$$q_k = \gamma_k^{1/2} Q_k \quad (5.31)$$

$$p_k = P_k/\gamma_k^{1/2}\hbar \quad (5.32)$$

$$\gamma_k = 2\pi c\omega_k/\hbar \quad (5.33)$$

The Coriolis coupling constant, $\zeta_{kl}^{(\alpha)}$, is a measure of the angular momentum about the α -axis induced by the interaction of two normal vibrational modes, Q_k and Q_l , having frequencies (in cm^{-1}) of ω_k and ω_l .

V.F. Band Analysis and Discussion.

Aminoborane's BH_2 -wag forms a C-type band whose appearance is characterized by a central spike, due to the asymmetry of the molecule causing low-K Q branches to pile up about the band origin (see Fig. 5.5).¹⁵⁸ At high resolution (Fig. 5.6), it can be seen that the spike is composed largely of the two lowest Q branches, PQ_1 and Q_0 (using the notation $\Delta K_a \Delta J_{K_a}$). The lines of the ^{11}B form of NH_2BH_2 were assigned by a process of successive refinement of the upper state constants. The ground state constants were held fixed at the best values available so far,¹³³ and the structure of the band was calculated using a prediction program. As the upper state constants were improved the prediction became more accurate so that more lines could be assigned. The assignments were limited to a maximum upper state value of K_a equal to 11, as a result of the Boltzmann distribution at room temperature. Lines of ammonia, present as an impurity in the spectrum, were used as an internal standard for absolute frequency calibration. The NH_3 frequencies were taken from the diode laser study by Job *et al.*¹⁵⁹

A complete set of molecular constants cannot be given at this time because the ν_5 fundamental has not yet been observed directly since its dipole derivative is very small. Without lines from ν_5 , it is extremely difficult to analyze the ν_5 - ν_7 - ν_{11} Coriolis interactions. However, it is hoped that a sufficient portion of the ν_5 band can be assigned in the near future to allow a fit to be made. The data were fitted to the matrix elements in equation (5.25) and (5.26) by means of a least-squares program written by Dr. Wyn Lewis-Bevan. In this program the Hellmann-Feynman theorem is used to calculate the

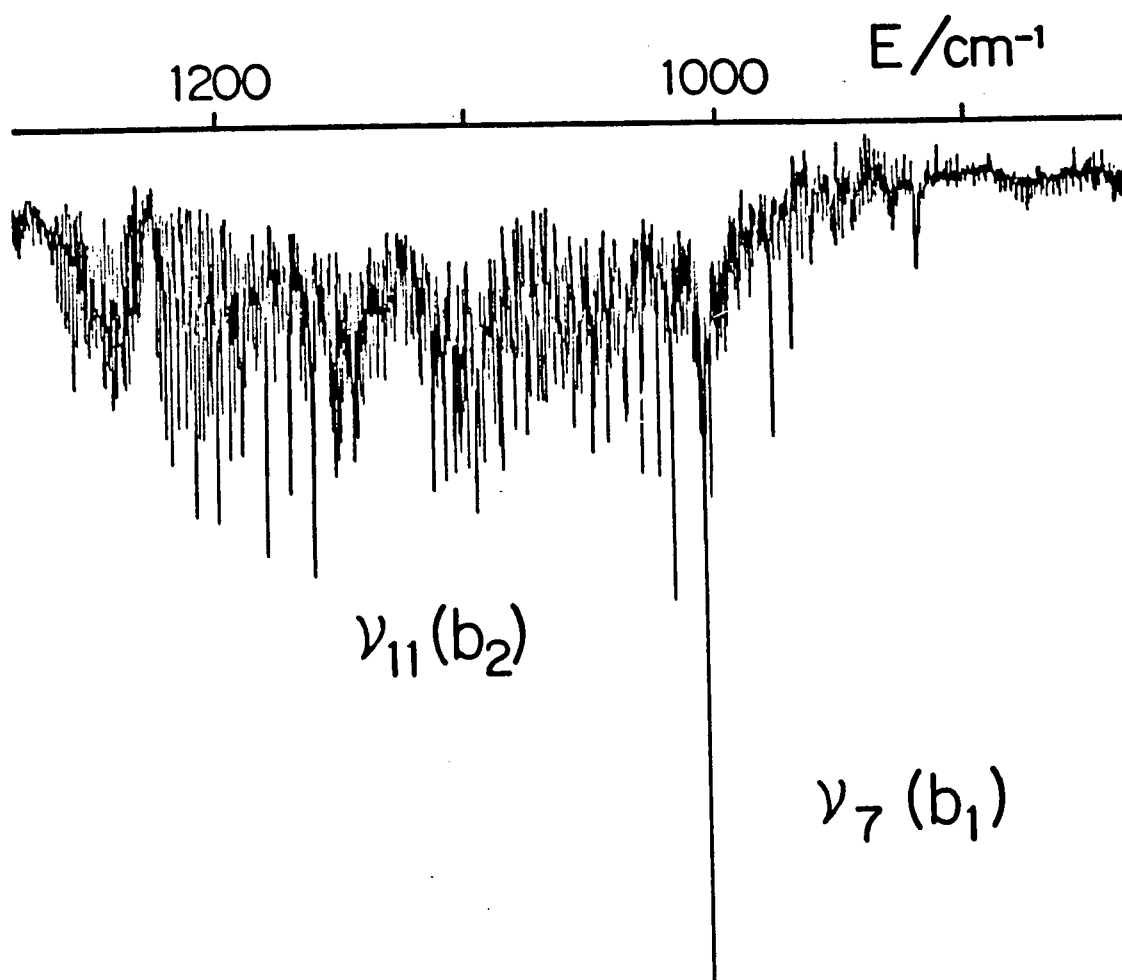


Fig. 5.5. NH_2BH_2 spectrum of the ν_7 band and the ν_5 and ν_{11} bands with which it undergoes Coriolis interactions.

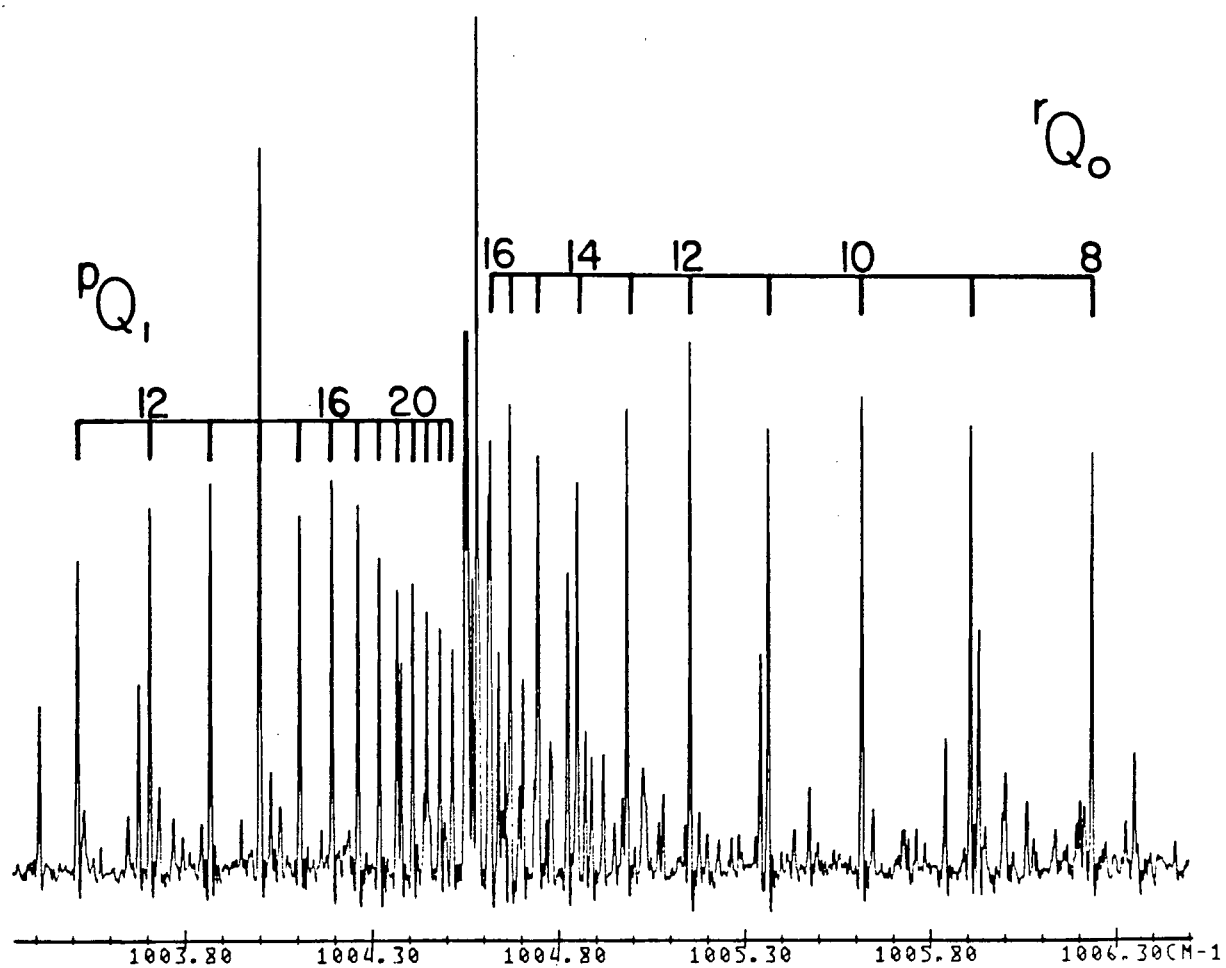


Fig. 5.6. Center of the ν_7 band of $\text{NH}_2^{11}\text{BH}_2$.

derivatives of the energy levels with respect to the parameters (see Section IV.C). The computations were performed on the University of British Columbia Computing Centre Amdahl 470 V/8 mainframe computer.

Two sets of molecular constants appear in Table 5.IV. Both were obtained by ignoring the Coriolis perturbation, but one was produced from a reduced data set of 606 transitions with a maximum K_a' of 6. In the excited state, all constants were floated except the off-diagonal sextics, namely ϕ_J , ϕ_{JK} , and ϕ_K . Eliminating all K_a' values above six reduces the standard deviation in the line positions from 0.001 cm^{-1} to 0.0003 cm^{-1} . This is expected from the K dependence of the Coriolis coupling. The standard errors of most constants improved when the data set was reduced, except for very small ones ($\approx 10^{-8} \text{ cm}^{-1}$) and with matrix elements dependent on K . Note in particular that Φ_{KJ} , L_{KKJ} and L_K , which accompany the variables K^6 , $J(J+1)K^6$ and K^8 , are very poorly determined in the reduced data set. This reflects the importance of a wide range of K values in determining terms containing high powers of K .

Without including Coriolis terms in the Hamiltonian, the constants in Table 5.IV are not true values. Rather, they comprise internally consistent sets which have incorporated the effects of the Coriolis interactions in order to fit the data. This is particularly evident in that the Δ_K and δ_K constants are negative, rather than positive as they should be. Since Δ_K and δ_K accompany the variables $-K^4$ and $-[(K \pm 2)^2 + K^2]$, these terms are the most sensitive to Coriolis interactions. An estimate of -0.406 was made for the ν_7 - ν_{11} a-axis Coriolis coupling constant ($\zeta_{7,11}$) from the ν_7

Table 5.IV. Molecular constants of the ν_7 band of $\text{NH}_2^{11}\text{BH}_2$ (in cm^{-1}), for both the full and reduced ($K_a' \leq 6$) data sets. The numbers in parentheses denote one standard deviation in units of the last significant figures. Where a ground state constant is blank, it was fixed to zero.

| | EXCITED STATE | | GROUND STATE |
|---------------|----------------------------|---------------------------|---------------------------|
| | Reduced | Full | |
| T_0 | 1004.68420(5) | 1004.6831(2) | |
| A | 4.51446(2) | 4.51512(3) | 4.610569(8) |
| B | 0.9060531(8) | 0.90605(2) | 0.916897(2) |
| C | 0.7646658(7) | 0.76467(2) | 0.763137(2) |
| Δ_J | $1.173(1) \times 10^{-6}$ | $1.161(3) \times 10^{-6}$ | $1.542(2) \times 10^{-6}$ |
| Δ_{JK} | $1.04(1) \times 10^{-5}$ | $1.15(2) \times 10^{-5}$ | $9.87(3) \times 10^{-6}$ |
| Δ_K | $-1.17(3) \times 10^{-4}$ | $-0.68(1) \times 10^{-4}$ | $8.692(8) \times 10^{-5}$ |
| δ_J | $1.116(6) \times 10^{-7}$ | $1.06(2) \times 10^{-7}$ | $2.86(3) \times 10^{-7}$ |
| δ_K | $-1.197(6) \times 10^{-5}$ | $-1.89(2) \times 10^{-5}$ | $1.016(2) \times 10^{-5}$ |
| Φ_{JK} | $6.7(2.2) \times 10^{-10}$ | $-3.3(2) \times 10^{-10}$ | |
| Φ_{KJ} | $-4.3(7) \times 10^{-8}$ | $5.7(4) \times 10^{-8}$ | $7.0(32) \times 10^{-11}$ |
| Φ_K | $-6.7(1.6) \times 10^{-7}$ | $3.7(2) \times 10^{-7}$ | $5.94(30) \times 10^{-9}$ |
| L_{JK} | $-2.5(7) \times 10^{-11}$ | $6.4(3) \times 10^{-11}$ | |
| L_{KKJ} | $4.6(1.3) \times 10^{-10}$ | | |
| L_K | $3.8(2.3) \times 10^{-9}$ | | |
| σ | 0.0003 | 0.001 | |

and v_{11} data.¹⁶⁰ This is in good agreement with a force field estimate of -0.40 .¹⁶¹

Appendix I. NbN $^3\Phi$ - $^3\Delta$ Correlation Matrix

| | B' | A _D ' | λ_D ' | A' | λ' | γ' | D' | h ₋₁ ' | h ₀ ' | h ₊₁ ' | b' | e ² qQ' |
|--------------------|----|------------------|---------------|--------|------------|-----------|--------|-------------------|------------------|-------------------|--------|--------------------|
| B' | 1 | -0.462 | 0.105 | 0.028 | -0.107 | 0.034 | 0.055 | -0.002 | 0.039 | 0.022 | 0.025 | 0.013 |
| A _D ' | | 1 | -0.159 | -0.258 | -0.158 | 0.333 | 0.157 | -0.032 | 0.022 | 0.047 | -0.319 | -0.004 |
| λ_D ' | | | 1 | 0.248 | -0.273 | 0.004 | 0.049 | -0.072 | 0.242 | -0.143 | 0.133 | -0.005 |
| A' | | | | 1 | 0.241 | -0.515 | -0.235 | 0.012 | -0.073 | -0.004 | 0.671 | 0.049 |
| λ' | | | | | 1 | -0.573 | -0.187 | 0.124 | -0.391 | 0.151 | 0.392 | 0.011 |
| γ' | | | | | | 1 | 0.517 | -0.117 | 0.121 | -0.011 | -0.706 | -0.013 |
| D' | | | | | | | 1 | 0.002 | 0.066 | 0.151 | -0.119 | -0.016 |
| h ₋₁ ' | | | | | | | | 1 | -0.027 | -0.004 | -0.002 | -0.068 |
| h ₀ ' | | | | | | | | | 1 | -0.027 | -0.075 | -0.002 |
| h ₊₁ ' | | | | | | | | | | 1 | 0.101 | -0.018 |
| b' | | | | | | | | | | | 1 | 0.041 |
| e ² qQ' | | | | | | | | | | | | 1 |

| | T_0 | B'' | A_D'' | λ_D'' | A'' | λ'' | γ'' | D'' | h_{-1}'' | h_0'' | h_{+1}'' | $b_{-1/0}''$ | $b_{0/+1}''$ |
|---------------|--------|--------|---------|---------------|--------|-------------|------------|--------|------------|---------|------------|--------------|--------------|
| B' | -0.038 | 0.995 | -0.462 | -0.017 | 0.026 | -0.113 | 0.011 | -0.131 | -0.025 | 0.032 | 0.021 | 0.027 | 0.023 |
| A_D' | -0.278 | -0.464 | 0.974 | -0.181 | -0.275 | -0.100 | 0.272 | 0.232 | 0.013 | 0.030 | 0.027 | -0.318 | -0.318 |
| λ_D' | -0.108 | 0.091 | -0.206 | 0.884 | 0.250 | -0.255 | -0.168 | -0.257 | -0.068 | 0.195 | -0.106 | 0.127 | 0.146 |
| A' | 0.152 | 0.026 | -0.355 | 0.396 | 0.999 | 0.235 | -0.882 | -0.455 | -0.026 | -0.078 | 0.041 | 0.670 | 0.672 |
| λ' | 0.592 | -0.091 | -0.060 | -0.114 | 0.242 | 0.965 | -0.268 | -0.067 | 0.084 | -0.345 | 0.150 | 0.398 | 0.377 |
| γ' | -0.902 | -0.004 | 0.227 | -0.267 | -0.520 | -0.382 | 0.680 | 0.284 | -0.063 | 0.123 | -0.050 | -0.701 | -0.701 |
| D' | -0.512 | -0.022 | 0.089 | -0.145 | -0.247 | -0.053 | 0.246 | 0.518 | 0.017 | 0.077 | 0.134 | -0.116 | -0.012 |
| h_{-1}' | 0.111 | 0.008 | -0.017 | -0.031 | 0.021 | 0.106 | -0.060 | 0.152 | 0.848 | -0.016 | 0.003 | 0.010 | 0.002 |
| h_0' | -0.116 | 0.036 | 0.005 | 0.221 | -0.073 | -0.415 | 0.072 | 0.105 | -0.011 | 0.910 | -0.012 | -0.082 | -0.062 |
| h_{+1}' | 0.034 | 0.034 | 0.073 | -0.110 | -0.020 | 0.151 | 0.056 | 0.356 | 0.000 | -0.006 | 0.933 | 0.096 | 0.081 |
| b' | 0.408 | 0.025 | -0.350 | 0.312 | 0.670 | 0.330 | -0.877 | -0.191 | -0.050 | -0.078 | 0.153 | 0.996 | 0.994 |
| e^2qQ' | -0.016 | 0.015 | -0.017 | -0.003 | 0.047 | 0.018 | -0.058 | -0.008 | -0.047 | 0.001 | -0.012 | 0.043 | 0.036 |
| T_0 | 1 | 0.007 | -0.097 | 0.147 | 0.159 | 0.368 | -0.301 | -0.110 | 0.074 | -0.112 | 0.050 | 0.401 | 0.400 |
| B'' | | 1 | -0.453 | -0.024 | 0.025 | -0.108 | 0.012 | -0.130 | -0.017 | 0.028 | 0.031 | 0.027 | 0.022 |
| A_D'' | | | 1 | -0.197 | -0.364 | -0.045 | 0.346 | 0.269 | 0.028 | 0.014 | 0.045 | -0.350 | -0.352 |
| λ_D'' | | | | 1 | 0.397 | -0.176 | -0.351 | -0.308 | -0.042 | 0.187 | -0.069 | 0.307 | 0.324 |
| A'' | | | | | 1 | 0.234 | -0.883 | -0.460 | -0.021 | -0.078 | 0.028 | 0.669 | 0.671 |
| λ'' | | | | | | 1 | -0.221 | -0.048 | 0.069 | -0.365 | 0.148 | 0.339 | 0.316 |
| γ'' | | | | | | | 1 | 0.442 | -0.005 | 0.078 | -0.008 | -0.877 | -0.880 |
| D'' | | | | | | | | 1 | 0.149 | 0.121 | 0.318 | -0.186 | -0.200 |
| h_{-1}'' | | | | | | | | | 1 | -0.010 | -0.004 | -0.051 | -0.051 |
| h_0'' | | | | | | | | | | 1 | -0.011 | -0.079 | -0.078 |
| h_{+1}'' | | | | | | | | | | | 1 | 0.153 | 0.150 |
| $b_{-1/0}''$ | | | | | | | | | | | | 1 | 0.993 |
| $b_{0/+1}''$ | | | | | | | | | | | | | 1 |

APPENDIX II. Transitions of the $3\Phi-3\Delta$ System of NbN.^aAppendix II.A. $3\Phi_2-3\Delta_1$.

| R | | | | Q | | | | P | | | |
|----|-----|----|-------------|----|------|----|-------------|----|------|----|-------------|
| J" | F" | | | J" | F" | | | J" | F" | | |
| 1 | 4.5 | pR | 16146.4540 | 2 | 5.5 | qQ | 16144.7074 | 3 | 6.5 | pP | 16141.7114 |
| 1 | 4.5 | qR | 16146.5474 | 2 | 6.5 | qQ | 16144.9179 | 3 | 7.5 | pP | 16141.8930 |
| 1 | 4.5 | rR | 16146.6629 | 3 | 5.5 | qQ | 16144.5975 | 4 | 3.5 | pP | 16140.4155 |
| 1 | 5.5 | pR | 16146.7154 | 3 | 6.5 | qQ | 16144.6982 | 4 | 4.5 | pP | 16140.4653 |
| 1 | 5.5 | qR | 16146.8310 | 3 | 7.5 | qQ | 16144.8162 | 4 | 5.5 | pP | 16140.5293 |
| 1 | 5.5 | rR | 16146.9692 | 4 | 5.5 | qQ | 16144.5255 | 5 | 4.5 | pP | 16139.4474 |
| 2 | 2.5 | pR | 16147.3250 | 4 | 6.5 | qQ | 16144.5854 | 5 | 5.5 | pP | 16139.4858 |
| 2 | 2.5 | qR | 16147.3517 | 4 | 8.5 | qQ | 16144.7337 | 5 | 6.5 | pP | 16139.5321 |
| 2 | 2.5 | co | 16147.3705 | 5 | 4.5 | qQ | 16144.4281 | 5 | 7.5 | pP | 16139.5875 |
| 2 | 2.5 | rR | 16147.3890 | 5 | 5.5 | qQ | 16144.4622* | 5 | 8.5 | pP | 16139.6506 |
| 2 | 3.5 | pR | 16147.3833 | 5 | 6.5 | qQ | 16144.5010 | 5 | 9.5 | pP | 16139.7216 |
| 2 | 3.5 | qR | 16147.4205 | 5 | 7.5 | qQ | 16144.5462 | 6 | 3.5 | pP | 16138.3884* |
| 2 | 3.5 | co | 16147.4442 | 5 | 8.5 | qQ | 16144.5975 | 6 | 4.5 | pP | 16138.4083* |
| 2 | 3.5 | rR | 16147.4682 | 5 | 9.5 | qQ | 16144.6555 | 6 | 5.5 | pP | 16138.4339 |
| 2 | 4.5 | pR | 16147.4643 | 6 | 5.5 | qQ | 16144.3961* | 6 | 6.5 | pP | 16138.4648 |
| 2 | 4.5 | qR | 16147.5121 | 6 | 6.5 | qQ | 16144.4232* | 6 | 7.5 | pP | 16138.5015 |
| 2 | 4.5 | rR | 16147.5698 | 6 | 7.5 | qQ | 16144.4556* | 6 | 8.5 | pP | 16138.5435 |
| 2 | 5.5 | qR | 16147.6272 | 6 | 9.5 | qQ | 16144.5314 | 6 | 9.5 | pP | 16138.5909 |
| 2 | 5.5 | rR | 16147.6948 | 6 | 10.5 | qQ | 16144.5764 | 6 | 10.5 | pP | 16138.6441 |
| 2 | 6.5 | qR | 16147.7669 | 7 | 2.5 | qQ | 16144.2829 | 7 | 2.5 | pP | 16137.3347 |
| 2 | 6.5 | rR | 16147.8436 | 7 | 3.5 | qQ | 16144.2937 | 7 | 3.5 | pP | 16137.3449 |
| 3 | 1.5 | pR | 16148.3506 | 7 | 4.5 | qQ | 16144.3069* | 7 | 4.5 | pP | 16137.3592 |
| 3 | 1.5 | qR | 16148.3604* | 7 | 5.5 | qQ | 16144.3241 | 7 | 5.5 | pP | 16137.3773 |
| 3 | 1.5 | co | 16148.3684* | 7 | 6.5 | qQ | 16144.3445* | 7 | 6.5 | pP | 16137.3992 |
| 3 | 1.5 | rR | 16148.3763 | 7 | 7.5 | qQ | 16144.3674 | 7 | 7.5 | pP | 16137.4251 |
| 3 | 2.5 | pR | 16148.3712* | 7 | 8.5 | qQ | 16144.3938 | 7 | 8.5 | pP | 16137.4548 |
| 3 | 2.5 | qR | 16148.3873 | 7 | 9.5 | qQ | 16144.4232 | 7 | 9.5 | pP | 16137.4886 |
| 3 | 2.5 | co | 16148.3985 | 7 | 10.5 | qQ | 16144.4556 | 7 | 10.5 | pP | 16137.5263 |
| 3 | 2.5 | rR | 16148.4098 | 7 | 11.5 | qQ | 16144.4915 | 7 | 11.5 | pP | 16137.5678 |
| 3 | 3.5 | pR | 16148.4032 | 8 | 3.5 | qQ | 16144.2216 | 8 | 3.5 | pP | 16136.2870 |
| 3 | 3.5 | qR | 16148.4257 | 8 | 4.5 | qQ | 16144.2325 | 8 | 4.5 | pP | 16136.2976 |
| 3 | 3.5 | co | 16148.4399 | 8 | 5.5 | qQ | 16144.2450 | 8 | 5.5 | pP | 16136.3108 |
| 3 | 3.5 | rR | 16148.4541 | 8 | 6.5 | qQ | 16144.2600 | 8 | 6.5 | pP | 16136.3270 |
| 3 | 4.5 | pR | 16148.4469 | 8 | 7.5 | qQ | 16144.2781* | 8 | 7.5 | pP | 16136.3461 |
| 3 | 4.5 | qR | 16148.4755 | 8 | 8.5 | qQ | 16144.2976 | 8 | 8.5 | pP | 16136.3682 |
| 3 | 4.5 | co | 16148.4930 | 8 | 9.5 | qQ | 16144.3198 | 8 | 9.5 | pP | 16136.3931 |
| 3 | 4.5 | rR | 16148.5103 | 8 | 10.5 | qQ | 16144.3445 | 8 | 10.5 | pP | 16136.4211 |
| 3 | 5.5 | qR | 16148.5375 | 8 | 11.5 | qQ | 16144.3719 | 8 | 11.5 | pP | 16136.4520 |
| 3 | 5.5 | co | 16148.5582 | 8 | 12.5 | qQ | 16144.4024 | 8 | 12.5 | pP | 16136.4858 |
| 3 | 5.5 | rR | 16148.5782 | 9 | 4.5 | qQ | 16144.1476* | 9 | 4.5 | pP | 16135.2249 |
| 3 | 6.5 | qR | 16148.6118 | 9 | 5.5 | qQ | 16144.1575* | 9 | 5.5 | pP | 16135.2350 |
| 3 | 6.5 | rR | 16148.6583 | 9 | 6.5 | co | 16144.1647* | 9 | 6.5 | pP | 16135.2472 |
| 3 | 7.5 | qR | 16148.6996 | 9 | 6.5 | qQ | 16144.1695* | 9 | 7.5 | pP | 16135.2616 |
| 3 | 7.5 | rR | 16148.7512 | 9 | 6.5 | co | 16144.1750* | 9 | 8.5 | pP | 16135.2784 |
| 4 | 0.5 | rR | 16149.3518 | 9 | 7.5 | qQ | 16144.1830 | 9 | 9.5 | pP | 16135.2974 |
| 4 | 1.5 | qR | 16149.3553 | 9 | 7.5 | co | 16144.1888* | 9 | 10.5 | pP | 16135.3187 |
| 4 | 1.5 | co | 16149.3607 | 9 | 8.5 | qQ | 16144.1989 | 9 | 11.5 | pP | 16135.3422 |
| 4 | 1.5 | rR | 16149.3661 | 9 | 8.5 | co | 16144.2049* | 9 | 12.5 | pP | 16135.3681 |
| 4 | 2.5 | qR | 16149.3725 | 9 | 9.5 | co | 16144.2092* | 9 | 13.5 | pP | 16135.3961 |
| 4 | 2.5 | co | 16149.3801 | 9 | 9.5 | qQ | 16144.2157 | | | | |
| 4 | 2.5 | rR | 16149.3875 | 9 | 9.5 | co | 16144.2226* | | | | |
| 4 | 3.5 | qR | 16149.3969 | 9 | 10.5 | co | 16144.2279* | | | | |
| 4 | 3.5 | co | 16149.4064 | 9 | 10.5 | qQ | 16144.2350 | | | | |
| 4 | 3.5 | rR | 16149.4159 | 9 | 10.5 | co | 16144.2431* | | | | |
| 4 | 4.5 | qR | 16149.4282 | 9 | 11.5 | co | 16144.2485* | | | | |
| 4 | 4.5 | co | 16149.4397 | 9 | 11.5 | qQ | 16144.2562 | | | | |
| 4 | 4.5 | rR | 16149.4514 | 9 | 11.5 | co | 16144.2645* | | | | |
| 4 | 5.5 | qR | 16149.4670 | 9 | 12.5 | co | 16144.2710* | | | | |
| 4 | 5.5 | co | 16149.4807 | 9 | 12.5 | qQ | 16144.2794 | | | | |

Appendix II.A, continued. $3\Phi_2-3\Delta_1$.

| <u>R</u> | | | <u>Q</u> | | | <u>P</u> | | |
|----------|------|---------------|----------|------|----------------|----------|----|--|
| J" | F" | | J" | F" | | J" | F" | |
| 4 | 5.5 | rR 16149.4943 | 9 | 13.5 | co 16144.2947* | | | |
| 4 | 6.5 | qR 16149.5134 | 9 | 13.5 | qQ 16144.3047* | | | |
| 4 | 6.5 | co 16149.5292 | 10 | 5.5 | qQ 16144.0616* | | | |
| 4 | 6.5 | rR 16149.5446 | 10 | 6.5 | qQ 16144.0707* | | | |
| 4 | 7.5 | qR 16149.5678 | 10 | 6.5 | co 16144.0749* | | | |
| 4 | 7.5 | rR 16149.6026 | 10 | 7.5 | qQ 16144.0815* | | | |
| 4 | 8.5 | qR 16149.6298 | 10 | 8.5 | co 16144.0888* | | | |
| 4 | 8.5 | rR 16149.6681 | 10 | 8.5 | qQ 16144.0937 | | | |
| 5 | 1.5 | co 16150.3267 | 10 | 8.5 | co 16144.0989* | | | |
| 5 | 1.5 | rR 16150.3306 | 10 | 9.5 | co 16144.1018* | | | |
| 5 | 2.5 | qR 16150.3348 | 10 | 9.5 | qQ 16144.1075 | | | |
| 5 | 2.5 | co 16150.3401 | 10 | 9.5 | co 16144.1132* | | | |
| 5 | 2.5 | rR 16150.3454 | 10 | 10.5 | co 16144.1167* | | | |
| 5 | 3.5 | qR 16150.3513 | 10 | 10.5 | qQ 16144.1226 | | | |
| 5 | 3.5 | co 16150.3581 | 10 | 10.5 | co 16144.1289* | | | |
| 5 | 3.5 | rR 16150.3649 | 10 | 11.5 | co 16144.1328* | | | |
| 5 | 4.5 | qR 16150.3726 | 10 | 11.5 | qQ 16144.1393 | | | |
| 5 | 4.5 | co 16150.3808 | 10 | 12.5 | co 16144.1507* | | | |
| 5 | 4.5 | rR 16150.3891 | 10 | 12.5 | qQ 16144.1575 | | | |
| 5 | 5.5 | qR 16150.3989 | 10 | 13.5 | qQ 16144.1775 | | | |
| 5 | 5.5 | co 16150.4086 | 10 | 14.5 | qQ 16144.1989 | | | |
| 5 | 5.5 | rR 16150.4184 | 11 | 7.5 | co 16143.9767 | | | |
| 5 | 6.5 | qR 16150.4302 | 11 | 8.5 | co 16143.9783 | | | |
| 5 | 6.5 | co 16150.4414 | 11 | 8.5 | qQ 16143.9824 | | | |
| 5 | 6.5 | rR 16150.4528 | 11 | 8.5 | co 16143.9869 | | | |
| 5 | 7.5 | qR 16150.4669 | 11 | 9.5 | co 16143.9889 | | | |
| 5 | 7.5 | co 16150.4795 | 11 | 9.5 | qQ 16143.9933 | | | |
| 5 | 7.5 | rR 16150.4921 | 11 | 9.5 | co 16143.9982 | | | |
| 5 | 8.5 | qR 16150.5088 | 11 | 10.5 | co 16144.0004 | | | |
| 5 | 8.5 | co 16150.5228 | 11 | 10.5 | qQ 16144.0053 | | | |
| 5 | 8.5 | rR 16150.5364 | 11 | 10.5 | co 16144.0106 | | | |
| 5 | 9.5 | rR 16150.5862 | 11 | 11.5 | co 16144.0134 | | | |
| 6 | 1.5 | rR 16151.2772 | 11 | 11.5 | qQ 16144.0188 | | | |
| 6 | 2.5 | co 16151.2838 | 11 | 11.5 | co 16144.0246 | | | |
| 6 | 2.5 | rR 16151.2878 | 11 | 12.5 | co 16144.0278 | | | |
| 6 | 3.5 | qR 16151.2917 | 11 | 12.5 | qQ 16144.0334 | | | |
| 6 | 3.5 | co 16151.2968 | 11 | 12.5 | co 16144.0396 | | | |
| 6 | 3.5 | rR 16151.3019 | 11 | 13.5 | co 16144.0431 | | | |
| 6 | 4.5 | qR 16151.3071 | 11 | 13.5 | qQ 16144.0494* | | | |
| 6 | 4.5 | co 16151.3133 | 11 | 14.5 | qQ 16144.0666* | | | |
| 6 | 4.5 | rR 16151.3195 | 11 | 15.5 | qQ 16144.0852 | | | |
| 6 | 5.5 | qR 16151.3260 | 12 | 7.5 | co 16143.8591 | | | |
| 6 | 5.5 | co 16151.3332 | 12 | 8.5 | co 16143.8609 | | | |
| 6 | 5.5 | rR 16151.3407 | 12 | 8.5 | co 16143.8671 | | | |
| 6 | 6.5 | qR 16151.3485 | 12 | 9.5 | co 16143.8684 | | | |
| 6 | 6.5 | co 16151.3569 | 12 | 9.5 | qQ 16143.8722 | | | |
| 6 | 6.5 | rR 16151.3652 | 12 | 9.5 | co 16143.8763 | | | |
| 6 | 7.5 | qR 16151.3748 | 12 | 10.5 | co 16143.8778 | | | |
| 6 | 7.5 | co 16151.3843 | 12 | 10.5 | qQ 16143.8819 | | | |
| 6 | 7.5 | rR 16151.3937 | 12 | 10.5 | co 16143.8864 | | | |
| 6 | 8.5 | qR 16151.4046 | 12 | 11.5 | co 16143.8882 | | | |
| 6 | 8.5 | co 16151.4153 | 12 | 11.5 | qQ 16143.8928 | | | |
| 6 | 8.5 | rR 16151.4256 | 12 | 11.5 | co 16143.8977 | | | |
| 6 | 9.5 | qR 16151.4385 | 12 | 12.5 | co 16143.8997 | | | |
| 6 | 9.5 | co 16151.4501 | 12 | 12.5 | qQ 16143.9046 | | | |
| 6 | 9.5 | rR 16151.4613 | 12 | 12.5 | co 16143.9097 | | | |
| 6 | 10.5 | rR 16151.5009 | 12 | 13.5 | co 16143.9121 | | | |
| 7 | 2.5 | rR 16152.2180 | 12 | 13.5 | qQ 16143.9175 | | | |
| 7 | 3.5 | co 16152.2246 | 12 | 13.5 | co 16143.9230 | | | |
| 7 | 3.5 | rR 16152.2287 | 12 | 14.5 | co 16143.9257 | | | |
| 7 | 4.5 | co 16152.2370 | 12 | 14.5 | qQ 16143.9315 | | | |
| 7 | 4.5 | rR 16152.2419 | 12 | 14.5 | co 16143.9374 | | | |
| 7 | 5.5 | qR 16152.2461 | 12 | 15.5 | co 16143.9405 | | | |
| 7 | 5.5 | co 16152.2521 | 12 | 15.5 | qQ 16143.9464 | | | |
| 7 | 5.5 | rR 16152.2578 | 12 | 15.5 | co 16143.9525 | | | |

Appendix II.A, continued. ${}^3\Phi_2$ - ${}^3\Delta_1$.

| R | | | | Q | | | | P | | | |
|----|------|----|------------|----|------|----|-------------|----|----|--|--|
| J" | F" | | | J" | F" | | | J" | F" | | |
| 7 | 6.5 | qR | 16152.2632 | 12 | 16.5 | co | 16143.9559 | | | | |
| 7 | 6.5 | co | 16152.2697 | 12 | 16.5 | qQ | 16143.9626* | | | | |
| 7 | 6.5 | rR | 16152.2762 | 13 | 9.5 | qQ | 16143.7435 | | | | |
| 7 | 7.5 | qR | 16152.2827 | 13 | 10.5 | qQ | 16143.7524 | | | | |
| 7 | 7.5 | co | 16152.2900 | 13 | 10.5 | co | 16143.7553 | | | | |
| 7 | 7.5 | rR | 16152.2972 | 13 | 11.5 | co | 16143.7562 | | | | |
| 7 | 8.5 | qR | 16152.3047 | 13 | 11.5 | qQ | 16143.7602 | | | | |
| 7 | 8.5 | co | 16152.3130 | 13 | 12.5 | qQ | 16143.7698 | | | | |
| 7 | 8.5 | rR | 16152.3210 | 13 | 12.5 | co | 16143.7744 | | | | |
| 7 | 9.5 | qR | 16152.3298 | 13 | 13.5 | co | 16143.7756 | | | | |
| 7 | 9.5 | co | 16152.3388 | 13 | 13.5 | qQ | 16143.7801 | | | | |
| 7 | 9.5 | rR | 16152.3477 | 13 | 13.5 | co | 16143.7851 | | | | |
| 7 | 10.5 | qR | 16152.3578 | 13 | 14.5 | co | 16143.7870 | | | | |
| 7 | 10.5 | co | 16152.3676 | 13 | 14.5 | qQ | 16143.7916 | | | | |
| 7 | 10.5 | rR | 16152.3772 | 13 | 14.5 | co | 16143.7966 | | | | |
| 7 | 11.5 | co | 16152.3995 | 13 | 15.5 | co | 16143.7986 | | | | |
| 7 | 11.5 | rR | 16152.4096 | 13 | 15.5 | qQ | 16143.8036 | | | | |
| 8 | 3.5 | rR | 16153.1443 | 13 | 15.5 | co | 16143.8099 | | | | |
| 8 | 4.5 | co | 16153.1507 | 13 | 16.5 | co | 16143.8113 | | | | |
| 8 | 4.5 | rR | 16153.1546 | 13 | 16.5 | qQ | 16143.8168 | | | | |
| 8 | 5.5 | co | 16153.1621 | 13 | 17.5 | qQ | 16143.8307 | | | | |
| 8 | 5.5 | rR | 16153.1668 | 14 | 10.5 | qQ | 16143.6131 | | | | |
| 8 | 6.5 | co | 16153.1758 | 14 | 11.5 | qQ | 16143.6199 | | | | |
| 8 | 6.5 | rR | 16153.1810 | 14 | 12.5 | qQ | 16143.6279 | | | | |
| 8 | 7.5 | co | 16153.1914 | 14 | 13.5 | qQ | 16143.6365 | | | | |
| 8 | 7.5 | rR | 16153.1973 | 14 | 14.5 | qQ | 16143.6459 | | | | |
| 8 | 8.5 | co | 16153.2091 | 14 | 15.5 | qQ | 16143.6557 | | | | |
| 8 | 8.5 | rR | 16153.2157 | 14 | 16.5 | qQ | 16143.6662 | | | | |
| 8 | 9.5 | co | 16153.2290 | 14 | 17.5 | qQ | 16143.6778 | | | | |
| 8 | 9.5 | rR | 16153.2362 | 14 | 18.5 | qQ | 16143.6901 | | | | |
| 8 | 10.5 | qR | 16153.2432 | 15 | 10.5 | qQ | 16143.4662* | | | | |
| 8 | 10.5 | co | 16153.2511 | 15 | 11.5 | qQ | 16143.4721* | | | | |
| 8 | 10.5 | rR | 16153.2589 | 15 | 12.5 | qQ | 16143.4787 | | | | |
| 8 | 11.5 | co | 16153.2754 | 15 | 13.5 | qQ | 16143.4854 | | | | |
| | | | | 15 | 14.5 | qQ | 16143.4931 | | | | |
| | | | | 15 | 15.5 | qQ | 16143.5011 | | | | |
| | | | | 15 | 16.5 | qQ | 16143.5100 | | | | |
| | | | | 15 | 17.5 | qQ | 16143.5193 | | | | |
| | | | | 15 | 18.5 | qQ | 16143.5293 | | | | |
| | | | | 15 | 19.5 | qQ | 16143.5401 | | | | |
| | | | | 16 | 12.5 | qQ | 16143.3211* | | | | |
| | | | | 16 | 13.5 | qQ | 16143.3267 | | | | |
| | | | | 16 | 14.5 | qQ | 16143.3331 | | | | |
| | | | | 16 | 15.5 | qQ | 16143.3393 | | | | |
| | | | | 16 | 16.5 | qQ | 16143.3465 | | | | |
| | | | | 16 | 17.5 | qQ | 16143.3544 | | | | |
| | | | | 16 | 18.5 | qQ | 16143.3625 | | | | |
| | | | | 16 | 19.5 | qQ | 16143.3713 | | | | |
| | | | | 16 | 20.5 | qQ | 16143.3805 | | | | |
| | | | | 17 | 12.5 | qQ | 16143.1555 | | | | |
| | | | | 17 | 13.5 | qQ | 16143.1602 | | | | |
| | | | | 17 | 14.5 | qQ | 16143.1650 | | | | |
| | | | | 17 | 15.5 | qQ | 16143.1706 | | | | |
| | | | | 17 | 16.5 | qQ | 16143.1763 | | | | |
| | | | | 17 | 17.5 | qQ | 16143.1824 | | | | |
| | | | | 17 | 18.5 | qQ | 16143.1890 | | | | |
| | | | | 17 | 19.5 | qQ | 16143.1963 | | | | |
| | | | | 17 | 20.5 | qQ | 16143.2037 | | | | |
| | | | | 17 | 21.5 | qQ | 16143.2118 | | | | |
| | | | | 18 | 13.5 | qQ | 16142.9849 | | | | |
| | | | | 18 | 14.5 | qQ | 16142.9887 | | | | |
| | | | | 18 | 15.5 | qQ | 16142.9932 | | | | |
| | | | | 18 | 16.5 | qQ | 16142.9978 | | | | |
| | | | | 18 | 17.5 | qQ | 16143.0028 | | | | |
| | | | | 18 | 18.5 | qQ | 16143.0081 | | | | |

Appendix II.A, continued. ${}^3\Phi_2\text{-}{}^3\Delta_1$.

| <u>R</u> | | <u>Q</u> | <u>P</u> |
|----------------|----------------|----------|-------------|
| J [*] | F [*] | | |
| 18 | 19.5 | qQ | 16143.0140 |
| 18 | 20.5 | qQ | 16143.0200 |
| 18 | 21.5 | qQ | 16143.0266 |
| 18 | 22.5 | qQ | 16143.0336 |
| 19 | 15.5 | qQ | 16142.8074 |
| 19 | 22.5 | qQ | 16142.8404 |
| 19 | 23.5 | qQ | 16142.8462 |
| 20 | 15.5 | qQ | 16142.6139 |
| 20 | 16.5 | qQ | 16142.6166 |
| 20 | 17.5 | qQ | 16142.6194 |
| 20 | 18.5 | qQ | 16142.6230 |
| 20 | 19.5 | qQ | 16142.6262 |
| 20 | 20.5 | qQ | 16142.6301 |
| 20 | 21.5 | qQ | 16142.6341 |
| 20 | 22.5 | qQ | 16142.6387 |
| 20 | 23.5 | qQ | 16142.6433 |
| 20 | 24.5 | qQ | 16142.6486 |
| 21 | 16.5 | qQ | 16142.4132 |
| 21 | 17.5 | qQ | 16142.4152 |
| 21 | 18.5 | qQ | 16142.4182 |
| 21 | 19.5 | qQ | 16142.4207 |
| 21 | 20.5 | qQ | 16142.4233 |
| 21 | 21.5 | qQ | 16142.4261 |
| 21 | 22.5 | qQ | 16142.4299 |
| 21 | 23.5 | qQ | 16142.4337 |
| 21 | 24.5 | qQ | 16142.4378 |
| 21 | 25.5 | qQ | 16142.4417 |
| 31 | 27.5 | qQ | 16139.8508* |
| 31 | 28.5 | qQ | 16139.8488* |
| 31 | 29.5 | qQ | 16139.8467* |
| 31 | 30.5 | qQ | 16139.8423* |
| 31 | 31.5 | qQ | 16139.8408* |
| 31 | 32.5 | qQ | 16139.8382* |
| 31 | 33.5 | qQ | 16139.8366* |
| 32 | 28.5 | qQ | 16139.5394* |
| 32 | 29.5 | qQ | 16139.5368* |
| 32 | 31.5 | qQ | 16139.5321* |
| 32 | 32.5 | qQ | 16139.5293* |
| 32 | 33.5 | qQ | 16139.5268* |
| 32 | 34.5 | qQ | 16139.5242* |
| 32 | 35.5 | qQ | 16139.5217* |
| 33 | 28.5 | qQ | 16139.2199 |
| 33 | 29.5 | qQ | 16139.2171 |
| 33 | 30.5 | qQ | 16139.2143 |
| 33 | 31.5 | qQ | 16139.2113 |
| 33 | 32.5 | qQ | 16139.2083 |
| 33 | 33.5 | qQ | 16139.2053 |
| 33 | 34.5 | qQ | 16139.2023 |
| 33 | 35.5 | qQ | 16139.1994 |
| 33 | 36.5 | qQ | 16139.1966 |
| 33 | 37.5 | qQ | 16139.1938 |
| 34 | 29.5 | qQ | 16138.8863 |
| 34 | 30.5 | qQ | 16138.8832 |
| 34 | 31.5 | qQ | 16138.8798 |
| 34 | 32.5 | qQ | 16138.8764 |
| 34 | 33.5 | qQ | 16138.8730 |
| 34 | 34.5 | qQ | 16138.8696 |
| 34 | 35.5 | qQ | 16138.8662 |
| 34 | 36.5 | qQ | 16138.8628 |
| 34 | 37.5 | qQ | 16138.8596 |
| 34 | 38.5 | qQ | 16138.8562 |
| 35 | 32.5 | qQ | 16138.5376* |
| 35 | 34.5 | qQ | 16138.5299 |
| 35 | 35.5 | qQ | 16138.5261 |
| 35 | 36.5 | qQ | 16138.5222 |

Appendix II.A, continued. ${}^3\Phi_2\text{-}{}^3\Delta_1$.

| <u>R</u> | | <u>Q</u> | <u>P</u> |
|----------|------|----------|-------------|
| J" | F" | | |
| 35 | 37.5 | qQ | 16138.5184 |
| 35 | 38.5 | qQ | 16138.5147 |
| 35 | 39.5 | qQ | 16138.5110 |
| 36 | 31.5 | qQ | 16138.1934 |
| 36 | 32.5 | qQ | 16138.1893 |
| 36 | 33.5 | qQ | 16138.1853 |
| 36 | 34.5 | qQ | 16138.1812 |
| 36 | 35.5 | qQ | 16138.1773 |
| 36 | 36.5 | qQ | 16138.1729 |
| 36 | 37.5 | qQ | 16138.1686 |
| 36 | 38.5 | qQ | 16138.1642 |
| 36 | 39.5 | qQ | 16138.1601 |
| 36 | 40.5 | qQ | 16138.1559 |
| 37 | 32.5 | qQ | 16137.8315 |
| 37 | 33.5 | qQ | 16137.8270 |
| 37 | 34.5 | qQ | 16137.8226 |
| 37 | 35.5 | qQ | 16137.8181 |
| 37 | 36.5 | qQ | 16137.8136 |
| 37 | 37.5 | qQ | 16137.8087 |
| 37 | 38.5 | qQ | 16137.8044 |
| 37 | 39.5 | qQ | 16137.7995 |
| 37 | 40.5 | qQ | 16137.7950 |
| 37 | 41.5 | qQ | 16137.7904 |
| 38 | 33.5 | qQ | 16137.4595 |
| 38 | 34.5 | qQ | 16137.4548* |
| 38 | 35.5 | qQ | 16137.4505 |
| 38 | 36.5 | qQ | 16137.4449 |
| 38 | 37.5 | qQ | 16137.4403 |
| 38 | 38.5 | qQ | 16137.4352 |
| 38 | 39.5 | qQ | 16137.4305 |
| 38 | 40.5 | qQ | 16137.4251* |
| 38 | 41.5 | qQ | 16137.4199 |
| 38 | 42.5 | qQ | 16137.4150 |
| 39 | 34.5 | qQ | 16137.0771 |
| 39 | 35.5 | qQ | 16137.0720 |
| 39 | 36.5 | qQ | 16137.0669 |
| 39 | 37.5 | qQ | 16137.0617 |
| 39 | 38.5 | qQ | 16137.0563 |
| 39 | 39.5 | qQ | 16137.0510 |
| 39 | 40.5 | qQ | 16137.0455 |
| 39 | 41.5 | qQ | 16137.0403 |
| 39 | 42.5 | qQ | 16137.0346 |
| 39 | 43.5 | qQ | 16137.0293 |
| 40 | 35.5 | qQ | 16136.6841 |
| 40 | 36.5 | qQ | 16136.6787 |
| 40 | 37.5 | qQ | 16136.6732 |
| 40 | 38.5 | qQ | 16136.6677 |
| 40 | 39.5 | qQ | 16136.6619 |
| 40 | 40.5 | qQ | 16136.6562 |
| 40 | 41.5 | qQ | 16136.6505 |
| 40 | 42.5 | qQ | 16136.6444 |
| 40 | 43.5 | qQ | 16136.6387 |
| 40 | 44.5 | qQ | 16136.6329 |
| 41 | 36.5 | qQ | 16136.2810 |
| 41 | 37.5 | qQ | 16136.2749 |
| 41 | 38.5 | qQ | 16136.2689 |
| 41 | 39.5 | qQ | 16136.2631 |
| 41 | 40.5 | qQ | 16136.2569 |
| 41 | 41.5 | qQ | 16136.2510 |
| 41 | 42.5 | qQ | 16136.2448 |
| 41 | 43.5 | qQ | 16136.2387 |
| 41 | 44.5 | qQ | 16136.2324 |
| 41 | 45.5 | qQ | 16136.2261 |
| 42 | 37.5 | qQ | 16135.8672 |

Appendix II.A, continued. $3\Phi_2-3\Delta_1$.

| R | | Q | P |
|----|------|----|------------|
| J" | F" | | |
| 42 | 38.5 | qQ | 16135.8612 |
| 42 | 39.5 | qQ | 16135.8549 |
| 42 | 40.5 | qQ | 16135.8485 |
| 42 | 41.5 | qQ | 16135.8421 |
| 42 | 42.5 | qQ | 16135.8356 |
| 42 | 43.5 | qQ | 16135.8293 |
| 42 | 44.5 | qQ | 16135.8227 |
| 42 | 45.5 | qQ | 16135.8158 |
| 42 | 46.5 | qQ | 16135.8091 |
| 43 | 38.5 | qQ | 16135.4427 |
| 43 | 39.5 | qQ | 16135.4362 |
| 43 | 40.5 | qQ | 16135.4298 |
| 43 | 41.5 | qQ | 16135.4230 |
| 43 | 42.5 | qQ | 16135.4164 |
| 43 | 43.5 | qQ | 16135.4093 |
| 43 | 44.5 | qQ | 16135.4024 |
| 43 | 45.5 | qQ | 16135.3961 |
| 43 | 46.5 | qQ | 16135.3889 |
| 43 | 47.5 | qQ | 16135.3816 |
| 44 | 39.5 | qQ | 16135.0081 |
| 44 | 40.5 | qQ | 16135.0014 |
| 44 | 41.5 | qQ | 16134.9947 |
| 44 | 42.5 | qQ | 16134.9875 |
| 44 | 43.5 | qQ | 16134.9804 |
| 44 | 44.5 | qQ | 16134.9733 |
| 44 | 45.5 | qQ | 16134.9664 |
| 44 | 46.5 | qQ | 16134.9588 |
| 44 | 47.5 | qQ | 16134.9515 |
| 44 | 48.5 | qQ | 16134.9442 |

Appendix II.B. $3\Phi_3-3\Delta_2$.

| J" | F" | | J" | F" | |
|----|-----|----|----|------|----|
| 2 | 2.5 | rR | 3 | 5.5 | qQ |
| 2 | 3.5 | pR | 3 | 5.5 | rQ |
| 2 | 3.5 | rR | 3 | 6.5 | qQ |
| 2 | 4.5 | pR | 3 | 6.5 | rQ |
| 2 | 4.5 | qR | 3 | 7.5 | qQ |
| 2 | 4.5 | rR | 4 | 1.5 | qQ |
| 2 | 5.5 | qR | 4 | 3.5 | qQ |
| 2 | 5.5 | rR | 4 | 4.5 | qQ |
| 2 | 6.5 | rR | 4 | 5.5 | qQ |
| 3 | 2.5 | qR | 4 | 6.5 | qQ |
| 3 | 3.5 | qR | 4 | 6.5 | rQ |
| 3 | 4.5 | pR | 4 | 7.5 | qQ |
| 3 | 4.5 | qR | 4 | 7.5 | rQ |
| 3 | 5.5 | pR | 4 | 8.5 | qQ |
| 3 | 5.5 | qR | 5 | 1.5 | co |
| 3 | 6.5 | qR | 5 | 2.5 | co |
| 3 | 6.5 | rR | 6 | 2.5 | qQ |
| 3 | 7.5 | qR | 6 | 2.5 | co |
| 3 | 7.5 | rR | 6 | 3.5 | qQ |
| 4 | 2.5 | qR | 6 | 4.5 | qQ |
| 4 | 2.5 | rR | 6 | 5.5 | qQ |
| 4 | 3.5 | qR | 6 | 6.5 | qQ |
| 4 | 3.5 | rR | 6 | 7.5 | qQ |
| 4 | 4.5 | qR | 6 | 8.5 | qQ |
| 4 | 4.5 | rR | 6 | 9.5 | qQ |
| 4 | 5.5 | qR | 6 | 10.5 | qQ |
| 4 | 5.5 | rR | 7 | 4.5 | qQ |
| 4 | 6.5 | qR | 7 | 5.5 | qQ |
| 4 | 6.5 | rR | 7 | 6.5 | qQ |
| 4 | 7.5 | qR | 7 | 7.5 | qQ |
| 4 | 7.5 | rR | 7 | 8.5 | qQ |

Appendix II.B, continued. ${}^3\Phi_3\text{-}{}^3\Delta_2$.

| R | | | Q | | | P | | |
|----|------|----------------|----|------|----------------|----|----|--|
| J" | F" | | J" | F" | | J" | F" | |
| 4 | 8.5 | qR 16547.7864* | 7 | 9.5 | qQ 16542.6473* | | | |
| 4 | 8.5 | rR 16547.8221* | 7 | 10.5 | qQ 16542.6544* | | | |
| 15 | 10.5 | rR 16557.3963 | 7 | 11.5 | qQ 16542.6623* | | | |
| 15 | 11.5 | rR 16557.3980 | 8 | 4.5 | qQ 16542.5271 | | | |
| 15 | 12.5 | rR 16557.4003 | 8 | 5.5 | qQ 16542.5310* | | | |
| 15 | 13.5 | rR 16557.4027 | 8 | 6.5 | qQ 16542.5344* | | | |
| 15 | 14.5 | rR 16557.4053 | 8 | 7.5 | qQ 16542.5377* | | | |
| 15 | 15.5 | rR 16557.4076 | 8 | 8.5 | qQ 16542.5420 | | | |
| 15 | 16.5 | rR 16557.4110 | 8 | 9.5 | qQ 16542.5469 | | | |
| 15 | 17.5 | rR 16557.4146 | 8 | 10.5 | qQ 16542.5526 | | | |
| 15 | 18.5 | rR 16557.4176 | 8 | 11.5 | qQ 16542.5589 | | | |
| 15 | 19.5 | rR 16557.4219 | 8 | 12.5 | qQ 16542.5657 | | | |
| 16 | 11.5 | rR 16558.1965* | 9 | 7.5 | qQ 16542.4283* | | | |
| 16 | 12.5 | rR 16558.1986 | 9 | 8.5 | qQ 16542.4318* | | | |
| 16 | 13.5 | rR 16558.2008 | 9 | 10.5 | qQ 16542.4407* | | | |
| 16 | 14.5 | rR 16558.2029* | 9 | 11.5 | qQ 16542.4458* | | | |
| 16 | 15.5 | rR 16558.2056 | 9 | 12.5 | qQ 16542.4515* | | | |
| 16 | 16.5 | rR 16558.2086 | 9 | 13.5 | qQ 16542.4580* | | | |
| 16 | 17.5 | rR 16558.2116 | 10 | 8.5 | qQ 16542.3107* | | | |
| 16 | 18.5 | rR 16558.2150 | 10 | 9.5 | qQ 16542.3142* | | | |
| 16 | 19.5 | rR 16558.2186 | 10 | 10.5 | qQ 16542.3181* | | | |
| 16 | 20.5 | rR 16558.2222 | 10 | 11.5 | qQ 16542.3227* | | | |
| 17 | 12.5 | rR 16558.9853* | 10 | 12.5 | qQ 16542.3273* | | | |
| 17 | 13.5 | rR 16558.9869 | 10 | 13.5 | qQ 16542.3325* | | | |
| 17 | 14.5 | rR 16558.9892 | 10 | 14.5 | qQ 16542.3382* | | | |
| 17 | 15.5 | rR 16558.9917 | 11 | 8.5 | qQ 16542.1788* | | | |
| 17 | 16.5 | rR 16558.9943 | 11 | 9.5 | qQ 16542.1816* | | | |
| 17 | 17.5 | rR 16558.9972 | 11 | 10.5 | qQ 16542.1849* | | | |
| 17 | 18.5 | rR 16559.0004 | 11 | 11.5 | qQ 16542.1888* | | | |
| 17 | 19.5 | rR 16559.0036 | 11 | 12.5 | qQ 16542.1927* | | | |
| 17 | 20.5 | rR 16559.0071 | 11 | 13.5 | qQ 16542.1970* | | | |
| 17 | 21.5 | rR 16559.0109 | 11 | 14.5 | qQ 16542.2020* | | | |
| 18 | 13.5 | rR 16559.7605* | 11 | 15.5 | qQ 16542.2074* | | | |
| 18 | 14.5 | rR 16559.7635* | 12 | 9.5 | qQ 16542.0373* | | | |
| 18 | 15.5 | rR 16559.7652* | 12 | 10.5 | qQ 16542.0400* | | | |
| 18 | 16.5 | rR 16559.7679 | 12 | 11.5 | qQ 16542.0434* | | | |
| 18 | 17.5 | rR 16559.7702 | 12 | 12.5 | qQ 16542.0468* | | | |
| 18 | 18.5 | rR 16559.7732 | 12 | 13.5 | qQ 16542.0508* | | | |
| 18 | 19.5 | rR 16559.7765 | 12 | 14.5 | qQ 16542.0548* | | | |
| 18 | 20.5 | rR 16559.7798 | 12 | 15.5 | qQ 16542.0595* | | | |
| 18 | 21.5 | rR 16559.7832 | 12 | 16.5 | qQ 16542.0648* | | | |
| 18 | 22.5 | rR 16559.7872 | 13 | 10.5 | qQ 16541.8833* | | | |
| 19 | 14.5 | rR 16560.5248 | 13 | 11.5 | qQ 16541.8864* | | | |
| 19 | 15.5 | rR 16560.5268 | 13 | 12.5 | qQ 16541.8894* | | | |
| 19 | 16.5 | rR 16560.5291 | 13 | 13.5 | qQ 16541.8929* | | | |
| 19 | 17.5 | rR 16560.5314 | 13 | 14.5 | qQ 16541.8964* | | | |
| 19 | 18.5 | rR 16560.5344 | 13 | 15.5 | qQ 16541.9005* | | | |
| 19 | 19.5 | rR 16560.5371 | 13 | 16.5 | qQ 16541.9050* | | | |
| 19 | 20.5 | rR 16560.5404 | 13 | 17.5 | qQ 16541.9100* | | | |
| 19 | 21.5 | rR 16560.5437 | 14 | 10.5 | qQ 16541.7165* | | | |
| 19 | 22.5 | rR 16560.5474 | 14 | 11.5 | qQ 16541.7191* | | | |
| 19 | 23.5 | rR 16560.5514 | 14 | 12.5 | qQ 16541.7215* | | | |
| 20 | 16.5 | rR 16561.2782 | 14 | 13.5 | qQ 16541.7245* | | | |
| 20 | 17.5 | rR 16561.2808 | 14 | 14.5 | qQ 16541.7278* | | | |
| 20 | 18.5 | rR 16561.2834 | 14 | 15.5 | qQ 16541.7313* | | | |
| 20 | 19.5 | rR 16561.2863 | 14 | 16.5 | qQ 16541.7355* | | | |
| 20 | 20.5 | rR 16561.2891 | 14 | 17.5 | qQ 16541.7397* | | | |
| 20 | 21.5 | rR 16561.2922 | 14 | 18.5 | qQ 16541.7445* | | | |
| 20 | 22.5 | rR 16561.2957 | 15 | 12.5 | qQ 16541.5414* | | | |
| 20 | 23.5 | rR 16561.2991 | 15 | 13.5 | qQ 16541.5438* | | | |
| 20 | 24.5 | rR 16561.3032 | 15 | 14.5 | qQ 16541.5469* | | | |
| 21 | 16.5 | rR 16562.0156 | 15 | 15.5 | qQ 16541.5501* | | | |
| 21 | 17.5 | rR 16562.0181 | 15 | 16.5 | qQ 16541.5536* | | | |
| 21 | 18.5 | rR 16562.0203 | 15 | 17.5 | qQ 16541.5575* | | | |

Appendix II.B, continued. ${}^3\Phi_3-{}^3\Delta_2$.

| R | | | Q | | | P | | |
|----|------|----|------------|----|------|----|-------------|--|
| J" | F" | | J" | F" | | | | |
| 21 | 19.5 | rR | 16562.0228 | 15 | 18.5 | qQ | 16541.5616* | |
| 21 | 20.5 | rR | 16562.0256 | 15 | 19.5 | qQ | 16541.5662* | |
| 21 | 21.5 | rR | 16562.0287 | 16 | 13.5 | qQ | 16541.3521* | |
| 21 | 22.5 | rR | 16562.0321 | 16 | 14.5 | qQ | 16541.3547* | |
| 21 | 23.5 | rR | 16562.0355 | 16 | 15.5 | qQ | 16541.3577* | |
| 21 | 24.5 | rR | 16562.0389 | 16 | 16.5 | qQ | 16541.3608* | |
| 21 | 25.5 | rR | 16562.0425 | 16 | 17.5 | qQ | 16541.3644* | |
| 22 | 17.5 | rR | 16562.7433 | 16 | 18.5 | qQ | 16541.3683* | |
| 22 | 18.5 | rR | 16562.7456 | 16 | 19.5 | qQ | 16541.3725* | |
| 22 | 19.5 | rR | 16562.7483 | 16 | 20.5 | qQ | 16541.3767* | |
| 22 | 20.5 | rR | 16562.7506 | 17 | 14.5 | qQ | 16541.1503* | |
| 22 | 21.5 | rR | 16562.7536 | 17 | 15.5 | qQ | 16541.1529* | |
| 22 | 22.5 | rR | 16562.7569 | 17 | 16.5 | qQ | 16541.1558* | |
| 22 | 23.5 | rR | 16562.7599 | 17 | 17.5 | qQ | 16541.1591* | |
| 22 | 24.5 | rR | 16562.7633 | 17 | 18.5 | qQ | 16541.1628* | |
| 22 | 25.5 | rR | 16562.7669 | 17 | 19.5 | qQ | 16541.1664* | |
| 22 | 26.5 | rR | 16562.7706 | 17 | 20.5 | qQ | 16541.1707* | |
| 23 | 18.5 | rR | 16563.4585 | 17 | 21.5 | qQ | 16541.1748* | |
| 23 | 19.5 | rR | 16563.4608 | 18 | 14.5 | qQ | 16540.9346* | |
| 23 | 20.5 | rR | 16563.4635 | 18 | 15.5 | qQ | 16540.9370* | |
| 23 | 21.5 | rR | 16563.4660 | 18 | 16.5 | qQ | 16540.9397* | |
| 23 | 22.5 | rR | 16563.4689 | 18 | 17.5 | qQ | 16540.9428* | |
| 23 | 23.5 | rR | 16563.4722 | 18 | 18.5 | qQ | 16540.9460* | |
| 23 | 24.5 | rR | 16563.4748 | 18 | 19.5 | qQ | 16540.9494* | |
| 23 | 25.5 | rR | 16563.4785 | 18 | 20.5 | qQ | 16540.9530* | |
| 23 | 26.5 | rR | 16563.4821 | 18 | 21.5 | qQ | 16540.9571* | |
| 23 | 27.5 | rR | 16563.4864 | 18 | 22.5 | qQ | 16540.9611* | |
| 24 | 19.5 | rR | 16564.1609 | 19 | 15.5 | qQ | 16540.7098 | |
| 24 | 20.5 | rR | 16564.1637 | 19 | 16.5 | qQ | 16540.7123 | |
| 24 | 21.5 | rR | 16564.1668 | 19 | 17.5 | qQ | 16540.7150 | |
| 24 | 22.5 | rR | 16564.1690 | 19 | 18.5 | qQ | 16540.7180 | |
| 24 | 23.5 | rR | 16564.1724 | 19 | 19.5 | qQ | 16540.7214 | |
| 24 | 24.5 | rR | 16564.1752 | 19 | 20.5 | qQ | 16540.7247 | |
| 24 | 25.5 | rR | 16564.1785 | 19 | 21.5 | qQ | 16540.7283 | |
| 24 | 26.5 | rR | 16564.1818 | 19 | 22.5 | qQ | 16540.7322 | |
| 24 | 27.5 | rR | 16564.1857 | 19 | 23.5 | qQ | 16540.7365 | |
| 24 | 28.5 | rR | 16564.1897 | 20 | 16.5 | qQ | 16540.4728 | |
| 25 | 20.5 | rR | 16564.8514 | 20 | 17.5 | qQ | 16540.4755 | |
| 25 | 21.5 | rR | 16564.8543 | 20 | 18.5 | qQ | 16540.4781 | |
| 25 | 22.5 | rR | 16564.8568 | 20 | 19.5 | qQ | 16540.4810 | |
| 25 | 23.5 | rR | 16564.8597 | 20 | 20.5 | qQ | 16540.4843 | |
| 25 | 24.5 | rR | 16564.8627 | 20 | 21.5 | qQ | 16540.4877 | |
| 25 | 25.5 | rR | 16564.8660 | 20 | 22.5 | qQ | 16540.4912 | |
| 25 | 26.5 | rR | 16564.8687 | 20 | 23.5 | qQ | 16540.4953 | |
| 25 | 27.5 | rR | 16564.8729 | 20 | 24.5 | qQ | 16540.4993 | |
| 25 | 28.5 | rR | 16564.8765 | 21 | 17.5 | qQ | 16540.2245 | |
| 25 | 29.5 | rR | 16564.8803 | 21 | 18.5 | qQ | 16540.2269 | |
| 26 | 21.5 | rR | 16565.5304 | 21 | 19.5 | qQ | 16540.2297 | |
| 26 | 22.5 | rR | 16565.5326 | 21 | 20.5 | qQ | 16540.2327 | |
| 26 | 23.5 | rR | 16565.5349 | 21 | 21.5 | qQ | 16540.2357 | |
| 26 | 24.5 | rR | 16565.5381 | 21 | 22.5 | qQ | 16540.2391 | |
| 26 | 25.5 | rR | 16565.5411 | 21 | 23.5 | qQ | 16540.2427 | |
| 26 | 26.5 | rR | 16565.5441 | 21 | 24.5 | qQ | 16540.2466 | |
| 26 | 27.5 | rR | 16565.5474 | 21 | 25.5 | qQ | 16540.2507 | |
| 26 | 28.5 | rR | 16565.5510 | 22 | 18.5 | qQ | 16539.9633 | |
| 26 | 29.5 | rR | 16565.5547 | 22 | 19.5 | qQ | 16539.9660 | |
| 26 | 30.5 | rR | 16565.5590 | 22 | 20.5 | qQ | 16539.9688 | |
| 27 | 22.5 | rR | 16566.1951 | 22 | 21.5 | qQ | 16539.9717 | |
| 27 | 23.5 | rR | 16566.1975 | 22 | 22.5 | qQ | 16539.9751 | |
| 27 | 24.5 | rR | 16566.2006 | 22 | 23.5 | qQ | 16539.9784 | |
| 27 | 25.5 | rR | 16566.2034 | 22 | 24.5 | qQ | 16539.9822 | |
| 27 | 26.5 | rR | 16566.2068 | 22 | 25.5 | qQ | 16539.9858 | |
| 27 | 27.5 | rR | 16566.2103 | 22 | 26.5 | qQ | 16539.9901 | |
| 27 | 28.5 | rR | 16566.2138 | 23 | 19.5 | qQ | 16539.6903 | |
| 27 | 29.5 | rR | 16566.2171 | 23 | 20.5 | qQ | 16539.6928* | |

Appendix II.B, continued. ${}^3\Phi_3\text{-}{}^3\Delta_2$.

| <u>R</u> | | | <u>Q</u> | | | <u>P</u> | | |
|----------|------|---------------|----------|------|---------------|----------|----|--|
| J" | F" | | J" | F" | | J" | F" | |
| 27 | 30.5 | rR 16566.2211 | 23 | 21.5 | qQ 16539.6956 | | | |
| 27 | 31.5 | rR 16566.2254 | 23 | 22.5 | qQ 16539.6988 | | | |
| | | | 23 | 23.5 | qQ 16539.7021 | | | |
| | | | 23 | 24.5 | qQ 16539.7054 | | | |
| | | | 23 | 25.5 | qQ 16539.7092 | | | |
| | | | 23 | 26.5 | qQ 16539.7130 | | | |
| | | | 23 | 27.5 | qQ 16539.7172 | | | |
| | | | 24 | 21.5 | qQ 16539.4074 | | | |
| | | | 24 | 22.5 | qQ 16539.4100 | | | |
| | | | 24 | 23.5 | qQ 16539.4131 | | | |
| | | | 24 | 24.5 | qQ 16539.4165 | | | |
| | | | 24 | 25.5 | qQ 16539.4200 | | | |
| | | | 24 | 26.5 | qQ 16539.4236 | | | |
| | | | 24 | 27.5 | qQ 16539.4275 | | | |
| | | | 24 | 28.5 | qQ 16539.4317 | | | |
| | | | 25 | 21.5 | qQ 16539.1073 | | | |
| | | | 25 | 22.5 | qQ 16539.1099 | | | |
| | | | 25 | 23.5 | qQ 16539.1129 | | | |
| | | | 25 | 24.5 | qQ 16539.1158 | | | |
| | | | 25 | 25.5 | qQ 16539.1191 | | | |
| | | | 25 | 26.5 | qQ 16539.1227 | | | |
| | | | 25 | 27.5 | qQ 16539.1264 | | | |
| | | | 25 | 28.5 | qQ 16539.1307 | | | |
| | | | 25 | 29.5 | qQ 16539.1344 | | | |
| | | | 26 | 22.5 | qQ 16538.7988 | | | |
| | | | 26 | 23.5 | qQ 16538.8014 | | | |
| | | | 26 | 24.5 | qQ 16538.8043 | | | |
| | | | 26 | 25.5 | qQ 16538.8077 | | | |
| | | | 26 | 26.5 | qQ 16538.8107 | | | |
| | | | 26 | 27.5 | qQ 16538.8146 | | | |
| | | | 26 | 28.5 | qQ 16538.8183 | | | |
| | | | 26 | 29.5 | qQ 16538.8225 | | | |
| | | | 26 | 30.5 | qQ 16538.8264 | | | |
| | | | 27 | 23.5 | qQ 16538.4771 | | | |
| | | | 27 | 24.5 | qQ 16538.4802 | | | |
| | | | 27 | 25.5 | qQ 16538.4829 | | | |
| | | | 27 | 26.5 | qQ 16538.4859 | | | |
| | | | 27 | 27.5 | qQ 16538.4895 | | | |
| | | | 27 | 28.5 | qQ 16538.4931 | | | |
| | | | 27 | 29.5 | qQ 16538.4969 | | | |
| | | | 27 | 30.5 | qQ 16538.5010 | | | |
| | | | 27 | 31.5 | qQ 16538.5050 | | | |

Appendix II.C. ${}^3\Phi_4\text{-}{}^3\Delta_3$.

| J" | F" | | J" | F" | | J" | F" | |
|----|-----|---------------|----|------|----------------|----|------|----------------|
| 3 | 3.5 | pR 16864.5123 | 7 | 2.5 | qQ 16860.1995* | 6 | 7.5 | pP 16854.1702 |
| 3 | 3.5 | qR 16864.5240 | 7 | 3.5 | qQ 16860.1811* | 6 | 8.5 | pP 16854.1221 |
| 3 | 3.5 | co 16864.5312 | 7 | 4.5 | qQ 16860.1613* | 6 | 9.5 | pP 16854.0689 |
| 3 | 3.5 | rR 16864.5385 | 7 | 5.5 | qQ 16860.1358* | 6 | 10.5 | pP 16854.0117 |
| 3 | 4.5 | pR 16864.4016 | 7 | 6.5 | qQ 16860.1061* | 7 | 3.5 | pP 16853.2286 |
| 3 | 4.5 | qR 16864.4167 | 7 | 8.5 | qQ 16860.0329* | 7 | 4.5 | pP 16853.2077 |
| 3 | 4.5 | co 16864.4255 | 7 | 10.5 | qQ 16859.9436* | 7 | 5.5 | pP 16853.1823 |
| 3 | 4.5 | rR 16864.4348 | 8 | 5.5 | qQ 16860.0412* | 7 | 6.5 | pP 16853.1531 |
| 3 | 5.5 | pR 16864.2657 | 9 | 4.5 | qQ 16859.9476* | 7 | 7.5 | pP 16853.1202 |
| 3 | 5.5 | qR 16864.2841 | 9 | 6.5 | qQ 16859.9134* | 7 | 8.5 | pP 16853.0836 |
| 3 | 5.5 | co 16864.2950 | 9 | 8.5 | qQ 16859.8685* | 7 | 9.5 | pP 16853.0431 |
| 3 | 5.5 | rR 16864.3058 | 9 | 9.5 | qQ 16859.8420* | 7 | 10.5 | pP 16852.9993 |
| 3 | 6.5 | pR 16864.1039 | 9 | 11.5 | qQ 16859.7819* | 7 | 11.5 | pP 16852.9518* |
| 3 | 6.5 | qR 16864.1256 | 9 | 12.5 | qQ 16859.7482* | 8 | 3.5 | pP 16852.1317 |
| 3 | 6.5 | co 16864.1383 | 10 | 6.5 | qQ 16859.7938* | 8 | 4.5 | pP 16852.1151 |
| 3 | 6.5 | rR 16864.1509 | 10 | 7.5 | qQ 16859.7770* | 8 | 5.5 | pP 16852.0958 |
| 3 | 7.5 | qR 16863.9396 | 10 | 8.5 | qQ 16859.7572 | 8 | 6.5 | pP 16852.0726* |

Appendix II.C, continued. ${}^3\Phi_4\text{-}{}^3\Delta_3$.

| R | | | | Q | | | | P | | | |
|----|-----|----|-------------|----|------|----|-------------|----|------|----|------------|
| J* | F* | | | J* | F* | | | J* | F* | | |
| 3 | 7.5 | co | 16863.9543 | 10 | 9.5 | qQ | 16859.7360 | 8 | 8.5 | pP | 16852.0184 |
| 3 | 7.5 | rR | 16863.9686 | 10 | 10.5 | qQ | 16859.7124* | 8 | 9.5 | pP | 16851.9865 |
| 4 | 0.5 | rR | 16865.5243* | 10 | 11.5 | qQ | 16859.6872 | 8 | 10.5 | pP | 16851.9520 |
| 4 | 2.5 | qR | 16865.4658* | 10 | 12.5 | qQ | 16859.6598 | 8 | 11.5 | pP | 16851.9147 |
| 4 | 2.5 | co | 16865.4690* | 10 | 13.5 | qQ | 16859.6301 | 8 | 12.5 | pP | 16851.8748 |
| 4 | 2.5 | rR | 16865.4729* | 10 | 14.5 | qQ | 16859.5991 | 9 | 4.5 | pP | 16851.0102 |
| 4 | 3.5 | pR | 16865.4072 | 11 | 7.5 | qQ | 16859.6461 | 9 | 5.5 | pP | 16850.9946 |
| 4 | 3.5 | qR | 16865.4154 | 11 | 8.5 | qQ | 16859.6301* | 9 | 6.5 | pP | 16850.9764 |
| 4 | 3.5 | co | 16865.4201 | 11 | 9.5 | qQ | 16859.6124 | 9 | 7.5 | pP | 16850.9558 |
| 4 | 3.5 | rR | 16865.4250* | 11 | 10.5 | qQ | 16859.5931 | 9 | 8.5 | pP | 16850.9325 |
| 4 | 4.5 | pR | 16865.3407 | 11 | 11.5 | qQ | 16859.5719 | 9 | 9.5 | pP | 16850.9072 |
| 4 | 4.5 | qR | 16865.3509 | 11 | 12.5 | qQ | 16859.5494 | 9 | 10.5 | pP | 16850.8793 |
| 4 | 4.5 | co | 16865.3568 | 11 | 13.5 | qQ | 16859.5251 | 9 | 11.5 | pP | 16850.8494 |
| 4 | 4.5 | rR | 16865.3630 | 11 | 14.5 | qQ | 16859.4999 | 9 | 12.5 | pP | 16850.8171 |
| 4 | 5.5 | pR | 16865.2600 | 11 | 15.5 | qQ | 16859.4725* | 9 | 13.5 | pP | 16850.7827 |
| 4 | 5.5 | qR | 16865.2726 | 12 | 8.5 | qQ | 16859.4874 | 10 | 5.5 | pP | 16849.8802 |
| 4 | 5.5 | co | 16865.2796 | 12 | 9.5 | qQ | 16859.4725* | 10 | 6.5 | pP | 16849.8656 |
| 4 | 5.5 | rR | 16865.2870 | 12 | 10.5 | qQ | 16859.4567 | 10 | 7.5 | pP | 16849.8488 |
| 4 | 6.5 | pR | 16865.1656 | 12 | 11.5 | qQ | 16859.4389 | 10 | 8.5 | pP | 16849.8298 |
| 4 | 6.5 | qR | 16865.1802 | 12 | 12.5 | qQ | 16859.4202 | 10 | 9.5 | pP | 16849.8089 |
| 4 | 6.5 | co | 16865.1886 | 12 | 13.5 | qQ | 16859.3998 | 10 | 10.5 | pP | 16849.7861 |
| 4 | 6.5 | rR | 16865.1970 | 12 | 14.5 | qQ | 16859.3781 | 10 | 11.5 | pP | 16849.7615 |
| 4 | 7.5 | pR | 16865.0577 | 12 | 15.5 | qQ | 16859.3552 | 10 | 12.5 | pP | 16849.7352 |
| 4 | 7.5 | qR | 16865.0743 | 12 | 16.5 | qQ | 16859.3310 | 10 | 13.5 | pP | 16849.7070 |
| 4 | 7.5 | co | 16865.0841 | 13 | 8.5 | qQ | 16859.3310* | 10 | 14.5 | pP | 16849.6771 |
| 4 | 7.5 | rR | 16865.0936 | 13 | 9.5 | qQ | 16859.3183 | 11 | 6.5 | pP | 16848.7402 |
| 4 | 8.5 | qR | 16864.9557 | 13 | 10.5 | qQ | 16859.3046 | 11 | 7.5 | pP | 16848.7261 |
| 4 | 8.5 | co | 16864.9664 | 13 | 11.5 | qQ | 16859.2896 | 11 | 8.5 | pP | 16848.7106 |
| 4 | 8.5 | rR | 16864.9773 | 13 | 12.5 | qQ | 16859.2736 | 11 | 9.5 | pP | 16848.6934 |
| 5 | 3.5 | qR | 16866.3218 | 13 | 13.5 | qQ | 16859.2564 | 11 | 10.5 | pP | 16848.6745 |
| 5 | 3.5 | co | 16866.3247 | 13 | 14.5 | qQ | 16859.2383 | 11 | 11.5 | pP | 16848.6534 |
| 5 | 3.5 | rR | 16866.3283 | 13 | 15.5 | qQ | 16859.2187 | 11 | 12.5 | pP | 16848.6316 |
| 5 | 4.5 | pR | 16866.2717 | 13 | 16.5 | qQ | 16859.1983 | 11 | 13.5 | pP | 16848.6086 |
| 5 | 4.5 | qR | 16866.2792 | 13 | 17.5 | qQ | 16859.1771 | 11 | 14.5 | pP | 16848.5835 |
| 5 | 4.5 | co | 16866.2833 | 14 | 9.5 | qQ | 16859.1494 | 11 | 15.5 | pP | 16848.5575 |
| 5 | 4.5 | rR | 16866.2876 | 14 | 10.5 | qQ | 16859.1377 | | | | |
| 5 | 5.5 | pR | 16866.2183 | 14 | 11.5 | qQ | 16859.1248 | | | | |
| 5 | 5.5 | qR | 16866.2274 | 14 | 12.5 | qQ | 16859.1112 | | | | |
| 5 | 5.5 | co | 16866.2326 | 14 | 13.5 | qQ | 16859.0964 | | | | |
| 5 | 5.5 | rR | 16866.2378 | 14 | 14.5 | qQ | 16859.0808 | | | | |
| 5 | 6.5 | pR | 16866.1563 | 14 | 15.5 | qQ | 16859.0642 | | | | |
| 5 | 6.5 | qR | 16866.1667 | 14 | 16.5 | qQ | 16859.0468 | | | | |
| 5 | 6.5 | co | 16866.1726 | 14 | 17.5 | qQ | 16859.0283 | | | | |
| 5 | 6.5 | rR | 16866.1785 | 14 | 18.5 | qQ | 16859.0092 | | | | |
| 5 | 7.5 | pR | 16866.0852 | 15 | 10.5 | qQ | 16858.9562 | | | | |
| 5 | 7.5 | qR | 16866.0975 | 15 | 11.5 | qQ | 16858.9451 | | | | |
| 5 | 7.5 | co | 16866.1043 | 15 | 12.5 | qQ | 16858.9332 | | | | |
| 5 | 7.5 | rR | 16866.1109 | 15 | 13.5 | qQ | 16858.9205 | | | | |
| 5 | 8.5 | qR | 16866.0198 | 15 | 14.5 | qQ | 16858.9070 | | | | |
| 5 | 8.5 | co | 16866.0273 | 15 | 15.5 | qQ | 16858.8928 | | | | |
| 5 | 8.5 | rR | 16866.0350 | 15 | 16.5 | qQ | 16858.8777 | | | | |
| 5 | 9.5 | qR | 16865.9338 | 15 | 17.5 | qQ | 16858.8617 | | | | |
| 5 | 9.5 | rR | 16865.9508 | 15 | 18.5 | qQ | 16858.8453 | | | | |
| 6 | 1.5 | rR | 16867.2702 | 15 | 19.5 | qQ | 16858.8279 | | | | |
| 6 | 2.5 | rR | 16867.2546 | 16 | 11.5 | qQ | 16858.7512 | | | | |
| 6 | 4.5 | qR | 16867.1976 | 16 | 12.5 | qQ | 16858.7407 | | | | |
| 6 | 4.5 | co | 16867.2007 | 16 | 13.5 | qQ | 16858.7298 | | | | |
| 6 | 4.5 | rR | 16867.2037 | 16 | 14.5 | qQ | 16858.7182 | | | | |
| 6 | 5.5 | qR | 16867.1611 | 16 | 15.5 | qQ | 16858.7057 | | | | |
| 6 | 5.5 | co | 16867.1647 | 16 | 16.5 | qQ | 16858.6926 | | | | |
| 6 | 5.5 | rR | 16867.1687 | 16 | 17.5 | qQ | 16858.6787 | | | | |
| 6 | 6.5 | qR | 16867.1182 | 16 | 18.5 | qQ | 16858.6644 | | | | |
| 6 | 6.5 | co | 16867.1225 | 16 | 19.5 | qQ | 16858.6499 | | | | |
| 6 | 6.5 | rR | 16867.1270 | 16 | 20.5 | qQ | 16858.6338 | | | | |
| 6 | 7.5 | qR | 16867.0689 | 17 | 12.5 | qQ | 16858.5344 | | | | |

Appendix II.C, continued. ${}^3\Phi_4$ - ${}^3\Delta_3$.

| R | | | Q | | | P | | |
|----|------|----|-------------|----|------|----|------------|--|
| J" | F" | | J" | F" | | J" | F" | |
| 6 | 7.5 | co | 16867.0742 | 17 | 13.5 | qQ | 16858.5253 | |
| 6 | 7.5 | rR | 16867.0792 | 17 | 14.5 | qQ | 16858.5158 | |
| 6 | 8.5 | qR | 16867.0141 | 17 | 15.5 | qQ | 16858.5037 | |
| 6 | 8.5 | co | 16867.0197 | 17 | 16.5 | qQ | 16858.4922 | |
| 6 | 8.5 | rR | 16867.0254 | 17 | 17.5 | qQ | 16858.4801 | |
| 6 | 9.5 | qR | 16866.9532 | 17 | 18.5 | qQ | 16858.4676 | |
| 6 | 9.5 | co | 16866.9597 | 17 | 19.5 | qQ | 16858.4546 | |
| 6 | 9.5 | rR | 16866.9659 | 17 | 20.5 | qQ | 16858.4412 | |
| 6 | 10.5 | qR | 16866.8867 | 17 | 21.5 | qQ | 16858.4269 | |
| 6 | 10.5 | co | 16866.8940 | 18 | 13.5 | qQ | 16858.3054 | |
| 6 | 10.5 | rR | 16866.9008 | 18 | 14.5 | qQ | 16858.2967 | |
| 7 | 2.5 | rR | 16868.1433 | 18 | 15.5 | qQ | 16858.2868 | |
| 7 | 3.5 | rR | 16868.1266 | 18 | 16.5 | qQ | 16858.2771 | |
| 7 | 5.5 | qR | 16868.0739 | 18 | 17.5 | qQ | 16858.2665 | |
| 7 | 5.5 | co | 16868.0768 | 18 | 18.5 | qQ | 16858.2556 | |
| 7 | 5.5 | rR | 16868.0795 | 18 | 19.5 | qQ | 16858.2439 | |
| 7 | 6.5 | qR | 16868.0420 | 18 | 20.5 | qQ | 16858.2325 | |
| 7 | 6.5 | co | 16868.0456 | 18 | 21.5 | qQ | 16858.2197 | |
| 7 | 6.5 | rR | 16868.0488 | 18 | 22.5 | qQ | 16858.2072 | |
| 7 | 7.5 | qR | 16868.0057 | 19 | 15.5 | qQ | 16858.0564 | |
| 7 | 7.5 | co | 16868.0097 | 19 | 16.5 | qQ | 16858.0475 | |
| 7 | 7.5 | rR | 16868.0136 | 19 | 17.5 | qQ | 16858.0383 | |
| 7 | 8.5 | qR | 16867.9650 | 19 | 18.5 | qQ | 16858.0284 | |
| 7 | 8.5 | co | 16867.9695 | 19 | 19.5 | qQ | 16858.0186 | |
| 7 | 8.5 | rR | 16867.9738 | 19 | 20.5 | qQ | 16858.0081 | |
| 7 | 9.5 | qR | 16867.9200 | 19 | 21.5 | qQ | 16857.9973 | |
| 7 | 9.5 | co | 16867.9247 | 19 | 22.5 | qQ | 16857.9862 | |
| 7 | 9.5 | rR | 16867.9297 | | | | | |
| 7 | 10.5 | qR | 16867.8706 | | | | | |
| 7 | 10.5 | co | 16867.8760 | | | | | |
| 7 | 10.5 | rR | 16867.8815 | | | | | |
| 7 | 11.5 | qR | 16867.8172 | | | | | |
| 7 | 11.5 | co | 16867.8234 | | | | | |
| 7 | 11.5 | rR | 16867.8292 | | | | | |
| 8 | 3.5 | rR | 16869.0122 | | | | | |
| 8 | 4.5 | rR | 16868.9957 | | | | | |
| 8 | 6.5 | qR | 16868.9467* | | | | | |
| 8 | 6.5 | co | 16868.9496* | | | | | |
| 8 | 6.5 | rR | 16868.9521 | | | | | |
| 8 | 7.5 | qR | 16868.9187* | | | | | |
| 8 | 7.5 | co | 16868.9219* | | | | | |
| 8 | 7.5 | rR | 16868.9250 | | | | | |
| 8 | 8.5 | qR | 16868.8873 | | | | | |
| 8 | 8.5 | co | 16868.8909 | | | | | |
| 8 | 8.5 | rR | 16868.8943 | | | | | |
| 8 | 9.5 | qR | 16868.8526 | | | | | |
| 8 | 9.5 | co | 16868.8566 | | | | | |
| 8 | 9.5 | rR | 16868.8604 | | | | | |
| 8 | 10.5 | qR | 16868.8144 | | | | | |
| 8 | 10.5 | co | 16868.8188 | | | | | |
| 8 | 10.5 | rR | 16868.8231 | | | | | |
| 8 | 11.5 | qR | 16868.7731 | | | | | |
| 8 | 11.5 | co | 16868.7779 | | | | | |
| 8 | 11.5 | rR | 16868.7826 | | | | | |
| 8 | 12.5 | qR | 16868.7289 | | | | | |
| 8 | 12.5 | co | 16868.7341 | | | | | |
| 8 | 12.5 | rR | 16868.7390 | | | | | |
| 9 | 4.5 | rR | 16869.8738 | | | | | |
| 9 | 5.5 | rR | 16869.8579 | | | | | |
| 9 | 6.5 | qR | 16869.8346 | | | | | |
| 9 | 6.5 | co | 16869.8369 | | | | | |
| 9 | 6.5 | rR | 16869.8391 | | | | | |
| 9 | 7.5 | qR | 16869.8123 | | | | | |
| 9 | 7.5 | co | 16869.8152 | | | | | |
| 9 | 7.5 | rR | 16869.8177 | | | | | |

Appendix II.C, continued. $3\Phi_4-3\Delta_3$.

| R | | | | Q | | | | P | | | |
|----|------|----|-------------|----|------|----|------------|---|--|--|--|
| J" | F" | | | J" | F" | | | | | | |
| 9 | 8.5 | qR | 16869.7877 | 19 | 23.5 | qQ | 16857.9745 | | | | |
| 9 | 8.5 | co | 16869.7907 | 20 | 15.5 | qQ | 16857.8116 | | | | |
| 9 | 8.5 | rR | 16869.7936 | 20 | 16.5 | qQ | 16857.8037 | | | | |
| 9 | 9.5 | qR | 16869.7600 | 20 | 17.5 | qQ | 16857.7960 | | | | |
| 9 | 9.5 | co | 16869.7635 | 20 | 18.5 | qQ | 16857.7872 | | | | |
| 9 | 9.5 | rR | 16869.7668 | 20 | 19.5 | qQ | 16857.7782 | | | | |
| 9 | 10.5 | qR | 16869.7299 | 20 | 20.5 | qQ | 16857.7689 | | | | |
| 9 | 10.5 | co | 16869.7335 | 20 | 21.5 | qQ | 16857.7593 | | | | |
| 9 | 10.5 | rR | 16869.7369 | 20 | 22.5 | qQ | 16857.7492 | | | | |
| 9 | 11.5 | qR | 16869.6975 | 20 | 23.5 | qQ | 16857.7390 | | | | |
| 9 | 11.5 | co | 16869.7013 | 20 | 24.5 | qQ | 16857.7286 | | | | |
| 9 | 11.5 | rR | 16869.7051 | 21 | 16.5 | qQ | 16857.5463 | | | | |
| 9 | 12.5 | qR | 16869.6621 | 21 | 17.5 | qQ | 16857.5393 | | | | |
| 9 | 12.5 | co | 16869.6663 | 21 | 18.5 | qQ | 16857.5318 | | | | |
| 9 | 12.5 | rR | 16869.6704 | 21 | 19.5 | qQ | 16857.5236 | | | | |
| 9 | 13.5 | qR | 16869.6246* | 21 | 20.5 | qQ | 16857.5155 | | | | |
| 9 | 13.5 | co | 16869.6292 | 21 | 21.5 | qQ | 16857.5070 | | | | |
| 9 | 13.5 | rR | 16869.6334 | 21 | 22.5 | qQ | 16857.4983 | | | | |
| 22 | 17.5 | rR | 16880.0768 | 21 | 23.5 | qQ | 16857.4894 | | | | |
| 22 | 18.5 | rR | 16880.0699 | 21 | 24.5 | qQ | 16857.4800 | | | | |
| 22 | 19.5 | rR | 16880.0628 | 21 | 25.5 | qQ | 16857.4706 | | | | |
| 22 | 20.5 | rR | 16880.0557 | 22 | 17.5 | qQ | 16857.2691 | | | | |
| 22 | 21.5 | rR | 16880.0476 | 22 | 18.5 | qQ | 16857.2621 | | | | |
| 22 | 22.5 | rR | 16880.0398 | 22 | 19.5 | qQ | 16857.2550 | | | | |
| 22 | 23.5 | rR | 16880.0313 | 22 | 20.5 | qQ | 16857.2480 | | | | |
| 22 | 24.5 | rR | 16880.0228 | 22 | 21.5 | qQ | 16857.2410 | | | | |
| 22 | 25.5 | rR | 16880.0151 | 22 | 22.5 | qQ | 16857.2330 | | | | |
| 22 | 26.5 | rR | 16880.0063 | 22 | 23.5 | qQ | 16857.2250 | | | | |
| 24 | 19.5 | rR | 16881.4627 | 22 | 24.5 | qQ | 16857.2167 | | | | |
| 24 | 20.5 | rR | 16881.4569 | 22 | 25.5 | qQ | 16857.2084 | | | | |
| 24 | 21.5 | rR | 16881.4512 | 22 | 26.5 | qQ | 16857.1997 | | | | |
| 24 | 22.5 | rR | 16881.4450 | 23 | 18.5 | qQ | 16856.9789 | | | | |
| 24 | 23.5 | rR | 16881.4387 | 23 | 19.5 | qQ | 16856.9727 | | | | |
| 24 | 24.5 | rR | 16881.4320 | 23 | 20.5 | qQ | 16856.9664 | | | | |
| 24 | 25.5 | rR | 16881.4251 | 23 | 21.5 | qQ | 16856.9598 | | | | |
| 24 | 26.5 | rR | 16881.4181 | 23 | 22.5 | qQ | 16856.9528 | | | | |
| 24 | 27.5 | rR | 16881.4113 | 23 | 23.5 | qQ | 16856.9457 | | | | |
| 24 | 28.5 | rR | 16881.4043 | 23 | 24.5 | qQ | 16856.9386 | | | | |
| 25 | 20.5 | rR | 16882.1360 | 23 | 25.5 | qQ | 16856.9309 | | | | |
| 25 | 21.5 | rR | 16882.1305 | 23 | 26.5 | qQ | 16856.9233 | | | | |
| 25 | 22.5 | rR | 16882.1254 | 23 | 27.5 | qQ | 16856.9157 | | | | |
| 25 | 23.5 | rR | 16882.1193 | 24 | 19.5 | qQ | 16856.6761 | | | | |
| 25 | 24.5 | rR | 16882.1138 | 24 | 20.5 | qQ | 16856.6706 | | | | |
| 25 | 25.5 | rR | 16882.1085 | 24 | 21.5 | qQ | 16856.6645 | | | | |
| 25 | 26.5 | rR | 16882.1020 | 24 | 22.5 | qQ | 16856.6585 | | | | |
| 25 | 27.5 | rR | 16882.0958 | 24 | 23.5 | qQ | 16856.6522 | | | | |
| 25 | 28.5 | rR | 16882.0897 | 24 | 24.5 | qQ | 16856.6461 | | | | |
| 25 | 29.5 | rR | 16882.0832 | 24 | 25.5 | qQ | 16856.6391 | | | | |
| 26 | 21.5 | rR | 16882.7961 | 24 | 26.5 | qQ | 16856.6324 | | | | |
| 26 | 22.5 | rR | 16882.7919 | 24 | 27.5 | qQ | 16856.6256 | | | | |
| 26 | 23.5 | rR | 16882.7862 | 24 | 28.5 | qQ | 16856.6185 | | | | |
| 26 | 24.5 | rR | 16882.7815 | 25 | 20.5 | qQ | 16856.3611 | | | | |
| 26 | 25.5 | rR | 16882.7766 | 25 | 21.5 | qQ | 16856.3560 | | | | |
| 26 | 26.5 | rR | 16882.7712 | 25 | 22.5 | qQ | 16856.3509 | | | | |
| 26 | 27.5 | rR | 16882.7660 | 25 | 23.5 | qQ | 16856.3454 | | | | |
| 26 | 28.5 | rR | 16882.7603 | 25 | 24.5 | qQ | 16856.3396 | | | | |
| 26 | 29.5 | rR | 16882.7548 | 25 | 25.5 | qQ | 16856.3342 | | | | |
| 26 | 30.5 | rR | 16882.7491 | 25 | 26.5 | qQ | 16856.3277 | | | | |
| | | | | 25 | 27.5 | qQ | 16856.3217 | | | | |
| | | | | 25 | 28.5 | qQ | 16856.3154 | | | | |
| | | | | 25 | 29.5 | qQ | 16856.3093 | | | | |
| | | | | 26 | 21.5 | qQ | 16856.0330 | | | | |
| | | | | 26 | 22.5 | qQ | 16856.0284 | | | | |
| | | | | 26 | 23.5 | qQ | 16856.0234 | | | | |
| | | | | 26 | 24.5 | qQ | 16856.0188 | | | | |

Appendix II.C, continued. ${}^3\Phi_4\text{-}{}^3\Delta_3$.

| <u>R</u> | | <u>Q</u> | <u>P</u> |
|----------|------|----------|-------------|
| J" | F" | | |
| 26 | 25.5 | qQ | 16856.0135 |
| 26 | 26.5 | qQ | 16856.0079 |
| 26 | 27.5 | qQ | 16856.0028 |
| 26 | 28.5 | qQ | 16855.9973 |
| 26 | 29.5 | qQ | 16855.9916 |
| 26 | 30.5 | qQ | 16855.9862 |
| 27 | 22.5 | qQ | 16855.6942 |
| 27 | 24.5 | qQ | 16855.6846 |
| 27 | 25.5 | qQ | 16855.6800 |
| 27 | 26.5 | qQ | 16855.6754 |
| 27 | 27.5 | qQ | 16855.6705 |
| 27 | 28.5 | qQ | 16855.6663 |
| 27 | 29.5 | qQ | 16855.6610 |
| 27 | 30.5 | qQ | 16855.6560 |
| 27 | 31.5 | qQ | 16855.6509 |
| 28 | 23.5 | qQ | 16855.3426* |
| 28 | 24.5 | qQ | 16855.3366 |
| 28 | 25.5 | qQ | 16855.3329 |
| 28 | 26.5 | qQ | 16855.3288 |
| 28 | 27.5 | qQ | 16855.3251 |
| 28 | 28.5 | qQ | 16855.3199 |
| 28 | 30.5 | qQ | 16855.3117 |
| 28 | 31.5 | qQ | 16855.3064 |
| 28 | 32.5 | qQ | 16855.3030 |
| 29 | 24.5 | qQ | 16854.9763 |
| 29 | 25.5 | qQ | 16854.9724 |
| 29 | 26.5 | qQ | 16854.9690 |
| 29 | 27.5 | qQ | 16854.9656 |
| 29 | 28.5 | qQ | 16854.9620 |
| 29 | 29.5 | qQ | 16854.9575 |
| 29 | 30.5 | qQ | 16854.9542 |
| 29 | 31.5 | qQ | 16854.9505 |
| 29 | 32.5 | qQ | 16854.9466 |
| 29 | 33.5 | qQ | 16854.9423 |

^aTransitions in units of cm^{-1} . Blended lines are denoted by an asterisk.

APPENDIX III. Transitions of the ν_7 Fundamental of $\text{NH}_2^{11}\text{BH}_2^{\text{a}}$

| R | | | Q | | | P | | |
|--------|----|------------|--------|----|------------|--------|----|------------|
| Branch | J" | | Branch | J" | | Branch | J" | |
| rRO | 0 | 1010.1049 | rQO | 1 | 1008.2841* | rPO | 2 | 1005.0696 |
| | 1 | 1011.9077 | | 2 | 1008.1281 | | 3 | 1003.5316* |
| | 2 | 1013.7738 | | 3 | 1007.9039 | | 4 | 1002.0797* |
| | 3 | 1015.7095 | | 4 | 1007.6227 | | 5 | 1000.7299* |
| | 4 | 1017.7244* | | 5 | 1007.2983* | | 6 | 999.4985 |
| | 5 | 1019.8287* | | 6 | 1006.9468 | | 7 | 998.4016* |
| | 6 | 1022.0408* | | 7 | 1006.5875* | | 8 | 997.4567* |
| | 7 | 1024.3696 | | 8 | 1006.2366 | | 9 | 996.6731 |
| | 8 | 1026.8280 | | 9 | 1005.9094 | | 10 | 996.0551 |
| | 9 | 1029.4214* | | 10 | 1005.6170 | | 11 | 995.6010 |
| | 10 | 1032.1525* | | 11 | 1005.3645 | | 12 | 995.3008 |
| | 11 | 1035.0115 | | 12 | 1005.1540 | | 13 | 995.1399* |
| | 12 | 1037.9854 | | 13 | 1004.9840* | | 14 | 995.0959 |
| | 13 | 1041.0538 | | 14 | 1004.8502 | | 15 | 995.1471* |
| | 14 | 1044.1942 | | 15 | 1004.7468* | | 16 | 995.2669 |
| | 15 | 1047.3830 | | 16 | 1004.6711* | | 17 | 995.4321 |
| | 16 | 1050.5983* | | 17 | 1004.6182* | | 18 | 995.6203 |
| | 17 | 1053.8206* | rQ1 | 3 | 1016.0602 | | 19 | 995.8127 |
| | 18 | 1057.0349 | | 2 | 1015.3731 | | 20 | 995.9953 |
| | 19 | 1060.2328* | rP1 | 2 | 1015.8385 | | 21 | 996.1585* |
| | 20 | 1063.4078 | | 3 | 1015.1179* | | 4 | 1008.1281* |
| | 21 | 1066.5582 | | 4 | 1016.3770* | | 5 | 1008.3194* |
| | 22 | 1069.6846* | | 4 | 1014.7801* | | 5 | 1006.0794* |
| | 23 | 1072.7885 | | 5 | 1016.8055 | | 6 | 1007.0793* |
| rR1 | 1 | 1019.0407* | | 5 | 1014.3608 | | 7 | 1005.9205* |
| | 1 | 1018.8912 | | 6 | 1017.3657 | | 7 | 1001.9174* |
| | 2 | 1020.8460* | | 6 | 1013.8658 | | 8 | 999.8510* |
| | 2 | 1020.4058* | | 7 | 1018.0803 | | 9 | 1003.8456 |
| | 3 | 1021.8576* | | 7 | 1013.2978 | | 9 | 997.8300 |
| | 3 | 1022.7189 | | 8 | 1018.9708* | | 10 | 1002.9319 |
| | 4 | 1024.6586* | | 8 | 1012.6643* | | 10 | 995.8851 |
| | 4 | 1023.2645 | | 9 | 1020.0551 | | 11 | 1002.1016* |
| | 5 | 1026.6682 | | 9 | 1011.9726 | | 11 | 994.0435* |
| | 5 | 1024.6459* | | 10 | 1021.3496* | | 12 | 992.3300* |
| | 6 | 1028.7450* | | 10 | 1011.2327 | | 13 | 1000.6831 |
| | 6 | 1026.0253 | | 11 | 1022.8611 | | 13 | 990.7678 |
| | 7 | 1030.8941 | | 11 | 1010.4563 | | 14 | 1001.0897* |
| | 7 | 1027.4255 | | 12 | 1024.5963 | | 14 | 989.3753 |
| | 8 | 1033.1127 | | 12 | 1009.6590 | | 15 | 999.5678* |
| | 8 | 1028.8737* | | 13 | 1008.8556 | | 15 | 988.1679 |
| | 9 | 1035.4025 | | 13 | 1026.5538 | | 16 | 987.1582* |
| | 9 | 1030.3893 | | 14 | 1008.0649 | | 17 | 986.3492 |
| | 10 | 1037.7617 | | 15 | 1007.2983* | | 18 | 985.7379* |
| | 10 | 1031.9923 | | 16 | 1006.5875* | | 19 | 985.3241* |
| | 11 | 1040.1900* | | 17 | 1005.9323 | | 20 | 985.0787* |
| | 11 | 1033.7003 | | 18 | 1005.3433 | | 21 | 984.9990 |
| | 12 | 1042.6999* | rQ2 | 19 | 1004.8253* | rP2 | 4 | 1015.9509* |
| | 12 | 1035.5309* | | 20 | 1004.3791* | | 5 | 1014.2566* |
| | 13 | 1045.2437 | | 21 | 1004.0011* | | 6 | 1012.5641* |
| | 13 | 1037.4928 | | 22 | 1003.6786 | | 7 | 1010.8849* |
| | 14 | 1048.8616* | | 23 | 1003.4115 | | 8 | 1009.2266 |
| | 14 | 1039.6025 | | 24 | 1003.1891 | | 9 | 1007.5971* |
| | 15 | 1050.5364* | | 25 | 1003.0034 | | 9 | 1006.2047* |
| | 15 | 1041.8683 | | 26 | 1002.8478* | | 10 | 1006.0037* |
| | 16 | 1053.2621 | | 27 | 1002.7176 | | 10 | 1004.0011* |
| | 16 | 1044.2964* | | 28 | 1002.6062* | | 11 | 1001.7142 |
| | 17 | 1058.0367* | | 29 | 1002.5345* | | 12 | 1002.9580 |
| | 17 | 1046.8873* | | 3 | 1022.6457* | | 12 | 999.3473* |
| | 18 | 1058.8497* | | 3 | 1022.6724* | | 13 | 1001.5208 |
| | 18 | 1049.6386* | | 4 | 1022.5746 | | 13 | 996.9305 |
| | 19 | 1061.7981* | | 4 | 1022.6457* | | 14 | 1000.1527* |
| | 19 | 1052.5335* | | 5 | 1022.4583 | | 14 | 994.4831* |
| | 20 | 1064.7856* | | 5 | 1022.6225* | | 15 | 998.8561* |
| | 20 | 1055.5552* | | 6 | 1022.2841 | | 15 | 992.0420 |

| R | | | Q | | | P | | |
|--------|----|------------|--------|----|------------|--------|----|-----------|
| Branch | J" | | Branch | J" | | Branch | J" | |
| rR1 | 21 | 1058.6813* | rQ2 | 6 | 1022.6132* | rP2 | 16 | 997.6372 |
| | 22 | 1061.8709* | | 7 | 1022.0408* | | 16 | 989.6367 |
| | 23 | 1065.1156* | | 7 | 1022.6225* | | 17 | 996.5003 |
| rR2 | 2 | 1027.7066* | 8 | 8 | 1021.6947 | 17 | 17 | 987.3044 |
| | 2 | 1027.7066* | | 8 | 1022.6619* | | 18 | 995.4475* |
| | 3 | 1029.3599 | | 9 | 1021.2534 | | 18 | 985.0787* |
| | 3 | 1029.3377* | | 9 | 1022.7473* | | 19 | 982.9912 |
| | 4 | 1031.0100 | | 10 | 1020.7012* | | 20 | 993.5984* |
| | 4 | 1030.9418 | | 10 | 1022.8919 | | 20 | 981.0716 |
| | 5 | 1032.6636 | | 11 | 1020.0366 | | 21 | 992.8029* |
| | 5 | 1032.5071 | | 11 | 1023.1151 | | 21 | 979.3436* |
| | 6 | 1034.3278* | | 12 | 1019.2616 | | 23 | 976.5387* |
| | 6 | 1034.0212* | | 12 | 1023.4372* | | 24 | 975.4816* |
| | 7 | 1036.0076 | | 13 | 1018.3825 | pP1 | 2 | 997.3140 |
| | 7 | 1035.4699 | | 13 | 1023.8812 | | 3 | 995.3837 |
| | 8 | 1037.7110 | | 14 | 1017.4096* | | 4 | 993.3620 |
| | 8 | 1036.8455 | | 14 | 1024.4698 | | 5 | 991.2423 |
| | 9 | 1039.4445 | | 15 | 1016.3552 | | 6 | 989.0151 |
| | 9 | 1038.1416 | | 15 | 1025.2282 | | 7 | 986.6704 |
| | 10 | 1041.2140 | | 16 | 1015.2320 | | 8 | 984.1997 |
| | 10 | 1039.3617 | | 16 | 1026.1794 | | 9 | 981.5953 |
| | 11 | 1043.0269 | | 17 | 1014.0559 | | 10 | 978.8544 |
| | 11 | 1040.5153 | | 17 | 1027.3419 | | 11 | 975.9802 |
| | 12 | 1044.8897* | | 18 | 1012.8439* | | 12 | 972.9832 |
| | 12 | 1041.6205 | | 18 | 1028.7324* | | 13 | 969.8798 |
| | 13 | 1046.8063 | | 19 | 1011.6111 | | 14 | 966.6919 |
| | 13 | 1042.6999* | | 19 | 1030.3594* | | 15 | 963.4440 |
| | 14 | 1048.7838* | | 20 | 1010.3800* | | 16 | 960.1606 |
| | 14 | 1043.7824 | | 20 | 1032.2262* | | 17 | 956.8643 |
| | 15 | 1050.8236 | | 21 | 1009.1683* | | 18 | 953.5738 |
| | 15 | 1044.8975* | | 22 | 1007.9954 | pP2 | 2 | 989.9796 |
| | 16 | 1052.9239* | | 23 | 1006.8817* | | 3 | 989.8431* |
| | 16 | 1046.0744 | | 24 | 1005.8420* | | 3 | 988.4041 |
| | 17 | 1055.1066 | | 25 | 1004.8886* | | 3 | 988.0031 |
| | 17 | 1047.3408 | | 26 | 1004.0550* | | 4 | 986.8626 |
| | 18 | 1057.3523 | | 27 | 1003.2674* | | 4 | 986.0845 |
| | 18 | 1048.7218* | | 28 | 1002.5995* | | 5 | 985.3387 |
| | 19 | 1059.6674 | | 29 | 1002.0207* | | 5 | 984.0876 |
| | 19 | 1050.2396* | rQ3 | 4 | 1029.5455* | | 6 | 983.8095 |
| | 20 | 1062.0510 | | 4 | 1029.5455* | | 6 | 982.0125 |
| | 20 | 1051.9110 | | 5 | 1029.4912* | | 7 | 982.2515 |
| | 21 | 1064.5001 | | 5 | 1029.4912* | | 7 | 979.8592 |
| | 21 | 1053.7518 | | 7 | 1029.3290* | | 8 | 980.6406* |
| | 22 | 1067.0120* | | 7 | 1029.3475 | | 8 | 977.6288 |
| | 23 | 1069.5835 | | 8 | 1029.2137 | | 9 | 978.9530 |
| | 23 | 1057.9821 | | 8 | 1029.2551 | | 9 | 975.3221* |
| | 24 | 1072.2165* | | 9 | 1029.0685 | | 10 | 977.1707* |
| | 24 | 1060.3822 | | 9 | 1029.1510* | | 10 | 972.9398 |
| | 25 | 1074.8836 | | 10 | 1028.8846 | | 11 | 975.2746 |
| | 25 | 1062.9708 | | 10 | 1029.0362* | | 11 | 970.4851 |
| | 26 | 1077.7030* | | 11 | 1028.6512 | | 12 | 973.2551* |
| | 26 | 1065.7372 | | 11 | 1028.9174 | | 12 | 967.9602 |
| | 27 | 1080.3614* | | 12 | 1028.3568 | | 13 | 971.1009 |
| rR3 | 3 | 1036.2744* | | 12 | 1028.7961 | | 13 | 965.3686 |
| | 3 | 1036.2744* | | 13 | 1027.9869 | | 14 | 968.7443* |
| | 4 | 1037.9060* | | 13 | 1028.6796 | | 14 | 962.7151 |
| | 4 | 1037.9060* | | 14 | 1027.5265 | | 15 | 960.0028 |
| | 5 | 1039.5262* | | 14 | 1028.5772 | | 16 | 963.7555 |
| | 5 | 1039.5262* | | 15 | 1026.9597* | | 16 | 957.2391 |
| | 6 | 1041.1383* | | 15 | 1026.9597* | | 17 | 960.9989 |
| | 6 | 1041.1304* | | 16 | 1026.2778* | | 17 | 954.4276 |
| | 7 | 1042.7363* | | 16 | 1028.4608 | | 18 | 951.5756 |
| | 7 | 1042.7184* | | 17 | 1025.4670 | | 19 | 955.0372 |
| | 8 | 1044.3233 | | 17 | 1028.4753 | | 19 | 948.6880 |
| | 8 | 1044.2834 | | 18 | 1024.5247* | | 20 | 951.8544 |

Appendix III, continued.

| R | | | Q | | | P | | |
|--------|----|------------|--------|----|------------|--------|----|-----------|
| Branch | J" | | Branch | J" | | Branch | J" | |
| rR3 | 9 | 1045.8996 | rQ3 | 18 | 1028.5612* | pP2 | 20 | 945.7720 |
| | 9 | 1045.8216 | | 19 | 1023.4506* | | 21 | 948.5616 |
| | 10 | 1047.4676* | | 20 | 1022.2521 | | 21 | 942.8300* |
| | 10 | 1047.3248 | | 20 | 1029.0362* | | 22 | 945.1839* |
| | 11 | 1049.0294 | | 21 | 1020.9383 | | 22 | 939.8683 |
| | 11 | 1048.7838* | | 21 | 1029.4670 | | 23 | 941.7475 |
| | 12 | 1050.5882* | | 22 | 1030.0639 | | 23 | 936.8755* |
| | 12 | 1050.1895 | | 22 | 1019.5236 | | 24 | 938.2798* |
| | 13 | 1052.1491 | | 23 | 1018.0056* | | 25 | 934.8032 |
| | 13 | 1051.5302 | rQ4 | 5 | 1036.2669* | pP3 | 4 | 978.7082 |
| | 14 | 1053.7169 | | 5 | 1036.2669* | | 4 | 978.6884 |
| | 14 | 1052.7941 | | 6 | 1036.2034* | | 5 | 977.0116 |
| | 15 | 1055.2980 | | 6 | 1036.2034* | | 5 | 976.9555* |
| | 15 | 1053.9720* | | 7 | 1036.1289* | | 6 | 975.3303* |
| | 16 | 1056.8992 | | 7 | 1036.1289* | | 6 | 975.1961 |
| | 16 | 1055.0612 | | 8 | 1036.0395* | | 7 | 973.6720 |
| | 17 | 1058.5274 | | 8 | 1036.0395* | | 7 | 973.4099 |
| | 17 | 1056.0591 | | 9 | 1035.9358* | | 8 | 972.0465* |
| | 18 | 1060.1880* | | 9 | 1035.9358* | | 8 | 971.5892* |
| | 18 | 1056.9737 | | 10 | 1035.8159* | | 9 | 970.4631 |
| | 19 | 1061.8923* | | 10 | 1035.8159* | | 9 | 969.7282 |
| | 19 | 1057.8196 | | 11 | 1035.6753* | | 10 | 968.9224 |
| | 20 | 1063.6434 | | 11 | 1035.6843* | | 10 | 967.8217 |
| | 20 | 1058.6198* | | 12 | 1035.5144 | | 11 | 967.4219* |
| | 21 | 1065.4484 | | 12 | 1035.5309* | | 11 | 965.8621 |
| | 21 | 1059.4005 | | 13 | 1035.3291 | | 12 | 965.9497 |
| | 22 | 1067.3136* | | 13 | 1035.3631 | | 12 | 963.8465 |
| | 22 | 1060.1829* | | 14 | 1035.1149* | | 13 | 964.4893 |
| | 24 | 1061.9630* | | 14 | 1035.1769 | | 13 | 961.7748* |
| | 25 | 1062.9990* | | 15 | 1034.8680 | | 14 | 963.0167 |
| | 26 | 1064.1769* | | 15 | 1034.9734 | | 14 | 959.6248* |
| rR4 | 4 | 1044.6741 | | 16 | 1034.5800 | | 15 | 961.5062 |
| | 4 | 1044.6741 | | 16 | 1034.7537 | | 15 | 957.4145* |
| | 5 | 1046.2965 | | 17 | 1034.5206 | | 16 | 959.9296 |
| | 5 | 1046.2965 | | 18 | 1033.8482* | | 16 | 955.1299 |
| | 6 | 1047.9076 | | 18 | 1034.2783 | | 17 | 958.2623 |
| | 6 | 1047.9076 | | 19 | 1033.3823 | | 17 | 952.7749 |
| | 7 | 1049.5070* | | 19 | 1034.0309* | | 18 | 956.4808 |
| | 7 | 1049.5070* | | 20 | 1032.8330 | | 18 | 950.3476 |
| | 8 | 1051.0941* | | 20 | 1033.7838* | | 19 | 954.5650* |
| | 8 | 1051.0941* | | 21 | 1032.1853* | | 19 | 947.8489 |
| | 9 | 1052.6676* | | 22 | 1031.4235 | | 20 | 952.5032 |
| | 9 | 1052.6676* | | 23 | 1030.5349 | | 20 | 945.2803 |
| | 10 | 1054.2260* | | 23 | 1033.1511 | | 21 | 950.2831 |
| | 10 | 1054.2260* | | 24 | 1029.5080 | | 21 | 942.6462* |
| | 11 | 1055.7739* | | 24 | 1033.0169 | | 22 | 947.8973 |
| | 11 | 1055.7658* | | 25 | 1028.3354* | | 22 | 939.9468 |
| | 12 | 1057.3044* | | 25 | 1032.9486 | | 23 | 945.3408 |
| | 12 | 1057.2868* | | 26 | 1027.0079 | | 23 | 937.1897* |
| | 13 | 1058.8177* | | 26 | 1032.9670 | | 24 | 942.6114 |
| | 13 | 1058.7858 | | 27 | 1025.5505 | | 24 | 934.3056* |
| | 14 | 1060.3155 | rQ5 | 27 | 1033.0915* | pP4 | 25 | 939.7111* |
| | 14 | 1060.2586* | | 6 | 1042.8357* | | 4 | 970.7243* |
| | 15 | 1061.7981* | | 6 | 1042.8357* | | 4 | 970.7243* |
| | 15 | 1061.7008* | | 7 | 1042.7645 | | 5 | 969.0060* |
| | 16 | 1063.2645 | | 7 | 1042.7645 | | 5 | 969.0060* |
| | 16 | 1063.1060 | | 9 | 1042.5844 | | 6 | 967.2789* |
| | 17 | 1064.7190* | | 9 | 1042.5844 | | 6 | 967.2789* |
| | 17 | 1064.4676 | | 10 | 1042.4754 | | 7 | 965.5417* |
| | 18 | 1066.1620 | | 10 | 1042.4754 | | 7 | 965.5467* |
| | 18 | 1065.7771 | | 11 | 1042.3520* | | 8 | 963.8095 |
| | 19 | 1067.5976 | | 11 | 1042.3520* | | 8 | 963.7943* |
| | 19 | 1067.0244* | | 12 | 1042.2139 | | 9 | 962.0712 |
| | 20 | 1069.0303* | | 12 | 1042.2139 | | 9 | 962.0391 |
| | 20 | 1068.1959* | | 13 | 1042.0604 | | 10 | 960.3347 |

Appendix III, continued.

| R | | | Q | | | P | | |
|--------|----|------------|--------|----|------------|--------|----|-----------|
| Branch | J" | | Branch | J" | | Branch | J" | |
| rR4 | 21 | 1070.4622* | rQ5 | 13 | 1042.0604 | pP4 | 10 | 960.2718 |
| | 21 | 1069.2947* | | 14 | 1041.8900* | | 11 | 958.6069 |
| | 22 | 1071.9036 | | 14 | 1041.8900* | | 11 | 958.4922* |
| | 22 | 1070.3068* | | 15 | 1041.7013* | | 12 | 956.8920 |
| | 23 | 1073.3239* | | 15 | 1041.7013* | | 12 | 956.6959 |
| rR5 | 23 | 1071.1956* | | 16 | 1041.4913* | | 13 | 955.1994 |
| | 5 | 1052.9239* | | 16 | 1041.4988* | | 13 | 954.8808 |
| | 6 | 1054.5354* | | 17 | 1041.2599 | | 14 | 953.5372 |
| | 7 | 1056.1367* | | 17 | 1041.2739 | | 14 | 953.0431 |
| | 8 | 1057.7263 | | 18 | 1041.0057 | | 15 | 951.9134* |
| | 9 | 1059.3049 | | 18 | 1041.0288 | | 15 | 951.1774 |
| | 10 | 1060.8713 | | 19 | 1040.7239 | | 16 | 950.3321 |
| | 11 | 1062.4240 | | 19 | 1040.7620 | | 16 | 949.2791 |
| | 12 | 1063.9636 | | 20 | 1040.4126 | | 17 | 948.7994 |
| | 12 | 1063.9636 | | 20 | 1040.4768 | | 17 | 947.3421 |
| | 13 | 1065.4879 | | 21 | 1040.0675 | | 18 | 947.3134 |
| | 13 | 1065.4879 | | 21 | 1040.1714 | | 18 | 945.3613 |
| | 14 | 1067.0112* | | 22 | 1039.8448* | | 19 | 945.8664 |
| | 14 | 1067.0112* | | 23 | 1039.2502* | | 19 | 943.3313 |
| | 15 | 1068.4896* | | 23 | 1039.4988* | | 20 | 944.4455 |
| | 15 | 1068.4896* | rQ6 | 7 | 1049.2726 | | 20 | 941.2457 |
| | 16 | 1069.9677* | | 7 | 1049.2726 | | 21 | 943.0298* |
| | 16 | 1069.9616* | | 8 | 1049.1907 | | 21 | 939.1012 |
| | 17 | 1071.4260* | | 8 | 1049.1907 | | 22 | 941.5931 |
| | 17 | 1071.4088* | | 9 | 1049.0974 | | 22 | 936.8755* |
| | 18 | 1072.8650 | | 9 | 1049.0974 | | 23 | 940.1075 |
| | 18 | 1072.8457 | | 10 | 1048.9930 | | 23 | 934.6179 |
| | 19 | 1074.2863 | | 10 | 1048.9930 | pP5 | 24 | 938.5446* |
| | 19 | 1074.2516 | | 11 | 1048.8757 | | 5 | 960.8783 |
| | 20 | 1075.6861* | | 11 | 1048.8757 | | 5 | 960.8783 |
| | 20 | 1075.6301 | | 12 | 1048.7456 | | 6 | 959.1505* |
| | 21 | 1077.0691 | | 12 | 1048.7456 | | 6 | 959.1505* |
| | 21 | 1076.9773 | | 13 | 1048.6023 | | 7 | 957.4145* |
| | 22 | 1078.4318* | | 13 | 1048.6023 | | 7 | 957.4145* |
| | 22 | 1078.2888 | | 14 | 1048.4444 | | 8 | 955.6703* |
| | 23 | 1079.5577 | | 14 | 1048.4444 | | 8 | 955.6703* |
| | 24 | 1081.1101* | | 15 | 1048.2726 | | 9 | 953.9166* |
| | 24 | 1080.7772 | | 15 | 1048.2726 | | 9 | 953.9166* |
| | 25 | 1081.9363* | | 16 | 1048.0851 | | 10 | 952.1558* |
| rR6 | 6 | 1061.0380 | | 16 | 1048.0851 | | 10 | 952.1558* |
| | 6 | 1061.0380 | | 17 | 1047.8814* | | 11 | 950.3875* |
| | 7 | 1062.6396 | | 17 | 1047.8814* | | 11 | 950.3875* |
| | 7 | 1062.6396 | | 18 | 1047.6606* | | 12 | 948.6166* |
| | 8 | 1064.2300* | | 18 | 1047.6606* | | 12 | 948.6099* |
| | 8 | 1064.2300* | | 19 | 1047.4220 | | 13 | 946.8395* |
| | 9 | 1065.8098 | | 19 | 1047.4220 | | 13 | 946.8262* |
| | 9 | 1065.8098 | | 20 | 1047.1643 | | 14 | 945.0593 |
| | 10 | 1067.3781 | | 20 | 1047.1643 | | 14 | 945.0298 |
| | 10 | 1067.3781 | | 21 | 1046.8878* | | 15 | 943.2808 |
| | 11 | 1068.9348 | | 21 | 1046.8878* | | 15 | 943.2365 |
| | 11 | 1068.9348 | | 22 | 1046.5863* | | 16 | 941.5041* |
| | 12 | 1070.4794 | | 22 | 1046.5950* | | 16 | 941.4301 |
| | 12 | 1070.4794 | | 23 | 1046.2623* | | 17 | 939.7341* |
| | 13 | 1072.0105 | | 23 | 1046.2773* | | 17 | 939.6135 |
| | 13 | 1072.0105 | | 24 | 1045.9127* | | 18 | 937.9768 |
| | 14 | 1073.5296 | | 24 | 1045.9401* | | 18 | 937.7859 |
| | 14 | 1073.5296 | rQ7 | 8 | 1055.5844* | | 19 | 936.2363* |
| | 15 | 1075.0336* | | 9 | 1055.5005 | | 19 | 935.9466* |
| | 15 | 1075.0336* | | 9 | 1055.5005 | | 20 | 934.5220* |
| | 16 | 1076.5238* | | 10 | 1055.3983 | | 23 | 928.3993* |
| | 16 | 1076.5238* | | 10 | 1055.3983 | pP6 | 6 | 950.8855 |
| | 17 | 1078.9823* | | 11 | 1055.2833 | | 6 | 950.8855 |
| | 17 | 1078.9823* | | 11 | 1055.2833 | | 7 | 949.1497 |
| | 18 | 1079.4562* | | 12 | 1055.1515* | | 7 | 949.1497 |
| | 18 | 1079.4562* | | 13 | 1055.0186 | | 8 | 947.4049 |

Appendix III, continued.

| R | | | Q | | | P | | |
|--------|----|------------|--------|----|------------|--------|----|-----------|
| Branch | J* | | Branch | J* | | Branch | J* | |
| rR6 | 19 | 1080.8983* | rQ7 | 13 | 1055.0186 | pP6 | 8 | 947.4049 |
| | 19 | 1080.8983* | | 14 | 1054.8669 | | 9 | 945.6509 |
| | 20 | 1082.3227* | | 14 | 1054.8669 | | 9 | 945.6509 |
| | 20 | 1082.3227* | | 15 | 1054.7023 | | 10 | 943.8883 |
| | 21 | 1083.7281* | | 15 | 1054.7023 | | 10 | 943.8883 |
| | 21 | 1083.7281* | | 16 | 1054.5236* | | 11 | 942.1175 |
| | 22 | 1085.1118* | | 17 | 1054.3329 | | 11 | 942.1175 |
| | 23 | 1086.4858* | | 17 | 1054.3329 | | 12 | 940.3385 |
| | 23 | 1086.4708* | | 18 | 1054.1259* | | 12 | 940.3385 |
| | 24 | 1087.8321* | | 19 | 1053.9050* | | 13 | 938.5518 |
| | 24 | 1087.8170* | | 20 | 1053.6692 | | 13 | 938.5518 |
| | 25 | 1089.1610* | | 20 | 1053.6692 | | 14 | 936.7573* |
| | 25 | 1089.1333 | | 21 | 1053.4223* | | 14 | 936.7573* |
| | 26 | 1090.4248* | | 21 | 1053.4223* | | 15 | 934.9561* |
| | 26 | 1090.3575* | | 22 | 1053.1481* | | 15 | 934.9561* |
| rR7 | 7 | 1069.0363* | | 22 | 1053.1481* | | 18 | 929.5201* |
| | 7 | 1069.0363* | rQ8 | 9 | 1061.8161* | | 18 | 929.5118* |
| | 8 | 1070.6266 | | 10 | 1061.7127* | | 19 | 927.6994* |
| | 8 | 1070.6266 | | 11 | 1061.5989 | | 19 | 927.6847* |
| | 9 | 1072.2067 | | 12 | 1061.4747 | | 20 | 925.8776* |
| | 9 | 1072.2067 | | 12 | 1061.4747 | | 20 | 925.8515* |
| | 10 | 1073.7749 | | 13 | 1061.3371 | | 21 | 924.0542* |
| | 10 | 1073.7749 | | 13 | 1061.3371 | | 21 | 924.0132* |
| | 11 | 1075.3329 | | 14 | 1061.1880 | | 22 | 922.2312* |
| | 11 | 1075.3329 | | 14 | 1061.1880 | | 22 | 922.1676* |
| | 12 | 1076.8785* | | 15 | 1061.0259* | pP7 | 7 | 940.7662 |
| | 12 | 1076.8785* | | 16 | 1060.8523* | | 7 | 940.7662 |
| | 13 | 1078.4125* | | 17 | 1060.6641 | | 8 | 939.0210 |
| | 14 | 1079.9289* | | 17 | 1060.6641 | | 8 | 939.0210 |
| | 15 | 1081.4438 | | 18 | 1060.4628* | | 9 | 937.2674* |
| | 15 | 1081.4438 | | 19 | 1060.2462* | | 10 | 935.5052 |
| | 16 | 1082.9402 | | 20 | 1060.0175 | | 10 | 935.5052 |
| | 16 | 1082.9402 | | 20 | 1060.0175 | | 11 | 933.7342 |
| | 17 | 1084.4232 | | 21 | 1059.7736 | | 11 | 933.7342 |
| | 17 | 1084.4232 | | 21 | 1059.7736 | | 12 | 931.9544 |
| | 18 | 1085.8867* | | 22 | 1059.5139* | | 12 | 931.9544 |
| | 19 | 1087.3487 | | 23 | 1059.2391 | | 13 | 930.1658 |
| | 19 | 1087.3487 | | 23 | 1059.2391 | | 13 | 930.1658 |
| | 20 | 1088.7940* | | 24 | 1058.9472* | | 14 | 928.3691 |
| | 21 | 1090.2200* | | 25 | 1058.6402* | | 14 | 928.3691 |
| | 21 | 1090.2200* | | 26 | 1058.3147 | | 15 | 926.5645 |
| | 23 | 1093.0102* | | 26 | 1058.3147 | | 15 | 926.5645 |
| | 23 | 1093.0102* | pQ1 | 1 | 1000.9813* | | 16 | 924.7520 |
| | 24 | 1094.3885* | | 2 | 1001.1124 | | 16 | 924.7520 |
| | 25 | 1095.7295* | | 3 | 1001.3015* | | 17 | 922.9322* |
| | 25 | 1095.7295* | | 4 | 1001.5405 | | 17 | 922.9322* |
| rR8 | 8 | 1076.9357 | | 5 | 1001.8174 | | 18 | 921.1042* |
| | 8 | 1076.9357 | | 6 | 1002.1190* | | 18 | 921.1042* |
| | 9 | 1078.5143 | | 7 | 1002.4287 | | 20 | 917.4283* |
| | 9 | 1078.5143 | | 8 | 1002.7353 | | 20 | 917.4283* |
| | 10 | 1080.0824* | | 9 | 1003.0237 | | 21 | 915.5818* |
| | 11 | 1081.6390 | | 10 | 1003.2853 | | 21 | 915.5818* |
| | 11 | 1081.6390 | | 11 | 1003.5143 | pP8 | 8 | 930.5386 |
| | 12 | 1083.1847 | | 12 | 1003.7086 | | 8 | 930.5386 |
| | 12 | 1083.1847 | | 13 | 1003.8702 | | 9 | 928.7860 |
| | 13 | 1084.7134* | | 14 | 1004.0011* | | 9 | 928.7860 |
| | 14 | 1086.2408* | | 15 | 1004.1081 | | 10 | 927.0244 |
| | 15 | 1087.7500 | | 16 | 1004.1938 | | 10 | 927.0244 |
| | 15 | 1087.7500 | | 17 | 1004.2634 | | 11 | 925.2535 |
| | 16 | 1089.2471 | | 18 | 1004.3205 | | 11 | 925.2535 |
| | 16 | 1089.2471 | | 19 | 1004.3688 | | 12 | 923.4737 |
| | 17 | 1090.7314 | | 20 | 1004.4104 | | 12 | 923.4737 |
| | 17 | 1090.7314 | | 21 | 1004.4480* | | 13 | 921.6856 |
| | 18 | 1092.2029* | | 22 | 1004.4830 | | 13 | 921.6856 |
| | 19 | 1093.6596 | | 23 | 1004.5169 | | 14 | 919.8884 |

Appendix III, continued.

| R | | | Q | | | P | | |
|--------|----|------------|--------|----|------------|--------|----|------------|
| Branch | J" | | Branch | J" | | Branch | J" | |
| rR8 | 19 | 1093.6596 | pQ1 | 24 | 1004.5503* | pP8 | 14 | 919.8884 |
| | 20 | 1095.1036* | | 25 | 1004.5828* | | 15 | 918.0830 |
| | 20 | 1095.1036* | | 26 | 1004.6182* | | 15 | 918.0830 |
| | 21 | 1096.5326* | | 27 | 1004.6495* | | 16 | 916.2684 |
| | 22 | 1097.9470 | | 28 | 1004.6954* | | 16 | 916.2684 |
| | 22 | 1097.9470 | | 29 | 1004.7359* | | 17 | 914.4465 |
| | 23 | 1099.3414* | | 30 | 1004.7790* | | 17 | 914.4465 |
| | 24 | 1100.7295 | pQ2 | 2 | 993.4676 | | 18 | 912.6160 |
| | 24 | 1100.7295 | | 2 | 993.0378 | | 18 | 912.6160 |
| | 25 | 1102.0978* | | 3 | 992.7770* | | 19 | 910.7782 |
| | 27 | 1104.7808* | | 3 | 993.6490 | | 19 | 910.7782 |
| | 28 | 1106.0987* | | 4 | 992.4059 | | 20 | 908.9318 |
| rR9 | 9 | 1084.7468 | | 4 | 993.8895* | | 20 | 908.9318 |
| | 9 | 1084.7468 | | 5 | 991.9070 | | 21 | 907.0794 |
| | 11 | 1087.8486 | | 5 | 994.1894 | | 21 | 907.0794 |
| | 11 | 1087.8486 | | 6 | 991.2583 | | 22 | 905.2186* |
| | 13 | 1090.9030 | | 6 | 994.5445 | | 23 | 903.3517* |
| | 13 | 1090.9030 | | 7 | 990.4366 | pP9 | 9 | 920.2284 |
| | 14 | 1092.4124 | | 7 | 994.9527 | | 9 | 920.2284 |
| | 14 | 1092.4124 | | 8 | 989.4200 | | 10 | 918.4668* |
| | 15 | 1093.9097 | | 8 | 995.4107 | | 10 | 918.4668* |
| | 15 | 1093.9097 | | 9 | 988.1900* | | 11 | 916.6970 |
| | 16 | 1095.3929* | | 9 | 995.9129 | | 11 | 916.6970 |
| | 17 | 1096.8673* | | 10 | 986.7319 | | 12 | 914.9177 |
| | 17 | 1096.8673* | | 10 | 996.4521* | | 12 | 914.9177 |
| | 18 | 1098.3274* | | 11 | 985.0383 | | 13 | 913.1299 |
| | 19 | 1099.7738 | | 11 | 997.0207* | | 13 | 913.1299 |
| | 19 | 1099.7738 | | 12 | 983.1079 | | 14 | 911.3330 |
| | 20 | 1101.2079 | | 12 | 997.6071 | | 14 | 911.3330 |
| | 20 | 1101.2079 | | 13 | 980.9447 | | 15 | 909.5262 |
| | 21 | 1102.6284* | | 13 | 998.1994 | | 15 | 909.5262 |
| | 21 | 1102.6284* | | 14 | 998.7843* | | 16 | 907.7126 |
| pR1 | 22 | 1104.0223* | | 15 | 999.3473* | | 16 | 907.7126 |
| | 1 | 1004.1651 | | 16 | 999.8737 | | 17 | 905.8895 |
| | 2 | 1005.6467 | | 17 | 1000.3537* | | 17 | 905.8895 |
| | 3 | 1007.0216 | | 18 | 1000.7778 | | 18 | 904.0587* |
| | 4 | 1008.2766* | | 19 | 1001.1414 | | 18 | 904.0587* |
| | 5 | 1009.3984 | | 20 | 1001.4443* | | 10 | 909.8565* |
| | 6 | 1010.3745* | | 21 | 1001.6879 | | 10 | 909.8565* |
| | 8 | 1011.8422 | | 22 | 1001.8780 | | 11 | 908.0866* |
| | 9 | 1012.3259* | | 23 | 1002.0207 | | 12 | 906.3071 |
| | 10 | 1012.6451 | | 24 | 1002.1190* | | 12 | 906.3071 |
| | 11 | 1012.8126 | | 25 | 1002.1934* | | 13 | 904.5200 |
| | 12 | 1012.8438* | | 26 | 1002.2361* | | 13 | 904.5200* |
| | 13 | 1012.7687* | | 27 | 1002.2564* | | 14 | 902.7215* |
| | 14 | 1012.6051 | | 28 | 1002.2851* | | 14 | 902.7215 |
| | 15 | 1012.3836 | | 29 | 1002.3037* | | 15 | 900.9151 |
| pR2 | 16 | 1012.1293* | pQ3 | 3 | 985.4164 | | 15 | 900.9151 |
| | 2 | 997.8488* | | 3 | 985.4382* | rPO | 16 | 899.1004* |
| | 3 | 999.1911* | | 4 | 985.4283* | | 16 | 899.1004* |
| | 4 | 1000.4591 | | 4 | 985.3671* | | 17 | 897.2758* |
| | 5 | 1001.6371* | | 5 | 985.4382* | | 2 | 1005.0696 |
| | 6 | 1006.3518* | | 5 | 985.2945 | | 3 | 1003.5316* |
| | 7 | 1008.2185* | | 6 | 985.4813* | | 4 | 1002.0797* |
| | 7 | 1003.7330 | | 6 | 985.1924* | | 5 | 1000.7299* |
| | 8 | 1010.0110 | | 7 | 985.5695 | | 6 | 999.4985 |
| | 8 | 1004.6495* | | 7 | 985.0520* | | 7 | 998.4016* |
| | 9 | 1011.7023 | | 8 | 985.7177* | | 8 | 997.4567* |
| | 9 | 1005.4748 | | 8 | 984.8605 | | 9 | 996.6731 |
| | 10 | 1013.2673 | | 9 | 985.9377 | | 10 | 996.0551 |
| | 10 | 1006.2160 | | 9 | 984.6054 | | 11 | 995.6010 |
| | 11 | 1014.6849 | | 10 | 986.2380 | | 12 | 995.3008 |
| | 11 | 1006.8750* | | 10 | 984.2701 | | 13 | 995.1399* |
| | 12 | 1015.9388 | | 11 | 986.6220 | | 14 | 995.0959 |
| | 12 | 1007.4514 | | 11 | 983.8347* | | 15 | 995.1471* |

Appendix III, continued.

| R | | | Q | | | P | | |
|--------|----|------------|--------|----|-----------|--------|----|------------|
| Branch | J" | | Branch | J" | | Branch | J" | |
| pR2 | 13 | 1017.0141 | pQ3 | 12 | 987.0907* | rPO | 16 | 995.2669 |
| | 13 | 1007.9534 | | 12 | 983.2784* | | 17 | 995.4321 |
| | 14 | 1017.9005 | | 13 | 987.6387* | | 18 | 995.6203 |
| | 14 | 1008.3822* | | 13 | 982.5775 | | 19 | 995.8127 |
| | 15 | 1018.5919 | | 14 | 988.2622 | | 20 | 995.9953 |
| | 15 | 1008.7512* | | 14 | 981.7067 | | 21 | 996.1585* |
| | 17 | 1019.3825* | | 15 | 988.9500 | rP1 | 4 | 1008.1281* |
| | 17 | 1009.3150* | | 15 | 980.6406* | | 5 | 1008.3194* |
| | 18 | 1019.5032 | | 16 | 989.6941 | | 5 | 1006.0794* |
| | 18 | 1009.5251 | | 16 | 979.3608* | | 6 | 1007.0793* |
| pR3 | 19 | 1009.6976* | | 17 | 990.4827 | | 7 | 1005.9205* |
| | 21 | 1018.9620* | | 17 | 977.8422* | | 7 | 1001.9174* |
| | 22 | 1018.5698 | | 18 | 991.3031 | | 8 | 999.8510* |
| | 5 | 995.5791* | | 19 | 992.1436 | | 9 | 1003.8456 |
| | 6 | 997.3516 | | 20 | 992.9882 | | 9 | 997.8300 |
| | 6 | 996.8616* | | 21 | 993.8224 | | 10 | 1002.9319 |
| | 7 | 999.1801* | | 22 | 994.6295* | | 10 | 995.8851 |
| | 7 | 998.3831* | | 23 | 995.3947 | | 11 | 1002.1016* |
| | 8 | 1001.0670* | | 24 | 996.1022 | | 11 | 994.0435* |
| | 8 | 999.8603* | | 25 | 996.7844* | | 12 | 992.3300* |
| pR4 | 9 | 1001.2852 | pQ4 | 26 | 997.4076* | rP2 | 13 | 1000.6831 |
| | 10 | 1002.6512 | | 28 | 998.4732* | | 13 | 990.7678 |
| | 11 | 1007.0793* | | 4 | 977.4141* | | 14 | 1001.0897* |
| | 11 | 1003.9510 | | 4 | 977.4141* | | 14 | 989.3753 |
| | 12 | 1009.1494 | | 5 | 977.3718* | | 15 | 999.5678* |
| | 12 | 1005.1782 | | 5 | 977.3718* | | 15 | 988.1679 |
| | 13 | 1006.3285* | | 6 | 977.3208* | | 16 | 987.1582* |
| | 14 | 1013.2431 | | 7 | 977.2778 | | 17 | 986.3492 |
| | 14 | 1007.3972 | | 7 | 977.2625 | | 18 | 985.7379* |
| | 15 | 1015.2062 | | 8 | 977.2310* | | 19 | 985.3241* |
| pR4 | 16 | 1017.0540* | | 8 | 977.1963* | | 20 | 985.0787* |
| | 17 | 1018.8015 | | 9 | 977.1891* | | 21 | 984.9990 |
| | 19 | 1021.7521* | | 9 | 977.1199* | rP2 | 4 | 1015.9509* |
| | 7 | 990.6643 | | 10 | 977.1609* | | 5 | 1014.2566* |
| | 8 | 992.2798* | | 10 | 977.0319 | | 6 | 1012.5641* |
| | 9 | 994.0085 | | 11 | 977.1526* | | 7 | 1010.8849* |
| | 10 | 995.6927 | | 11 | 976.9286 | | 8 | 1009.2266 |
| | 10 | 995.4825 | | 12 | 977.1707* | | 9 | 1007.5971* |
| | 11 | 997.4076* | | 12 | 976.8040 | | 9 | 1006.2047* |
| | 11 | 997.0645 | | 13 | 977.2397* | | 10 | 1006.0037* |
| | 12 | 999.1627* | | 13 | 976.6517 | | 10 | 1004.0011* |
| | 12 | 998.6270 | | 14 | 977.3603* | | 11 | 1001.7142 |
| pR4 | 13 | 1000.9692* | | 14 | 976.4627 | | 12 | 1002.9580 |
| | 13 | 1000.1659* | | 15 | 977.5502 | | 12 | 999.3473* |
| | 14 | 1002.8357 | | 15 | 976.2262 | | 13 | 1001.5208 |
| | 14 | 1001.6739 | | 16 | 977.8212* | | 13 | 996.9305 |
| | 15 | 1003.1454 | | 16 | 975.9274 | | 14 | 1000.1527* |
| | 16 | 1006.7696* | | 17 | 978.1846 | | 14 | 994.4831* |
| | 17 | 1008.8357* | | 17 | 975.5511 | | 15 | 998.8561* |
| | 17 | 1006.9491* | | 18 | 978.6466 | | 15 | 992.0420 |
| | 18 | 1007.1670* | | 18 | 975.0783 | | 16 | 997.6372 |
| | 19 | 1008.5181* | | 19 | 979.2104 | | 16 | 989.6367 |
| pR4 | 20 | 1009.6976* | | 19 | 974.4872 | | 17 | 996.5003 |
| | 21 | 1010.8008* | | 20 | 979.8744 | | 17 | 987.3044 |
| | | | | 20 | 973.7537 | | 18 | 995.4475* |
| | | | | 21 | 980.6335* | | 18 | 985.0787* |
| | | | | 21 | 972.8532 | | 19 | 982.9912 |
| | | | | 22 | 981.4764* | | 20 | 993.5984* |
| | | | | 22 | 971.7609 | | 20 | 981.0716 |
| | | | | 23 | 982.3944* | | 21 | 992.8029* |
| | | | | 23 | 970.4513 | | 21 | 979.3436* |
| | | | | 24 | 983.3726* | | 23 | 976.5387* |
| | | | | 25 | 984.3966 | | 24 | 975.4816* |
| | | | | 26 | 985.4507 | | | |
| | | | | 27 | 986.5186* | | | |

Appendix III, continued.

| <u>R</u> | | <u>Q</u> | <u>P</u> |
|----------|-----------|-----------|----------|
| | Branch J* | | |
| | pQ4 28 | 987.5992* | |
| | pQ5 5 | 969.2386* | |
| | 5 | 969.2386* | |
| | 6 | 969.1859* | |
| | 6 | 969.1859* | |
| | 7 | 969.1260* | |
| | 7 | 969.1260* | |
| | 8 | 969.0586* | |
| | 8 | 969.0586* | |
| | 9 | 968.9853* | |
| | 9 | 968.9853* | |
| | 10 | 968.9064* | |
| | 10 | 968.9064* | |
| | 11 | 968.8264* | |
| | 11 | 968.8202* | |
| | 12 | 968.7435* | |
| | 12 | 968.7285 | |
| | 13 | 968.6588 | |
| | 13 | 968.6318 | |
| | 14 | 968.5784 | |
| | 14 | 968.5291 | |
| | 15 | 968.5041 | |
| | 15 | 968.4193 | |
| | 16 | 968.4421* | |
| | 16 | 968.3020 | |
| | 17 | 968.3970* | |
| | 17 | 968.1728 | |
| | 18 | 968.3793 | |
| | 18 | 968.0280* | |
| | 19 | 968.3970* | |
| | 19 | 967.8656* | |
| | 20 | 968.4421* | |
| | 20 | 967.6744* | |
| | 21 | 968.5614* | |
| | pQ6 6 | 960.9167 | |
| | 6 | 960.9167 | |
| | 8 | 960.7837 | |
| | 8 | 960.7837 | |
| | 9 | 960.7057* | |
| | 9 | 960.7057* | |
| | 10 | 960.6200 | |
| | 10 | 960.6200 | |
| | 11 | 960.5279 | |
| | 11 | 960.5279 | |
| | 12 | 960.4291 | |
| | 12 | 960.4291 | |
| | 13 | 960.3237* | |
| | 13 | 960.3237* | |
| | 14 | 960.2128* | |
| | 14 | 960.2128* | |
| | 15 | 960.0969* | |
| | 15 | 960.0969* | |
| | 16 | 959.9748* | |
| | 17 | 959.8587* | |
| | 17 | 959.8487* | |
| | 18 | 959.7366* | |
| | 18 | 959.7183* | |
| | 19 | 959.5839 | |
| | 19 | 959.6133* | |
| | 20 | 959.4937 | |
| | 20 | 959.4453* | |
| | 21 | 959.3002* | |
| | 21 | 959.3758* | |
| | 22 | 959.1627* | |
| | 23 | 958.9872* | |

Appendix III, continued.

| <u>R</u> | | <u>Q</u> | <u>P</u> |
|----------|----|-----------|----------|
| Branch | J* | | |
| pQ7 | 8 | 952.3931* | |
| | 8 | 952.3931* | |
| | 9 | 952.3136* | |
| | 9 | 952.3136* | |
| | 10 | 952.2261 | |
| | 10 | 952.2261 | |
| | 11 | 952.1301 | |
| | 11 | 952.1301 | |
| | 12 | 952.0267 | |
| | 12 | 952.0267 | |
| | 13 | 952.9134* | |
| | 13 | 952.9134* | |
| | 14 | 951.7966 | |
| | 14 | 951.7966 | |
| | 15 | 951.6714 | |
| | 15 | 951.6714 | |
| | 16 | 951.5399 | |
| | 16 | 951.5399 | |
| | 17 | 951.4016* | |
| | 17 | 951.4016* | |
| pQ8 | 18 | 951.2580* | |
| | 18 | 951.2580* | |
| | 19 | 951.1094* | |
| | 19 | 951.1094* | |
| | 20 | 950.9490* | |
| | 8 | 943.9068 | |
| | 8 | 943.9068 | |
| | 9 | 943.8256 | |
| | 9 | 943.8256 | |
| | 10 | 943.7367 | |
| | 10 | 943.7367 | |
| | 11 | 943.6391 | |
| | 11 | 943.6391 | |
| | 12 | 943.5336 | |
| | 12 | 943.5336 | |
| | 13 | 943.4193 | |
| | 13 | 943.4193 | |
| | 14 | 943.2973 | |
| | 14 | 943.2973 | |
| | 15 | 943.1668 | |
| | 15 | 943.1668 | |
| pQ9 | 16 | 943.0298* | |
| | 17 | 942.8855* | |
| | 18 | 942.7328 | |
| | 18 | 942.7328 | |
| | 19 | 942.5744 | |
| | 19 | 942.5744 | |
| | 20 | 942.4087 | |
| | 20 | 942.4087 | |
| | 21 | 942.2373* | |
| | 21 | 942.2373* | |
| | 22 | 942.0601* | |
| | 22 | 942.0601* | |
| | 24 | 941.6879* | |
| | 24 | 941.6879* | |
| | 12 | 934.9675* | |
| | 12 | 934.9675* | |
| | 13 | 934.8515* | |
| | 13 | 934.8515* | |
| | 14 | 934.7237* | |
| | 14 | 934.7237* | |
| | 15 | 934.5948* | |
| | 15 | 934.5948* | |
| | 16 | 934.4536* | |
| | 16 | 934.4536* | |

Appendix III, continued.

| <u>R</u> | | <u>Q</u> | <u>P</u> |
|----------|--------|----------|-----------|
| | Branch | J" | |
| | pQ9 | 17 | 934.3056* |
| | | 17 | 934.3056* |
| | | 18 | 934.1575* |
| | | 18 | 934.1575* |
| | | 21 | 933.6237* |
| | | 21 | 933.6237* |

^aTransitions in units of cm^{-1} . Blended lines are denoted by an asterisk.

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