RADIATIVE LIFETIME OF THE $B^{3}\Pi_{o^{+}u}$ **STATE OF** Br_{2}

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Abstract

The absorption and fluorescence spectra of the molecule bromine corresponding to the transition between the ground state, $X^1\Sigma_{o+g}$, and excited state, $B^3\Pi_{o+u}$, have been measured from approximately 17464 cm^{-1} to 17480 cm^{-1} . This region of the spectra covered the 14' - 1'', 15' - 1'', 17' - 2'', 18' - 2'', and 19' - 2'' vibrational bands. The frequency of each absorption line was calculated and the integrated absorption coefficient under each absorption line was measured. At room temperature, the number of molecules per cm^3 for $^{(79,79)}Br_2$, $^{(79,81)}Br_2$ and $^{(81,81)}Br_2$ have been calculated. By using both theory and experiment the radiative lifetime τ_{rad} from B state to X state of $^{(79,79)}Br_2$, $^{(79,81)}Br_2$ and $^{(81,81)}Br_2$ for v' = 14,15,17,18,19 have been obtained. The predissociation of Br_2 in the $B^3\Pi_{o+u}$ state is discussed.

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Chapter 1

Introduction

For a number of years the spectroscopy of halogen molecules, especially I_2 , has attracted considerable interest. The spectrum of the B - X system of I_2 has been studied successfully and extensively by various research groups.

Bromine, being on the same column (VIIA) of the periodic table as iodine, has properties that closely resemble those of iodine. Of special spectroscopic interest is the B -X system of Br_2 which is very similar to the B - X system of I_2 , the absorption and fluoresence spectra of both lying in the visible region. The B - X system of Br_2 has also been extensively investigated [5,9,10,19].

The bromine atom with atomic number 35 and international atomic weight of 79.909 a.m.u. has 35 electrons, 5 of which lie in the outermost, or valence, shell. The electronic configuration is expressed as

> Br(35): $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^5$ or KLM $4s^2$ $4p^5$

Bromine occurs natually in two isotopes, yielding three types of Br_2 which are $^{79,79}Br_2$, $^{79,81}Br_2$, and $^{81,81}Br_2$ in a relative abundance of 1.0216: 2.0: 0.9784.

The combination of two bromine atoms to form a molecule gives rise to a $X^1 \Sigma_{o^+u}$ ground state and the first excited state $B^3 \prod_{o^+u}$ (see Figure 1.1) [24]. A few other states lying above the ground states are also shown in Figure 1.1.

Chapter II describes the theoretical work of dealing with the internal motion of a diatomic molecule. We consider molecular bromine as a non-translating rigid rotator

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Figure 1.1: Potential energy curves for Br_2

Chapter 1. Introduction

and this rigid rotator moves around the center of mass which are the origins of both space and molecular coordinate system. We also consider the vibration as a simple harmonic motion. From the Born-Oppenheimer approximation, the wave function of the system can be separated to a good approximation into an electronic part ψ_e and a vibrational part ψ_n so that the coupled Schrödinger equation of the system be separated. From solving the two Schrödinger equations we can obtain the electronic and nuclear (vibrational and rotational) energies.

In fact, the vibration of molecule is a non-simple harmonic motion and the rotation of molecular bromine is not a rigid rotator. Therefore we have to amend the results obtained from the approximation to obtain finally the total energy of the system.

In Chapter III we describe the apparatus used to study the radiative lifetime of $B^3\Pi_{0^+u}$ state of Br_2 and the construction of bromine sample cell. We also report the absorption spectum in this chapter.

Chapter IV describes the procedure of analysing the data. We use the iodine atlas obtained by another research group [21] to calibrate the bromine spectrum. By checking the dispersion of each scan region we found the frequency of each absorption line. We used a digitizer to get two sets of data and then to calculate the area under each absorption line by using those data. In order to make sure the lines are not overlapped we assume the line is a Gaussian distrubution and then compare the two values of $\int k_{\nu} d\nu$ between the Gaussian distrubution and the real $\int k_{\nu} d\nu$. We also calculate the half width of each absorption spectral line to check whether the line is overlapped or not. In order to obtain the radiative lifetime we also calculate the density of Br_2 in the different vibrational and rotational energy levels.

Chapter V provides a discussion of the results; we compare our results of radiative lifetime with the results obtained by other authors. The predissociation rate of molecular bromine in the $B^3\Pi_{o^+u}$ state is also discussed in this chapter.

Chapter 2

Theory

2.1 Internal motion of a diatomic molecule

An atom has only one nucleus and some electrons moving around it. Because the nucleus has much greater mass than the electrons, one can assume that all the electrons move approximately in a central potential produced by the nucleus and so estimate the energy levels. The simplest molecule consists of two atoms; for example, molecular bromine consists of two bromine atoms. The electrons in this kind of molecule move in the potential produced by the two nuclei, and nuclei will vibrate about their equilibrium positions (where the potential energy is at a minimum), and rotate around its center of mass. Therefore, both the electron and nuclear motions should be taken into account at the same time in the study of molecular internal motions. Because it has been found that there is a certain structure for every kind of molecule and this structure is determined by the equilibrium positions of nuclei, one can divide the molecular internal motion into three kinds: electronic motion, and rotational, vibrational motion of the nuclei.

Before we start to look these three kinds of motions, two kinds of coordinate systems should be introduced. One is the normal Cartesian system which will be fixed in space and will not move with molecule; another one is called the molecular coordinate system which will be fixed on the molecule (actually nuclei's equilibrium positions) and will rotate with the molecule (Fig.2.2). Both of the two systems will take the center of mass of the molecule as their origins. The relation between the two systems can be described

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Figure 2.2: The Cartesian and Molecule Coordinate Systems o -xyz is the molecule coordinate systems $o-\xi\eta\zeta$ is the space coordinate systems

by the Eulerian angles (ϕ, θ, δ) [6].

For the molecular rotations, we can assume that each nucleus is fixed at its equilibrium position, the two nuclei can be recognized as a rigid rotor like a dumbell fixed on the z axis of the molecular coordinate system (Fig.2.2). This "dumbell" can rotate freely around the original point (center of mass).

The vibrations can be described in the molecular coordinate system.

2.2 Born-Oppenheimer method

In quantum mechanics, the quantum states of a physical system are charaterized by a wave function, Ψ , which contain all the information about the physical system. The

probability of finding the system in such a state Ψ is

$$|\Psi|^2 = \int \Psi^* \Psi d\tau \tag{2.1}$$

The dynamical evolution of the state vector Ψ is governed by the Schrödinger equation:

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi \tag{2.2}$$

where H is the Hamiltonian, an observable associated with the total energy of the system. That is,

$$H = T + U \tag{2.3}$$

where T and U are the kinetic and potential energy of this dynamical system. The Hamiltonian of the Br_2 molecule can be expressed, to the first order, as [26]

$$H = \sum_{i=1}^{2} \frac{P_i^2}{2M_i} + \sum_{j=1}^{Z_1+Z_2} \frac{p_j^2}{2m_i} - \sum_{j=1}^{Z_1+Z_2} \frac{Z_1e^2}{r_{1j}} - \sum_{j=1}^{Z_1+Z_2} \frac{Z_2e^2}{r_{2j}} + \frac{Z_1Z_2e^2}{R_{12}} + \sum_{i>j} \frac{e^2}{r_{ij}}$$
(2.4)

where

 Z_1, Z_2 : atomic numbers of atom one and atom two

 $\mathbf{P_i}$: the linear momentum of nucleus i

 $\mathbf{p}_{\mathbf{j}}$: the linear momentum of electron j

 M_i : the mass of nucleus i

 m_i : the mass of electron i

 r_{1j} : the distance between nucleus 1 and electron j

 r_{2j} : the distance between nucleus 2 and electron j

 R_{12} : the internuclear distance

r_{ij} : the distance between electrons i and j

In the above equation, the first term describes the kinetic energy of the two bromine nuclei; the second term the electron kinetic energy; the third and the fourth are the coulomb potential energy between electrons and the nucleus one and nucleus two, respectively; the fifth term is the coulomb potential energy between the two nuclei; and the last term is the coulomb potential energy between all electrons.

In general, it is impossible to solve this Schrödinger equation exactly for such a system. Since the mass of electrons is much smaller than the mass of nucleus, the velocity of electron is much greater than that of nucleus. Whenever the nucleus moves a little bit, the electron has already moved through many orbits around it. Accordingly, Born and Oppenheimer introduced an approximation in which they separated the electronic and nuclear motions by supposing that the nuclei are fixed at their equilibrium positions and electrons move in a stable potential produced by the two nuclei, the distance between the two nuclei being regarded as a parameter. From solving the Schrödinger equation for the electrons, they could get the electron eigenenergy with the coordinate of nuclei as a parameter. Then, they solved the Schrödinger equation for the nuclear motions (i.e. vibrations and rotations) by substituting the electronic eigenenergy in.

In order to realize that, they wrote the wavefunction as,

$$\Psi = \psi_e \psi_n \tag{2.5}$$

where ψ_e is electronic eigenfunction and ψ_n is the nuclear eigenfunction. Substituting this eigenfunction Ψ into the Eqn.(2.2), we can get two equations:

$$\left[-\frac{\hbar^2}{2m}\sum_{i}\nabla_{i}^2 - \sum_{j=1}^{Z_1+Z_2}\frac{Z_1e^2}{r_{1j}} - \sum_{j=1}^{Z_1+Z_2}\frac{Z_2e^2}{r_{2j}} + \sum_{i>j}\frac{e^2}{r_{ij}}\right]\psi_e(R_{12}) = E_e(R_{12})\psi_e(R_{12}) \qquad (2.6)$$

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$$\left[-\sum_{j}^{2} \frac{\hbar^{2}}{2M_{j}} \bigtriangledown_{j}^{2} + E_{e}(R_{12}) + \frac{Z_{1}Z_{2}e^{2}}{R_{12}}\right]\psi_{n} = E\psi_{n}$$
(2.7)

When solving Eqn.(2.6), one can recognize R_{12} as a parameter in the electronic eigenvalues and eigenfunctions. The third term of Eqn.(2.7) can be removed by supposing that it has be included in this parameter. Therefore the Eqn.(2.7) can be written as

$$\left[-\sum_{j}^{2} \frac{\hbar^{2}}{2M_{j}} \bigtriangledown_{j}^{2} + E_{e}^{'}(R_{12})\right]\psi_{n} = E\psi_{n}$$
(2.8)

So, one can solve the Eqn.(2.6) to get a set of eigenvalues E_e^{μ} :

$$E_e^{\mu} = E_e^{\mu}(r_{ij}, R_{12}) \tag{2.9}$$

and eigenfunctions ψ_e^{μ} :

$$\psi_e^{\mu} = \psi_e^{\mu}(r_{ij}, R_{12}) \tag{2.10}$$

where $E_e^{\mu}(r_{ij}, R_{12})$ and $\psi_e^{\mu}(r_{ij}, R_{12})$ should be the sum of electronic kinetic and potential energy, and the electronic eigenfunctions for a certain molecular state.

It is quite obvious that in the Eqn.(2.8), the $E'_e(R_{12})$ actually takes the role of potential energy in the Schrödinger equation. It is well known that whenever the $E'_e(R_{12})$ has a minimum, there should be a stable structure corresponding to it. So, theoretically speaking, once one obtained $\psi^{\mu}_e(r_{ij}, R_{12})$ and an electronic energy $E^{\mu}_e(r_{ij}, R_{12})$, i.e. a stable molecular structure, from solving Eqn.(2.6), one can in principle determine the nuclear motion: vibrations and rotations, from Eqn.(2.8).

2.2.1 The vibration and rotation of diatomic molecules

In order to seperate the molecular vibrations and rotations, one can write down the Schrödinger Eqn.(2.3) in terms of a set of polar coordinates: r, θ , and ϕ [6]

$$[T_e + T_v + T_r + U(R, x_3, y_3, z_3, \dots x_N, y_N, z_N) - E_{rve}]\Phi_{rve}(R, \theta, \phi, x_3, \dots z_N) = 0 \quad (2.11)$$

where T_e is the electron kinetic energy operator,

$$T_e = -\frac{\hbar^2}{2m} \sum_{i=3}^N \nabla_i^2 - \frac{\hbar^2}{2M_N} \sum_{i,j=3}^N \nabla_i \cdot \nabla_j \qquad (2.12)$$

where M_N is the total nuclear mass, i.e.

$$M_N = m_1 + m_2 \tag{2.13}$$

 T_{v} is the nuclear vibrational kinetic energy operator,

$$T_{\nu} = -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R}\right) \tag{2.14}$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{2.15}$$

while the T_r is the nuclear rotational kinetic energy operator,

$$T_r = -\frac{\hbar^2}{2\mu R^2} \left[\frac{1}{\sin^2\theta} \left(\frac{\partial}{\partial \phi} + i \frac{L_x}{\hbar} \sin\theta - i \frac{L_z}{\hbar} \cos\theta \right)^2 + \frac{1}{\sin\theta} \left(\frac{\partial}{\partial \theta} - i \frac{L_y}{\hbar} \right) \sin\theta \left(\frac{\partial}{\partial \theta} - i \frac{L_y}{\hbar} \right) \right]$$
(2.16)

where L_x , L_y and L_z are the electron angular momentum operators in the molecular coordinate system.

From Eqn.(2.16), one can see that it is impossible to separate the electron and molecular coordinates except for neglecting L_x , L_y and L_z . People usually neglect these angular momenta first, solve the simplified equations to get the electron, vibration and rotation energy, and then to discuss the coupling between these motions. From Herzberg, for the first approximation (small rotation) the wavefunction of the system can be written as [17]

$$\Psi_{rve} = \psi_e \cdot \frac{1}{R_{12}} \psi_v (R_{12} - R_e) \cdot \psi_r$$
(2.17)

where R_e is the distance between two nuclei at the equilibrium position. Ψ_{rve} in the above equation is called the rovibronic wavefunction. The total energy of the system is

$$E_{tot.} = E_e + E_v + E_r \tag{2.18}$$

Eqn.(2.17) holds to a good approximation expect for the high vibrational and rotational energy levels of the molecule. When the vibrational quantum number, v, increases, the amplitude of the vibration will increase, while when the rotational quantum number, J, increases, the distance between the two nulei will increase. Therefore, we have to use the model of the anharmonic oscillator and consider the molecule as a non-rigid rotator.

After adding the potential of the anharmonic oscillator and the non-rigid rotator to the potential in Eqn.(2.8), we can ultimately obtain the rovibronic energy,

$$E = hc\{T_e + [\omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + ...] + [B_e - \alpha_e(v + \frac{1}{2})]J(J+1) + [D_e - \beta_e(v + \frac{1}{2})]J^2(J+1)^2 + ...\}$$
(2.19)

All the constants ω_e , $\omega_e x_e$, α_e , $\beta_e T_e$, B_e , D_e can be obtain from [2,20] An important property is

$$B_e \ll \omega_e \ll T_e$$

That means

 $\Delta E_e \gg \Delta E_v \gg \Delta E_r$

From the above equation, it can be seen that the rotational energy levels are added to the vibrational energy levels, while the vibrational energy levels are added to the electronic energy levels.

2.3 Electronic states of a diatomic molecule

There is only an axial symmetry about the internuclear axis in a diatomic molecule. The constant of the motion is only the component of the electronic orbital angular momentum, L, along internuclear axis. That component M_L of L is called Λ and $\Lambda = |M_L|$ [13]. The value of Λ corresponding to each electronic state of molecule are shown in following table

The Λ value:0123 \ldots The molecular state: Σ Π Δ Φ \ldots

All the states except for $\Lambda = 0$ are doubly degenerate because M_L can have the two values $+\Lambda$ and $-\Lambda$.

The spin of an electron is not affected by the electronic field. There is a magneitic field along the internuclear axis. For states $\Lambda \neq 0$, the magneitic field causes a precession of S about the internuclear axis with a constant component Σ ,

$$\Sigma = S, S - 1, \dots, -S. \tag{2.20}$$

For each state Λ the spin degeneracy is 2S+1.

The total electronic angular momentum (in units \hbar) along the internuclear axis is:

$$\Omega = |\Lambda + \Sigma| \tag{2.21}$$

where

 Λ : the projection of L along internucler axis

S: the electron spin

 Σ : the projection of S along internucler axis

Each electronic state finally is labelled by

$$^{2S+1}\Lambda_{|\Lambda+\Sigma|}$$

2.4 Coupling of electronic motion and rotation

We consider the case where the interaction of nuclear and electronic motion is very weak and the electronic motion is coupled very strongly to the internuclear axis (Hund's case a), when the total angular momentum is:

$$J = \Omega + R \tag{2.22}$$

where R is the rotation of the nuclei. In this thesis we are interested in the cases in which Ω is equal to zero. Hence,

$$\mathbf{J} = \mathbf{R} \tag{2.23}$$

2.5 The symmetry properties of a diatomic molecule

2.5.1 The symmetry of the electronic wavefunction

In a diatomic molecule, any plane through the internuclear axis is a plane of symmetry. So for a Σ state ($\Lambda = 0$), the electronic wavefunction eighter remains unchanged (for a Σ^+ state), or changes sign (for a Σ^- state) upon reflection through such a plane of symmetry.

2.5.2 g and u symmetry of electronic states

For homonuclear diatomic molecule the electronic wavefunction has a fixed parity. The wavefunction either remains unchanged (even or g (gerade)) upon inversion or change sign (odd or u (ungerade)). Because only homonuclear molecules have the inversion symmetry property, so the subscripts g and u are applicable to only homonuclear molecules.

2.5.3 +, - parity of rotational states

Rotational levels have '+' or '-' parity depending on the symmetry of the total wavefunction with respect to inversion at the origin of a space coordinate system.

2.5.4 s and a symmetry of rotational states

s(symmetry) and a(antisymmetry) refer to the symmetry of the total wavefuction on exchanging the two identical nuclei (where the nuclear spin has been omitted).

2.6 The selection rules of molecular bromine for transitions

The selection rules can be summerized as following [18]:

2.6.1 For the electronic transitions

For electric dipole transitions between the electronic states, the selection rules are:

$$\Delta \Lambda = 0, \pm 1 \tag{2.24}$$

$$\Delta \Omega = 0, \pm 1 \tag{2.25}$$

 $\Delta \Sigma = 0 \tag{2.26}$

 $\Sigma^+ \longleftrightarrow \Sigma^+ \tag{2.27}$

$$\Sigma^{-} \longleftrightarrow \Sigma^{-} \tag{2.28}$$

$$g \longleftrightarrow u$$
 (2.29)

For the bromine molecule, the third selection rule (2.26) cannot be used at all. Because Br_2 is a heavy molecule, the interaction between L and S may be stronger than the interaction with the internuclear axis. Σ is not a good quantum number any more, so that $\Delta \Sigma = 0$ is no longer true.

2.6.2 For the vibrational transitions

For the transitions between the vibrational states, the selection rules are:

$$\Delta v = 0, \pm 1, \pm 2, \dots \tag{2.30}$$

But in the electronic transition the intensity of the vibrational spectrum band is proportional to the Franck-Condon Factor (F.C.F.). (See appendix B)

2.6.3 For the rotational transitions

The selection rules for the transitions between the rotational states of a homonulear molecule are:

$$\Delta J = \pm 1 \tag{2.31}$$

$$+ \longleftrightarrow -$$
 (2.32)

$$s \longleftrightarrow s$$
 (2.33)

$$a \longleftrightarrow a$$
 (2.34)

From Eqn (2.31) we can obtain

P branch:

$$J' = J'' - 1 \tag{2.35}$$

and R branch:

$$J' = J'' + 1 \tag{2.36}$$

where the single prime and double prime represent the excited state and initial state, respectively.

2.7 The distribution of the number of molecules

Bromine molecules may exist in a variety of different states, each of which may be described by rotational, vibrational and electronic quantum numbers. When a molecular gas is at thermal equilibrium, the number of molecules in each state obeys the Boltzmann distribution:

$$N_i = N_0 e^{-\beta E_i} \tag{2.37}$$

where.

 N_i is the number of molecules in state i

 N_0 is the total number of molecules

 E_i is the energy of state of i relative to the lowest state

$$\beta$$
: $(kT)^{-1}$

k is the Boltzmann constant

T is the temperature

If a state has degeneracy g_i , then the Boltzmann law becomes:

$$N_i = N_0 q_i e^{-\beta E_i} \tag{2.38}$$

We can apply the Boltzmann law to rotation, vibrational and electronic energy levels in turn. Because the energy separations of electron levels is much bigger than the one of vibrational and rotational levels, we can think that molecules stay in the electronic ground state at room temperature.

2.8 The effect of nuclear spin

There is a further symmetry property which must be considered, and which turns out to have very important implications for the population of different rotational levels. This symmetry property is the behaviour of the total wavefunction when equivalent nuclei are interchanged. As is known, nuclei with integer spin obey Bose-Einstein statistics, according to which the total wavefunction must be symmetric with respect to exchange of identical nuclei. Nuclei with half-integer spin obey Fermi-Dirac statistics, according to which the total wavefunction is antisymmetric with respect to exchange of nuclei. For Br_2 , exchange of nuclei leaves the electronic wavefunction unchanged. The vibrational wavefunction is also unchanged on nuclear exchange, because the vibrational wavefunction only deponds on the magnitude of the bond length. But, the nuclear exchange influences the rotational wavefunction. Rotational wavefunctions are symmetric if J is even and are antisymmetric if J is odd. The bromine nucleus has spin I, the degeneracy introduced by nuclear spin is shown in table 2.1

The intensity of spectral lines are proportional to degeneracy. The neighbouring spectral lines in the same P branch and R branch will have symmetry and antisymmetry, respectively. When the nuclear spin I is equal to a integer, the ratio of the intensity of

Nuclear spin	Integer		Half-integer	
Ψ_{rve}	S	a	S	a
Degeneracy	(I+1)(2I+1)	I(2I+1)	(I+1)(2I+1)	I(2I+1)

Table 2.1: The degeneracy introduced by nuclear spin

neighbour spectral lines is

$$\frac{I_a}{I_s} = \frac{I}{I+1} \tag{2.39}$$

When I has a half-integral value, we have

$$\frac{I_a}{I_s} = \frac{I+1}{I} \tag{2.40}$$

Where the subscript s indicates a symmetric and a indicates an antisymmetric state. The nuclear spin, I, of each bromine atom is $\frac{3}{2}$. So, the total nuclear spin, $I = I_1 + I_2$, is 0,1,2,3.

In the ground electronic state, $X^1\Sigma_{0+g}$, bromine molecules with odd J values are referred to as ortho-bromine and those with even J values as para-bromine. For odd J (ortho), we have I = 1 (2I + 1 = 3 states) and I = 3 (2I + 1 = 7 states), i.e. totally we have 10 antisymmetric states. For even J (para), we have I = 0 (2J + 1 = 1 state) and I = 2 (2J + 1 = 5 states), i.e. we totally have 6 symmetric states. Hence the hyperfine partition factor is $\frac{10}{16} = \frac{5}{8}$ for ortho states, and $\frac{6}{16} = \frac{3}{8}$ for para states.

Thus, at room temperature, we can get the number of moleculer per cm^3 in a particular vibrational and rotational states.

The density of ortho state of (odd J) $^{(79,79)}Br_2$ and $^{(81,81)}Br_2$ satisfies Eqn.(2.41), and para state (even J) of $^{(79,79)}Br_2$ and $^{(81,81)}Br_2$ satisfies Eqn.(2.42). (For more details see appendix C)

$$N_{mv''J''} = \frac{N_0}{V} \times M \\ \times \frac{e^{-\beta E_{v''}}}{\sum_{v''} e^{-\beta E_{v''}}} \times \frac{5}{4} \frac{(2J''+1)e^{-\beta E_{J''}}}{\sum_{J''} (2J''+1)e^{-\beta E_{J''}}} \times e^{-\beta E_{e}}$$
(2.41)

$$N_{mv''J''} = \frac{N_0}{V} \times M \\ \times \frac{e^{-\beta E_{v''}}}{\sum_{v''} e^{-\beta E_{v''}}} \times \frac{3}{4} \frac{(2J''+1)e^{-\beta E_{J''}}}{\sum_{J''} (2J''+1)e^{-\beta E_{J''}}} \times e^{-\beta E_e}$$
(2.42)

where the sum over J'' is from 0 to infinit.

There are no para and ortho states defined for ${}^{(79,81)}Br_2$ where the two nuclei are inequivalent. The density of ${}^{(79,81)}Br_2$, at room temperature, satisfies Eqn.(2.43)

$$N_{mv''J''} = \frac{N_0}{V} \times M \times \frac{e^{-\beta E_{v''}}}{\sum_{v''} e^{-\beta E_{v''}}} \times \frac{(2J''+1)e^{-\beta E_{J''}}}{\sum_{J''} (2J''+1)e^{-\beta E_{J''}}} \times e^{-\beta E_e}$$
(2.43)

where J'' includes odd J'' and even J''.

M is the fractional abundances of the type of molecule studied, where M is equal to 0.2554 for $^{(79,79)}Br_2$, 0.2446 for $^{(81,81)}Br_2$ and 0.5 for $^{(79,81)}Br_2$.

For the ground electronic state E_e is equal to zero.

The partition function $\frac{e^{-\beta E_{v''}}}{\sum_{v''} e^{-\beta E_{v''}}}$ is the probability of molecules in vibrational states.

$$\frac{N_0}{V} = \frac{P}{RT} = 2.08 \times 10^{17} (molecules/cm^3)$$
(2.44)

P : pressure in the cell

R : molar gas constant

T : room temperature





2.9 Absorption of light by a diatomic molecule

2.9.1 Definition of the absorption coefficient

When a beam of light is sent through a bromine gas cell the intensity of the transmitted light, I_{ν} , may show a frequency distribution similar to the one depicted in Figure 2.3.[23] where ν_0 is the frequency at the centre of the line.

In general, the absorption coefficient k_{ν} of the gas, is defined by the equation

$$I_{\nu} = I_0 e^{-k_{\nu}L} \tag{2.45}$$

that is,

$$k_{\nu} = (1/L)\ln(I_0/I_{\nu}) \tag{2.46}$$

where

 I_0 is the intensity incident on the cell

L is the length of the cell

When L is meassured in cm, k_{ν} is expressed in cm^{-1} , and ν is the wavenumber of the radiation in cm^{-1} . From Fig.2.3 and Eqn.(2.46), we have a curve in Figure 2.4 [23].





where $\Delta \nu$ is called the half-width of the absorption line.

2.9.2 The relations between the Einstein coefficients and the integrated absoption coefficient

The intensity of an absorption line can be defined by equation [13]

$$I_{\nu}^{nm} = I_{0}^{nm} N_{m} B_{nm} h \nu_{nm} L \tag{2.47}$$

where

m is initial(lower energy) state

n is excited(higher energy) state

 N_m is the number of molecule per cm^3 in the initial state m

 B_{nm} is the Einstein transition probability of absorption

 ν_{nm} is the transition frequency

The intensity of a spectral line in emission is written as

$$I_{\nu'}^{nm} = N_n h c \nu_{nm} A_{nm}$$

(2.48)

where c is the speed of light and A_{nm} is the Einstein transition probability of spontaneous emission.

From wave mechanics [13], we find for transitions between non-degenerate levels is

$$A_{nm} = \frac{64\pi^4 \nu_{nm}^3}{3h} | \mathbf{R}^{nm} |^2$$
 (2.49)

and

.so,

$$B_{mn} = \frac{8\pi^3}{3h^2c} |\mathbf{R}^{nm}|^2$$
(2.50)

where
$$\mathbf{R^{nm}}$$
 is a transition dipole moment.

$$A_{nm} = 8\pi h \nu_{nm}^3 B_{mn} \tag{2.51}$$

For the case of a transition between the two levels n and m of degeneracy d_n and d_m , respectively, we have

$$A_{nm} = \frac{64\pi^4 \nu_{nm}^3}{3hd_n} \sum_{m_{J''}} |\mathbf{R}^{\mathbf{n}_{J'}\mathbf{m}_{J''}}|^2$$
(2.52)

$$B_{mn} = \frac{8\pi^3}{3h^2 c d_m} \sum_{m_{J''}} |\mathbf{R}^n \mathbf{J}'^m \mathbf{J}''||^2$$
(2.53)

$$A_{nm} = \frac{d_m}{d_n} 8\pi h c \nu_{nm}^3 B_{mn}$$
(2.54)

Because the absorption coefficient k_{ν} varies across an absorption line (or band), the light absorbed by the transition n - m for a small ΔL is given by [16]

$$I_{abs.}^{nm} = \int (I_{\nu}^{0} - I_{\nu}) d\nu = I_{\nu}^{0} \Delta L \int k_{\nu} d\nu$$
(2.55)

where the incident intensity I_{ν}^{0} is assumed to be constant over the width of the line or band. Substituting Eqn.(2.47) into the above equation and taking I_{0}^{nm} as I_{ν}^{0} we obtain for the integrated absorption coefficient

$$\int k_{\nu} d\nu = N_m B_{mn} h \nu_{nm} \tag{2.56}$$

2.9.3 The relation between the Einstein coefficient and transition probabilities

From Herzberg [15], the transition probability $B_{mn,v''v',J''J'}$ for absorption is given by

$$B_{mn,v''v',J''J'} = \frac{8\pi^3}{3h^2c} |\mathbf{R}_{e}^{nm}|^2 |\mathbf{R}_{vib.}^{v'v''}|^2 \frac{\sum_{M'M''} |\mathbf{R}_{rot.}^{JJ''}|^2}{2J''+1}$$
(2.57)

where the total matrix element R^{nm} for the system is

$$\mathbf{R}^{\mathbf{n}\mathbf{m}} = \mathbf{R}_{\mathbf{e}}^{\mathbf{n}\mathbf{m}} \mathbf{R}_{\mathbf{v}\mathbf{i}\mathbf{b}.}^{\mathbf{v}'\mathbf{v}''} \mathbf{R}_{\mathbf{rot}.}^{\mathbf{J}'\mathbf{J}''}$$
(2.58)

and the summation is over all values of the magnetic quantum numbers M' and M'' of upper and lower states.

The electronic transition probability is given by

$$|\mathbf{R}_{\mathbf{e}}^{\mathbf{mn}}|^{2} = |\int \psi_{\mathbf{e}'}^{*} \mathbf{M}_{\mathbf{e}} \psi_{\mathbf{e}''} \mathbf{d} \tau_{\mathbf{e}}|^{2}$$
(2.59)

where M_e is the electric moment which only depends on the electrons.

The vibrational transition probability is given by

$$|\mathbf{R}_{\mathbf{v}\mathbf{i}\mathbf{b}}^{\mathbf{v}'\mathbf{v}''}|^{2} = |\int \psi_{\mathbf{v}'}^{*}\psi_{\mathbf{v}''} d\mathbf{r}|^{2} = |\langle \mathbf{v}'|\mathbf{v}''\rangle|^{2}$$
(2.60)

The $|\langle v'|v''\rangle|^2$ is the well-known Franck-Condon Factor (F.C.F.) for the transition v' - v'' (see appendix B). Usually people use the symbol

$$q_{v',v''} = |\langle v'|v''\rangle|^2 \tag{2.61}$$

The rotational transition probability

For rotational transition probability we have to consider three directions, x, y, and z, in space coordinate system. For example, the transition probability in the z direction is

$$|\mathbf{R}_{\text{rot.}}^{\mathbf{J}'\mathbf{J}''}|^{2} = |\int \sin\theta \cos\theta \psi_{\mathbf{r}'}^{*} \psi_{\mathbf{r}''} d\theta d\phi|^{2}$$
(2.62)

In appendix A, we have shown the derivation of these three equations in detail. The F.C.F. and rotational part are given in appendix B.

We used both theory and experiment to obtain the electronic transition probability. $|\mathbf{R}_{e}|^{2}$ is a more fundamental measure of the transition probability. From Eqn.(2.56) and (2.57), we can get

$$|\mathbf{R}_{e}|^{2} = \frac{3h^{2}c \int k_{\nu}d\nu}{8\pi^{3}N_{mv''J''}h\nu_{nm,v'v''J'J''}|\mathbf{R}_{vib}^{v''v'}|^{2}\frac{\Sigma_{M'M''|\mathbf{R}_{rot}^{J''J'}|^{2}}}{2J''+1}}$$
(2.63)

where ν_{nm} is in wavenumber units.

2.9.4 The radiative lifetime of $B^3 \prod_{0^+ u}$ state of Br_2

The radiative lifetime of an molecule in a definite excited electronic state n can be calculated theoretically. We have in general,

$$\tau_{rad.} = \frac{1}{\sum_{m} A_{nm}} \tag{2.64}$$

The radiative lifetime of rovibronic levels in the $B^3\Pi_{0^u}$ state of molecular bromine is:

$$\tau_{rad.} = \frac{1}{\sum_{v'',J''} A_{v'v'',J'J''}}$$
(2.65)

where $A_{v',v'',J',J''}$ is the Einstein coefficient for spontaneous emission from the state J'which is in the v' state into the state J'' of v'' state. τ_{rad} varies with v' and this variation can be substantial over the whole vibrational energy range of an electronically-excited manifold.

In order to compare the magnitudes of τ_{rad} obtained for different v' levels in various investigations, it is desirable first to transform from τ_R values into the corresponding electronic transition probability $|\mathbf{R}_{\mathbf{e}}|^2$. In the Born-Oppenheimer approximation, $|\mathbf{R}_{\mathbf{e}}|^2$ is a strictly electronic transition probability and the vibrational and rotational-energy dependences of τ_{rad} are factored out by the transformation from τ_{rad} to $|\mathbf{R}_{\mathbf{e}}|^2$. The expression of τ_{rad} is as follows [8],

$$\tau_{rad.} = \frac{1}{\sum_{\nu''} A_{\nu',\nu''}} = \frac{3h \cdot d_n}{64\pi^4 \cdot d_m \sum_{\nu''} q_{\nu'\nu''} \nu^3 |\mathbf{R}_e|^2 \frac{\sum_{\mathbf{J}''} |\mathbf{R}_{rot}^{\mathbf{J}'\mathbf{J}''}|^2}{2\mathbf{J}''+1}}$$
(2.66)

From the absorption spectrum we can get the value of $|\mathbf{R}_e|^2$ by using Eqn.(2.63). Also we know that $\frac{d_m}{d_n} = 1$ in our case and the rotation part of Eqn.(2.66) when the P and R branches are considered together is equal to 1 (see appendix B), so we finally can obtain the Eqn.(2.67),

$$\tau_{rad.} = \frac{3h}{64\pi^4 \mid \mathbf{R_e} \mid^2 \sum_{\mathbf{v}''} \mathbf{q}_{\mathbf{v}'\mathbf{v}''} \nu^3}$$
(2.67)

In our case, it is possible to calculate a $\tau_{rad.}$ value for v' = 14, 15, 17, 18, 19 by using the $|\mathbf{R}_e|^2$ values obtained from theory and experiment.

2.9.5 The predissociation of Br_2 in the $B^3\Pi_{o^+u}$ state

From Fig. 1.1 one can see that there is a crossing point between the excited state $B^3\Pi_{o^+u}$ and the unbound state ${}^{1}\Pi_{1u}$. The vibrational energy levels of the the $B^3\Pi_{o^+u}$ near the crossing point have a higher probability of producing a non-radiative transition to the ${}^{1}\Pi_{1u}$ state; then the atoms will separate, the entire process being called predissociation.

The density of molecular bromine in the excited states, N^* , changing with time, can be written as [4]

$$\frac{dN^*}{dt} = B_{NN^*} \cdot I_{laser} \cdot (N - N^*) - (\Gamma_R + \Gamma_P + \Gamma_C) \cdot N^*$$
(2.68)

Where

 $B_{NN^{\bullet}} \cdot I_{laser}$: the laser excitation rate N: the density of Br_2 in the ground state Γ_R : the radiative decay rate $(\Gamma_R = \frac{1}{\tau_{rad}})$ Γ_P : the predissociation rate Γ_C : the collisional decay rate

Taking
$$\frac{dN^*}{dt} = 0$$
, we can get

$$N^* = \frac{B_{NN^*} I_{laser} N}{B_{NN^*} I_{laser} + \Gamma_R + \Gamma_P + \Gamma_C}$$
(2.69)

For iodine,

$$\Gamma_P = k_{\nu'} J'(J'+1) + a_{\nu'}^2 \tag{2.70}$$

One can model bromine in the same way.

The fluoresence intensity, I_F , is proportional to N^* . So, one knows that $\frac{1}{I_F} \propto J'(J'+1)$

One can draw a graph of $\frac{1}{I_F}$ vs. J'(J'+1) to measure the predissociation rate, Γ_P .
Chapter 3

Experimental apparatus and spectrum

In this chapter we describe the apparatus used to measure the radiative lifetime of the $B^3\Pi_{0+u}$ state of Br_2 molecule.

3.1 Preparation of the sample cell

A pyrex sample cell, of length 14.09 ± 0.05 cm, was continuously heated and evacuated to a background pressure of 3.8×10^{-6} torr. Part of the vacuum system was also cooled with liquid nitrogen. The sample cell was filled with dry Br_2 vapour, and a mixed methanol and liquid nitrogen bath was used to cool the liquid bromine to a temperature of $-(32.5 \pm 0.2)^{\circ}$ C. This environment was maintained for about ten mintues to allow bromine vapour to diffuse into the sample cell. The molecules were contained in T-shape pyrex sample cell, filled with isotopic bromine (79-79), (79-81), (81-81) whose relative abundances were 1.0216:2.0:0.9784, respectively. The sample cell was then sealed and removed from the vacuum system. Under these conditions the Br_2 pressure inside the sample cell was 3.6 ± 0.2 torr, which was sufficient to obtain a peak absorption of about 30% for the rotational lines of bromine molecule under study. For stronger absorption, we could increase the pressure of the sample cell. Then, the collisions probability among bromine molecules will increase; this is a method of broadening the absorption line.

Using the same techniques we can prepare an iodine sample cell. The spectrum of the B - X system of I_2 has been studied successfully and extensively by various research groups. Therefore we can use a I_2 sample cell to get the fluorescence spectrum of I_2 and



Figure 3.5: Experimental arrangment. M_1, M_2 : total reflectional mirror; S: splitter; F_1, F_2, F_3, F_4, F_5 : filter; PM: photomultiplier; PD: photodiode; MC: monochrameter; PC: photo counter; TLR1, TLR2: two line recorder

then we can use the I_2 fluorescence spectrum obtained by [21] to calibrate the spectrum of Br_2 .

3.2 Experimental set-up

A block diagram of the experimental arrangement used for measuring the lifetime of the $B^3\Pi_{0+u}$ state of Br_2 is shown in figure 3.5.

A Coherent CR-15 SG argon ion laser tuned to the 5145 Å line, and an output power of 6W was used to pump a Cohererent CR-699-21 scanning dye laser. The dye laser, using Rhodamine 6G dye, gave a peak output power of 800mW. This dye laser was connected to an electronic scanning system capable of tuning the laser at different scan speeds. In our experiment we tuned the dye laser from approximately 17464 cm^{-1} to 17480 cm^{-1} , with the electronic scanner set to scan a 30GHz ($\simeq 1cm^{-1}$) region per scan period of 5 minutes. This allowed us to excite the specific rovibrational levels (v', J')of $Br_2B^3\prod_{0+u}$ state from the $X^1\Sigma_{0+g}$ ground state. The dye laser beam was split into two by a beam splitter S. One of the beams was passed through the Br_2 sample cell while the other was directed through an I_2 sample cell. Less than 1 mW intensity of the beam was going into the Br_2 sample cell. The beam area $3.14mm^2$. The spectrum of iodine, which has already been studied extensively by other research groups, served as a reference for calibration. Both, absorption and fluorescence spectra were recorded for Br_2 , whereas, only the fluoresence spectrum was recorded for I_2 . A photodiode (HP PIN 5082-4220) and two photomultipliers (EMI 9558 B, EMI 9558 QB) were used as detectors for absorption and fluorescence, respectively. Several glass color filters were used in the path of the dye laser beam to reduce the intensity of the beam before it entered the sample cells and the detectors, in order to avoid saturation. Two double line recorders (PM 8252A) were used for recording purpose. One was used to record simultaneously the fluorescence spectra of Br_2 and I_2 with the other used to trace the absorption spectrum of Br_2 and the fluorescence spectrum of I_2 . A monochrometer was used as an aid to obtain the accurate frequencies which were needed during the experiment.

3.3 Absorption spectrum of molecular bromine







Chapter 4

Data Analysis

4.1 Assignment of Br_2 lines

An arbitrary zero on the horizontal axis of the spectrum was established. The distance to each I_2 fluoresence peak was measured and the frequency ν_{I_2} in cm^{-1} was plotted against the distance d in cm. From this graph we can find the slope, a, and the intercept b on each scan of the laser. If ν vs. d is linear then an average dispersion can be taken and we can use this dispersion a to find the frequency ν_{Br_2} on each Br_2 line which is

$$\nu_{Br_2} = ad' + b' \tag{4.71}$$

where d' is the distance from an arbitrary zero on the horizontal axis to each Br_2 absorption line, and b' is the intercept for Br_2 lines on each scan of dye laser, that is

$$b' = b + 0.428a \tag{4.72}$$

where the number 0.428 is the separation distance between I_2 and Br_2 lines. (Because the two line recorder (PM 8252A) has a fixed separation between the two pens)

Using Eqn.(4.71) we obtained the frequencies of all the absorption lines from the experimental data. Then all these frequencies were compared with theoretical ones calculated using Eqns.(4.73) and (4.74). The difference between the two values should vary smoothly and in the same direction.

Here we gave a example, $^{(79,79)}Br_2$, band 15' - 1" in table 4.2

line no.	R(J),P(J)	$\mu(cm^{-1})$	$\nu(cm^{-1})$	$\nu - \mu$
195	R(58)	17478.7155	17478.691	-0.025
153	R(59)	17475.1262	17475.099	-0.027
102	R(60)	17471.4733	17471.445	-0.028
50	R(61)	17467.7568	17467.732	-0.025
188	P(55)	17478.1605	17478.132	-0.029
149	P(56)	17474.5676	17474.530	-0.038
92	P(57)	17470.9113	17470.882	-0.029
42	P(58)	17467.1916	17467.161	-0.031

Table 4.2: Obtaining the band $15' \cdot 1''$ of $(^{79,81})Br_2$

In the table 4.2 μ and ν are theoretical and experimental frequencies, respectively.

4.2 Calculating the Br_2 transition energies

The transition energies for $^{79,79}Br_2$ and $^{81,81}Br_2$ can be calculated by using the following formula:

$$E_{X-state} = T_{v''} + B_{v''}(J''(J''+1)) - D_{v''}(J''(J''+1))^2 + H_{v''}(J''(J''+1))^3$$
(4.73)

$$E_{B-state} = T_{v'} + B_{v'}(J'(J'+1)) - D_{v'}(J'(J'+1))^2 + H_{v'}(J'(J'+1))^3$$
(4.74)

Where

 $T_{v} = T_{v,J=0}$ is the vibrational term value relative to $X^{1}\Sigma_{0+g}$ state.

The energy is measured in wave number (cm^{-1}) units and the $X \to B$ transitions for the P and R branches in $(^{79,79})Br_2$ and $(^{81,81})Br_2$ were calculated. The constants, T_v, B_v, D_v , and H_v were obtained from [2]. For $(^{79,81})Br_2$, the transition energies were calculated by averaging the results of $(^{79,79})Br_2$ and $(^{81,81})Br_2$.

Chapter 4. Data Analysis

4.3 The absorption band strengths

From Eqn.(2.41),(2.42) and (2.43) we can obtain the number of bromine molecules in each rotational state of each vibrational state. (The probability of being in a vibrational state is estimated by summation from v = 0 to v = 10. The probability of being in a rotational state is integrated from J = 0 to $J = \infty$ for both R branch and P branch). At room temperature, the B-state levels are sparsely populated so only the X-state levels need to be calculated. From calculating the partition function $\frac{e^{-\beta E_v''}}{\sum_{v''} e^{-\beta E_v''}}$, one can assume that most bromine molecules occupy the states v'' = 0, 1 and 2 only.

From Eqn.(2.38), the Boltzmann distribution law for rotational levels is now [22]

$$N_{J''} \cong N_0(2J''+1)e^{-\beta B_v J''(J''+1)}$$
(4.75)

The particle density will not be affected by nuclear spin.

By differentiation Eqn.(4.75) it can be shown that the quantum number of the state with the greatest population is

$$J_{max} = \sqrt{2\beta B_v} - \frac{1}{2}$$
 (4.76)

Taking the value of $B_v \cong 0.08 cm^{-1}$ [2], we can obtain

$$J_{max} \cong 35 \tag{4.77}$$

In the table 4.4 we gave the part of particle densities on para and ortho states of v'' = 1. The constants used for calculating the particle density are shown in table 4.3 [2].

Franck-Condon factors gives an approximation to the relative intensities. A chart of F.C.F.'s for $0 \le v' \le 48$ to $0 \le v'' \le 14$ is given in [12]. From that chart we can see that

State	Mol. Const.	$^{(79,79)}Br_2$	$^{(81,81)}Br_2$	$^{(79,81)}Br_2$
$1\Sigma_{0+u}$	ω_e	325.3213	321.29	323.3056
	$\omega_e x_e$	1.07742	1.064	1.0707
$v'' \leq 10$	$10^3 \omega_e y_e$	-2.29798	-2.2134	-2.2556
v'' = 1	$10^{2}B_{v}$	8.1627	7.9618	8.0622
	$10^{8}D_{v}$	2.108	2.005	2.011
	$-10^{13}H_{v}$	2.89	0.0	1.445
v'' = 2	$10^2 B_v$	8.1304	7.9306	8.0305
	$10^{8}D_{v}$	2.116	2.013	2.0645
	$-10^{13}H_{v}$	2.88	0.0	1.44

Table 4.3: Molecular constants (cm^{-1}) for the ${}^{1}\Sigma_{0+u}$ state

Table 4.4: A part of the particle densities (in cm^{-3}) on v'' = 1, ${}^{(79,79)}Br_2$

v''	P,R(J = even)	Density	P,R(J = odd)	Density
1	0	1.4624×10^{12}	1	$7.3060 imes 10^{12}$
1	2	7.2945×1012	3	$1.6980 imes 10^{13}$
1	4	$1.3058 imes 10^{13}$	5	2.6494×10^{13}
1	6	1.8698×10^{13}	7	$3.5758 imes10^{13}$
1	8	2.4162×10^{13}	9	4.4689×10^{13}
1	10	2.9402×10^{13}	11	5.3206×10^{13}
1	12	3.4372×10^{13}	13	6.1237×10^{13}
1	14	3.9029×10^{13}	15	$6.8715 imes 10^{13}$
1	16	4.3337×10^{13}	17	$7.5583 imes 10^{13}$
1	18	4.7264×10^{13}	19	$8.1793 imes 10^{13}$
1	20	$5.0783 imes 10^{13}$	21	$8.7305 imes 10^{13}$
1	22	5.3874×10^{13}	23	9.2091×10^{13}
1	24	5.6523×10^{13}	25	9.6132×10^{13}
1	26	5.8721×10^{13}	27	9.9417×10^{13}
1	28	6.0466×10^{13}	29	$1.0195 imes 10^{14}$
1	30	6.1761×10^{13}	31	1.0374×10^{14}
1	32	6.2614×10^{13}	33	1.0480×10^{14}
1	34	6.3039×10^{13}	35	$1.0516 imes 10^{14}$
1	36	6.3054×10^{13}	37	1.0486×10^{14}
1	38	6.2681×10^{13}	39	1.0393×10^{14}
1	40	6.1947×10^{13}	41	1.0242×10^{14}

transitions 17' - 2'' should be very strong. Transitions 14' - 1'', 23' - 3'' will be strong but not as strong as the 17' - 2'' transition. The Franck-Condon factors used for our calculation are listed in appendix B.

The distribution of bromine isotopes also affects the transition intensity. Since the $(^{79,81})Br_2$ are twice as numerous as $(^{79,79})Br_2$ and $(^{81,81})Br_2$, $(^{79,81})Br_2$ transitions will have intensities twice as big as similar transitions in $(^{79,79})Br_2$ and $(^{81,81})Br_2$.

4.4 Calculating the integrated absorption coefficient

From Eqn (2.63) we knew that we have to obtain the integrated absorption coefficient $\int k_{\nu}d\nu$ in order to obtain the experimental measure of the total strength of an electronic transition. We used several steps to obtain the integrated area, $\int k_{\nu}d\nu$.

First, the coordinates of the lower left and upper right corners of each Br_2 absorption line were calculated and fixed. Then we used a digitizer to obtain a set of data, x and y coordinates. The abscissa x represented ν in cm^{-1} and the ordinate y represented the intensity I_{ν} . The program VDIGIT (provided by the Computing Center at UBC) run from a VICTOR9000 terminal was used to create data files. Moving the cursor along the absorption line one can obtained a set of data, i.e. a set of ν and I_{ν} values. Since the input intensity I_0 varies with time, a line between A and B was choosen to represent an approximate I_0 (see figure 4.7).

If several absorption lines overlap each other (see figure 4.8), we digitized them together.

Second, one can obtain a series of k_{ν} values by using Eqn.(2.46), and then one can obtain a set of ν and k_{ν} values for each absorption line. By using those ν and k_{ν} values one can obtain the values of $\int k_{\nu}d\nu$ using a computer.

Third, some apparently single lines were checked to see if they were, in fact, overlapped



or not. We used two different methods to get two areas, using trapezoidal rule to get area A_1 and assuming k_{ν} as a Gaussian distrubution to get area A_2 . Then we compared the two areas. If the area A_2 was same as the area A_1 (A_2 may be somewhat larger than A_1 because the Gaussian distrubution has long wings which may have been neglected by the first method), the line was not overlapped. If the area A_2 was much larger than A_1 , the line was overlapped.

We also checked the half width, $\Delta \nu$, for each absorption line. If the line is overlapped, the measured half width will be wider than the Gaussian width. At the half-height of the band, we have

$$k_{\frac{1}{2}} = \frac{k_{max} - k_{min}}{2} = -\frac{1}{2L} \ln \frac{I_{min}}{I_0}$$
(4.78)

From Fig.2.4 we can find





$$\Delta \nu = \nu_2 - \nu_1 \tag{4.79}$$

Independently measurements of $\int k_{\nu} d\nu$ agreed to within $\pm 3.0\%$ except for the weakest lines where the difference approached $\pm 6.0\%$.

Chapter 5

The Results and Discussions

After analysing the spectrum, we obtained data for the following bands:

14' - 1''	$(79,79)Br_2$	$1 \le J'' \le 19$
15' - 1''	$^{(79,79)}Br_2$	$57 \leq J^{''} \leq 63$
17' - 2''	$^{(79,79)}Br_2$	$0 \leq J^{''} \leq 21$
18' - 2''	$^{(79,79)}Br_2$	$53 \leq J'' \leq 59$
19' - 2''	$^{(79,79)}Br_2$	$74 \leq J'' \leq 78$
14' - 1''	$^{(79,81)}Br_2$	$1 \leq J^{''} \leq 11$
15' - 1''	$^{(79,81)}Br_2$	$55 \leq J'' \leq 61$
17' - 2''	$^{(79,81)}Br_2$	$0 \leq J^{''} \leq 16$
18' - 2''	$^{(79,81)}Br_2$	$51 \leq J'' \leq 57$
19' - 2''	$^{(79,81)}Br_2$	$73 \leq J'' \leq 78$
15' - 1''	$^{(81,81)}Br_2$	$53 \leq J'' \leq 60$
17'-2''	$^{(81,81)}Br_2$	$0 \leq J^{''} \leq 8$
18' - 2''	$^{(81,81)}Br_2$	$50 \le J'' \le 56$

By using Eqn.(2.63) we estimated values for the electronic transition probability $|\mathbf{R}_{e}|^{2}$ for each band. Here we give a detailed sample calculation that shows how one goes from $\int k_{\nu} d\nu$ to $|R_{e}|^{2}$ with all factors explicitly given.

From Eqn.(2.63), one can obtain Eqn.(5.80):

Chapter 5. The Results and Discussions

$$|R_{e}|^{2} = \frac{\int k_{\nu} d\nu}{N_{mv''J''}\nu_{nm,v''J''}(\frac{8\pi^{3}}{3hc}) |R_{vib.}^{v'v''}|^{2} \frac{\sum_{M'M''}|R_{rot.}^{j'J''}|^{2}}{2J''+1}}$$
(5.80)

For P(11) of band 14' - 1'' of $(79,79)Br_2$, the $|R_e|^2$ value is given by

$$|R_e|^2 = \frac{2.3694 \times 10^{-4}}{5.3206 \times 10^{13} \cdot 17469.499 \cdot (4.1623 \times 10^{17}) \cdot 0.00509 \cdot \frac{11}{23}} = 2.52 \times 10^{-37} (erg \cdot cm^3)$$
(5.81)

For the overlapped lines, a $\int k_{\nu} d\nu$ over the total area has been used. For example, the overlap of the three lines, P(54): 18' - 2'' of ${}^{(79,79)}Br_2$; R(8): 14' - 1'' of ${}^{(79,79)}Br_2$ and R(77): 19' - 2'' of ${}^{(79,79)}Br_2$, Eqn.(5.80) can be written as:

$$|R_{e}|^{2} = \frac{\int k_{\nu_{1}} d\nu + \int k_{\nu_{2}} d\nu + \int k_{\nu_{3}} d\nu}{C_{1} + C_{2} + C_{3}}$$
(5.82)

where C_1, C_2 and C_3 are the denominators in Eqn.(5.80) for P(54), R(8) and R(77), respectively.

The results of $|R_e|^2$ for the band 14' - 1'' of $(^{79,79})Br_2$ is shown in table 5.5. The results for all other measured lines are showed in appendix D.

Taking the average of all values of $|\mathbf{R}_{e}|^{2}$ from table 5.5 we obtained Eqn.(5.83), the average value and standard diviation of the electronic transition probability.

$$|\mathbf{R}_{e}|^{2} = (2.54 \pm 0.28) \times 10^{-37} (\mathrm{erg} \cdot \mathrm{cm}^{3})$$
 (5.83)

Because we only obtained the small part of spectrum of molecular bromine from our experiment, some of the lines in the spectrum were overlapped with some other lines which cannot be identified. So, for those lines we cannot obtain better values of $|\mathbf{R}_{e}|^{2}$ in the band. Therefore when we calculate the values of $|\mathbf{R}_{e}|^{2}$, we did not take into

P(J)	$\nu \ cm^{-1}$	N _{mv"J"}	$\int k_{\nu} d\nu \ cm^{-2}$	$ \mathbf{R}_{\mathbf{e}} ^2$	$\Delta \nu \ cm^{-1}$
P(1)	17474.510	7.3066×10^{12}	2.3747×10^{-4}	2.82×10^{-37}	2.30×10^{-2}
P(4)	17473.655	1.3058×10^{13}	$3.8263 imes 10^{-4}$	$2.11 imes 10^{-37}$	$2.07 imes 10^{-2}$
P(6)	17472.770	1.8698×10^{13}	0.7201×10^{-4}	$2.25 imes10^{-37}$	1.46×10^{-2}
P(7)	17472.237	3.5758×10^{13}	1.8767×10^{-4}	2.85×10^{-37}	2.01×10^{-2}
P(8)	17471.645	2.4162×10^{13}	1.0942×10^{-4}	2.60×10^{-37}	$2.25 imes 10^{-2}$
P(9)	17470.987	4.4689×10^{13}	1.8651×10^{-4}	2.37×10^{-37}	$2.27 imes10^{-2}$
P(11)	17469.499	$5.3206 imes 10^{13}$	2.3694×10^{-4}	$2.52 imes10^{-37}$	2.12×10^{-2}
P(12)	17468.656	$3.4372 imes 10^{13}$	1.5725×10^{-4}	2.58×10^{-37}	2.17×10^{-2}
P(13)	17467.756	$6.1237 imes 10^{14}$	1.5741×10^{-4}	2.27×10^{-37}	$2.07 imes 10^{-2}$
P(14)	17466.796	$3.9029 imes 10^{13}$	$3.0943 imes10^{-4}$	2.89×10^{-37}	$2.39 imes10^{-2}$
P(15)	17465.771	6.8715×10^{13}	4.5367×10^{-4}	2.06×10^{-37}	$2.47 imes 10^{-2}$
P(16)	17464.684	4.3337×10^{13}	1.9524×10^{-4}	2.51×10^{-37}	$2.05 imes 10^{-2}$
R(J)	$\nu \ cm^{-1}$	N _{mv''J''}	$\int k_{\nu} d\nu \ cm^{-2}$	$ \mathbf{R}_{\mathbf{e}} ^2$	$\Delta \nu \ cm^{-1}$
R(4)	17474.546	1.3058×10^{13}	10.4649×10^{-4}	2.82×10^{-37}	2.78×10^{-2}
R(5)	17474.359	2.6494×10^{13}	1.5968×10^{-4}	2.98×10^{-37}	$2.21 imes 10^{-2}$
R(7)	17473.761	3.5758×10^{13}	2.5813×10^{-4}	2.12×10^{-37}	1.94×10^{-2}
R(8)	17473.368	2.4162×10^{13}	1.5832×10^{-4}	3.00×10^{-37}	2.18×10^{-2}
R(9)	17472.926	4.4689×10^{13}	3.8333×10^{-4}	2.38×10^{-37}	2.17×10^{-2}
R(11)	17471.841	5.3206×10^{13}	2.3285×10^{-4}	2.27×10^{-37}	1.94×10^{-2}
R(12)	17471.199	3.4372×10^{13}	1.6754×10^{-4}	2.53×10^{-37}	2.42×10^{-2}
R(13)	17470.501	6.1237×10^{14}	2.6743×10^{-4}	2.28×10^{-37}	1.96×10^{-2}
R(14)	17469.749	3.9029×10^{13}	1.4127×10^{-4}	2.22×10^{-37}	1.88×10^{-2}
R(15)	17468.925	6.8715×10^{14}	3.0055×10^{-4}	2.78×10^{-37}	2.03×10^{-2}
R(16)	17468.042	4.3337×10^{13}	2.7618×10^{-4}	2.65×10^{-37}	2.53×10^{-2}
R(17)	17467.095	7.5583×10^{14}	3.6602×10^{-4}	2.54×10^{-37}	2.09×10^{-2}
R(18)	17466.096	4.7264×10^{13}	7.0570×10^{-4}	2.65×10^{-37}	2.25×10^{-2}
R(19)	17465.032	8.1793×10^{14}	4.6456×10^{-4}	2.29×10^{-37}	2.46×10^{-2}

Table 5.5: $|\mathbf{R}_{\mathbf{e}}|^2$ values for 14' - 1'' of ${}^{(79,79)}Br_2$

P,R(J)	$\nu \ cm^{-1}$	$N_{mv''J''}$	$\int k_{\nu} d\nu \ cm^{-2}$	$ \mathbf{R}_{\mathbf{e}} ^2$	$\Delta \nu \ cm^{-1}$
P(2)	17474.273	$7.2945 imes 10^{12}$	1.0087×10^{-4}	9.34×10^{-37}	2.36×10^{-2}
P(3)	17473.990	1.6980×10^{13}	$1.0253 imes 10^{-4}$	3.81×10^{-37}	2.58×10^{-2}
P(5)	17473.234	$2.6494 imes 10^{13}$	1.7751×10^{-4}	3.98×10^{-37}	$2.80 imes 10^{-2}$
P(10)	17470.271	2.9402×10^{13}	2.9105×10^{-4}	5.62×10^{-37}	$0.83 imes 10^{-2}$
R(6)	17474.090	1.8689×10^{14}	1.2210×10^{-4}	3.28×10^{-37}	2.47×10^{-72}
R(10)	17472.412	2.9402×10^{13}	2.4368×10^{-4}	4.27×10^{-37}	$2.09 imes 10^{-2}$

Table 5.6: $|R_e|^2$ value for overlapped lines

account those lines, for instance, in band 14' - 1'' of $^{(79,79)}Br_2$, the value of $|\mathbf{R}_e|^2$ of those lines overlapped with the line cannot be identified are showed in table 5.6.

After calculating the electronic transition probability for all bands which we have analysed, we obtained the table 5.7. The mean value of $|\mathbf{R}_{e}|^{2}$ is $(2.52 \pm 0.25) \times 10^{-37} (erg \cdot cm^{3})$

The average radiative lifetime, τ_{rad} , for each vibrational state v' was obtained by using Eqn.(2.67) and the results are summarized in table 5.8 for the region 17464 cm^{-1} to 17480 cm^{-1} . In the ground electronic state there are around 137 vibrational levels v''. F.C.F. were only available to evaluate $\Sigma q_{v'v''} v^3$ up to v'' = 10 for v' = 14, 15, 17, 18, 19 for ${}^{(79,79)}Br_2$ and ${}^{(81,81)}Br_2$; v'' = 20 for v' = 14, 15, 17; v'' = 12 for v' = 18, 19 for ${}^{(79,81)}Br_2$ (see appendix E). The frequency of each observed line was used during the calculation of τ_{rad} .

The results of radiative lifetime measurements obtained by Clyne [8] are showed in table 5.9 where the calculated τ_{rad} values are based on Le Roy's work [24].

Le Roy used radial wavefunction to calculate diatomic molecule absorption coefficients. In Clyne's work, τ_{rad} were obtained from measurements of collision-free lifetimes τ_0 of Br_2 (B) excited molecules. The collision-free lifetime is given by Eqn.(5.84).

Band	Average $ R_e ^2$	Standard diviation	Error
$(14' - 1'')^{79-79}$	2.54×10^{-37}	0.28×10^{-37}	11%
$(15' - 1'')^{79-79}$	$2.43 imes10^{-37}$.	0.18×10^{-37}	7%
$(17'-2'')^{79-79}$	$2.58 imes 10^{-37}$	0.24×10^{-37}	9%
$(18'-2'')^{79-79}$	2.62×10^{-37}	0.25×10^{-37} .	10%
$(19' - 2'')^{79-79}$	2.66×10^{-37}	0.27×10^{-37}	10%
$(14' - 1'')^{79-81}$	2.67×10^{-37}	0.23×10^{-37}	9%
$(15' - 1'')^{79-81}$	$2.45 imes 10^{-37}$	0.21×10^{-37}	9%
$(17'-2'')^{79-81}$	2.58×10^{-37}	0.20×10^{-37}	8%
$(18' - 2'')^{79-81}$	2.48×10^{-37}	0.27×10^{-37}	11%
$(19'-2'')^{79-81}$	$2.47 imes 10^{-37}$	0.27×10^{-37}	11%
$(15' - 1'')^{81-81}$	2.40×10^{-37}	0.24×10^{-37}	10%
$(17' - 2'')^{81-81}$	2.47×10^{-37}	0.32×10^{-37}	13%
$(18' - 2'')^{81-81}$	2.47×10^{-37}	0.31×10^{-37}	13%

Table 5.7: Mean $\mid \mathbf{R_e} \mid^2$ for all identified bands

Table 5.8: $\tau_{rad.}$ for the excited state v'

Isotope Br_2	Excited state v'	Average $\tau_{rad.}$	Error
Br_2 (79-79)	14	17.1 μs	1.9 µs
Br_2 (79-81)	14	9.8 μs	$1.1 \ \mu s$
Br_2 (79-79)	17	22.2 μs	$2.4 \ \mu s$
Br_2 (79-81)	17	17.5 μs	1.9 μs
Br_2 (81-81)	17	23.6 μs	$2.6 \ \mu s$
Br_2 (79-79)	18	24.3 μs	$2.7 \ \mu s$
Br_2 (79,81)	18	$22.0 \ \mu s$	$2.4 \ \mu s$
Br_2 (81-81)	18	$24.5 \ \mu s$	$2.7 \ \mu s$
Br_2 (79-79)	19	$24.5 \ \mu s$	$2.7 \ \mu s$
Br_2 (79-81)	19	23.4 μs	$2.6 \ \mu s$
Br_2 (79-79)	15	18.0 μs	$2.0 \ \mu s$
Br_2 (79-81)	15	11.0 μs	$1.2 \ \mu s$
Br_2 (81-81)	15	18.4 μs	$2.0 \ \mu s$

v'	Mean $ R_e ^2$	$ au_{rad.} \ \mu s \ (cal.)$	$ au_{rad.} \ \mu s \ (obs.)$	Error
11	2.04×10^{-37}	15.8	5.1	+1.5
•				-0.9
14	1.97×10^{-37}	15.9	7.4	+1.5
				-1.0
19	1.87×10^{-37}	20.8	11.3	+2.0
				-1.5
20	1.85×10^{-37}	21.9	6.1	+2.5
				-1.9

Table 5.9: The $\tau_{rad.}$ of $^{(79,79)}Br_2$ obtained by Clyen

$$\frac{1}{\tau_0} = \frac{1}{\tau_{rad}} + k_{v'} J' (J' + 1)$$
(5.84)

where $k_{v'}$ is a constant dependent on v'. For such a case, a plot of $\frac{1}{\tau_0}$ vs. J'(J'+1) has been given and the intercept equal to $\frac{1}{\tau_{rad}}$. From table 5.9 one can note that the calculated values are two to three times larger than the observed one, while our results (see table 5.8) are closer to Le Roy's estimates.

The values of $\tau_{rad.}$ are very sensitive to the values of $\Sigma q_{v'v''} v^3$ used in Eqn.(2.67). As more terms are added to the sum, the smaller $\tau_{rad.}$ becomes. Table 5.10 shows the difference among the values of $\Sigma q_{v'v''} v^3$ as more terms are added for the case of the 17' - 2'' band of $(^{79,81})Br_2$. If we can obtain all the F.C.F. and sum over them, the value of $\Sigma q_{v'v''}$ should equal to 1 and then Eqn.(2.67) approximately can be written as Eqn.(5.85).

$$\tau_{rad.} = \frac{3h}{64\pi^4 \mid \mathbf{R_e} \mid^2 \nu^3} \tag{5.85}$$

the radiative lifetime τ_{rad} has been given in table 5.11 by using Eqn.(5.85).

Terms of F.C.F.	$\Sigma q_{v'v''} \nu^3$	Terms of F.C.F.	$\Sigma q_{\nu'\nu''} \nu^3$
3	18.707×10^{10}	13	58.959×10^{10}
4	32.259×10^{10}	14	62.480×10^{10}
5	36.552×10^{10}	15	62.625×10^{10}
6	36.873×10^{10}	16	64.518×10^{10}
7	43.126×10^{10}	17	67.299×10^{10}
8	48.417×10^{10}	18	$67.395 imes 10^{10}$
9	48.466×10^{10}	19	68.991×10^{10}
10	51.961×10^{10}	20	71.198×10^{10}
11 .	56.377×10^{10}	21	71.248×10^{10}
12	56.519×10^{10}		

Table 5.10: The values of $\sum q_{\nu'\nu''}\nu^3$

However, now there is a difficulty in choosing a suitable value for ν . We used the frequency of each observed line to calculate $\Sigma q_{v'v''}\nu^3$. One can chose the frequency which corresponds to the strongest F.C.F.

Based on Le Roy's study, Clyne obtained the values of $|R_e|^2$ from Eqn.(5.86).

$$|R_e|^2 = [0.3905 + 0.265(r - 2.3)]^2$$
(5.86)

the mean $|R_e|^2$ were given in table 5.9. From table 5.8 one can also see that the electronic transition probability, $|R_e|^2$, are in close agreement with Clyne's work.

In order to see the spontaneous predissociation rate, Γ_{ρ} , of $Br_2 \ B^3 \Pi_{o+u}$ state one can draw a graph $\frac{1}{I_F}$ vs. J'(J'+1). The graphs shown in figure 5.9 does not follow Eqn.(2.70). From reference [25], we can obtain figure 5.10 (by using their data). In contract, one can obtain the firgure 5.11 from our data using the same method.

Comparing figure 5.10 and figure 5.11 one can see that they both have very similar shape. Figure 5.11 suggests that there is probably a predissociation in v' = 14 level near J'(J' + 1). This method cannot be used for v' = 15, 17, 18, 19 levels because most of





Isotope	Excited state v'	Average $\tau_{rad.}$	Error
Br_2 (79-79)	14	2.5 μs	0.3 μs
Br_2 (79-81)	14	2.7 μs	$0.2 \ \mu s$
Br_2 (79-79)	17	2.6 µs	$0.2 \ \mu s$
Br_2 (79-81)	17	2.6 μs	$0.2 \ \mu s$
Br_2 (81-81)	17 .	$2.5 \ \mu s$	$0.3 \ \mu s$
Br_2 (79-79)	18	$2.6 \ \mu s$	$0.3 \ \mu s$
Br_2 (79,81)	18	$2.5 \ \mu s$	$0.3 \ \mu s$
Br_2 (81-81)	18	$2.5 \ \mu s$	0.3 μs
Br_2 (79-79)	19	2.7 μs	0.3 μs
Br_2 (79-81)	19	$2.5 \ \mu s$	0.3 µs
Br_2 (79-79)	15	$2.4 \ \mu s$	$0.2 \ \mu s$
Br_2 (79-81)	15	$2.5 \ \mu s$	0.2 μs
Br_2 (81-81)	15	$2.4 \ \mu s$	0.2 μs

Table 5.11: τ_{rad} for the excited state v'









lines from those v' states are overlapped. Therefore it is hard to determine if there is a predissociation or not for those vibrational states.

In this thesis, we have presented a detailed research of radiative lifetime, $\tau_{rad.}$, of $^{(79,79)}Br_2$, $^{(79,81)}Br_2$ and $^{(81,81)}Br_2$. The apparatus and methods used to obtain the spectra and construction of the sample cells are described. The absorption and fluorescence spectra of the molecule bromine corresponding to the transitions between the ground state, $X^1\Sigma_{o^+g}$, and excited state, $B^3\Pi_{o^+u}$, have been measured from approximately 17464 cm^{-1} to 17480 cm^{-1} . The radiative lifetimes $\tau_{rad.}$ for v' = 14, 15, 17, 18, 19 of $^{(79,79)}Br_2$, $^{(79,81)}Br_2$ and $^{(81,81)}Br_2$ have been calculated from the spectra. However, there is a difficulty to determine the predissociations for some levels because of limited data.

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Appendix A

The derivation of the transition probabilities

From quantum mechanics, we have

$$\mathbf{R} = \int \boldsymbol{\psi}^{\prime *} \mathbf{M} \boldsymbol{\psi}^{\prime \prime} \mathbf{d} \tau \tag{A.87}$$

where

$$d\tau = d\tau_e r^2 \sin\theta dr d\theta d\phi \tag{A.88}$$

and

$$M = M_e + M_n \tag{A.89}$$

 $d au_e$ is the volume element in the configuration space of the electrons.

M is the electronic momnent.

 M_e and M_n depend on electrons and nuclei, respectrly.

In the z direction, we have

$$M_z = M\cos\theta = (M_e + M_N)\cos\theta \tag{A.90}$$

The complete eigenfunction of a molecule, to a first order approximation, is

$$\psi = \psi_e \cdot \frac{1}{r} \psi_v \cdot \psi_r \tag{A.91}$$

where

 ψ_e the electron eigenfunction.

 ψ_v the eigenfunction of a non simple harmonic vibration.

 ψ_{τ} the eigenfunction of a rigid rotor.

Thus,

$$R_z = \int \psi_{e'}^* M_e \psi_{e''} d\tau_e \int \psi_{v'}^* \psi_{v''} dr \int \sin \theta \cos \theta \psi_{r'}^* \psi_{r''} d\theta d\varphi \tag{A.92}$$

Where we have used

$$\int \psi_{e'}^* \psi_{e''} d\tau_e = 0 \tag{A.93}$$

Considering three dimensions, we can obtain the total matrix element for the system

$$\mathbf{R}^{\mathbf{n}\mathbf{m}} = \mathbf{R}_{\mathbf{e}}^{\mathbf{n}\mathbf{m}} \mathbf{R}_{\mathbf{v}\mathbf{i}\mathbf{b}}^{\mathbf{v}'\mathbf{v}''} \mathbf{R}_{\mathbf{rot}}^{\mathbf{J}'\mathbf{J}''} \tag{A.94}$$

The transition probability is proportional to $|\mathbf{R^{nm}}|^2$.

Appendix B

The vibrational and rotational transition probabilities

B.1 Vibrational transition probability

From Eqn.(A.89) one know that in the electronic transition the intensity of the vibrational spectrum band is proportional to $|\int \psi_{v'}^* \psi_{v''} dr |^2$ (F.C.F.). Where $\psi_{v'}$ and $\psi_{v''}$ belong to different electronic states, and they are not orthogonal. The integral $\int \psi_{v'}^* \psi_{v''}$ is called overlap integral. The intensity of a vibrational band depends on the level of overlap between $\psi_{v'}$ and $\psi_{v''}$. If we knew the electronic and vibrational wavefunctions, we can obtain the transition probability from Eqn.(A.89).

For the $B^3 \prod_{o^+u^-} X^1 \Sigma_{0^+g}$ system of Br_2 , all the Franck-Condon factors in the $B^3 \prod_{o^+u}$ state were obtained from several papers.[3,12]

B.2 Calculation of the rotational transition probabilty

First one can consider the z direction,

$$\sum_{M'M''} |\mathbf{R}_{rot}^{\mathbf{J}'\mathbf{J}''}|^2 = \sum_{M'M''} |\int \sin\theta\cos\theta\psi_{\mathbf{r}'}^*\psi_{\mathbf{r}''}^* d\theta d\varphi|^2$$
(B.95)

where

$$\psi_r^{J,M} = N_r P_J^{|M|}(\cos\theta) e^{iM\varphi} \tag{B.96}$$

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Appendix B. The vibrational and rotational transition probabilities

Thus

$$\int \sin\theta \cos\theta [N_{r'}N_{r''} \int e^{i(M'-M'')} d\varphi] P_{J'}^{|M'|}(\cos\theta) P_{J''}^{|M''|}(\cos\theta) d\theta$$

= $2\pi N_{r'}N_{r''} \int_{-1}^{+1} P_{J'}^{|M|}(x) x P_{J''}^{|M|}(x) dx$ (B.97)

where we have used

$$\int e^{i(M'-M'')} d\varphi = 2\pi \delta_{M'M''}$$
(B.98)

Using the formulas

$$zP_{\nu}^{\mu}(z) = \frac{1}{2\nu+1} [(\nu-\mu+1)P_{\nu+1}^{\mu}(z) + (\nu+\mu)P_{\nu-1}^{\mu}(z)]$$
(B.99)

$$\int_{-1}^{+1} P_{l^m}(\mu) P_{l'}^m(\mu) d\mu = \frac{2}{2l+1} \frac{(l+m)}{(l-m)!} \delta_{ll'}$$
(B.100)

$$N_r = (-1)^m \sqrt{\frac{(2J+1)(J-M)!}{4\pi(J+M)!}}$$
(B.101)

In this case,

$$z = x \tag{B.102}$$

$$\nu = \mu \tag{B.103}$$

$$\mu = M \tag{B.104}$$

$$l = J' \tag{B.105}$$

$$l' = J^{"} \tag{B.106}$$

$$m = M \tag{B.107}$$

So, in z direction one can obtain the transition probability,

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$$\sum_{M'M''} |\mathbf{R}_{rot,J'J''}|^{2} = \sum_{M'M''} |\frac{2\pi(-1)^{2m}}{2J''+1} \sqrt{\frac{(2J'+1)(J'-M)!}{4\pi(J'+M)!}} \sqrt{\frac{(2J''+1)(J''-M)!}{4\pi(J''+M)!}} \\ [(J''-M+1)\delta_{J',J''+1} + (J''+M)\delta_{J',J''}]$$
(B.108)

Finally, for the three dimensional system one obtains

$$\sum_{M'M''} | \mathbf{R}_{\mathbf{rot.}}^{\mathbf{J}'\mathbf{J}''} |^2 = \mathbf{J}''$$
(B.109)

for the P branch, and

Ξ

$$\sum_{M'M''} |\mathbf{R}_{\rm rot.}^{\mathbf{J}'\mathbf{J}''}|^2 = \mathbf{J}'' + \mathbf{1}$$
(B.110)

for the R branch.

Therefore,

$$\frac{\sum_{M'M''} |\mathbf{R}_{rot}^{\mathbf{J}'\mathbf{J}''}|^2}{2\mathbf{J}'' + 1} = 1$$

(B.111)

Appendix C

The density of molecular bromine in a particular rovibronic state

The hyperfine partition factor is $\frac{10}{16} = \frac{5}{8}$ for an ortho state (odd J), and $\frac{6}{10} = \frac{3}{8}$ for a para state (even J).

The density of a para state of $(^{79,79})Br_2$, at room temperature, satisfies the following equation

$$N_{v''J''} = \frac{N_0}{V} \times 0.2554 \times \frac{e^{-\beta E_{v''}}}{\sum_{v''} e^{-\beta E_{v''}}} \times \frac{e^{-\beta E_e}}{\sum_n e^{-\beta E_e}} \times \left[\frac{3(2J''+1)e^{-\beta E_{J''}}}{5\sum_{oddJ''}(2J''+1)e^{-\beta E_{J''}}+3\sum_{evenJ''}(2J''+1)e^{-\beta E_{J''}}}\right] \quad (C.112)$$

The equation above can be written as

$$N_{v''J''} = \frac{N_0}{V} \times 0.2554 \times \frac{e^{-\beta E_{v''}}}{\sum_{v''} e^{-\beta E_{v''}}} \times \left[\frac{3(2J''+1)e^{-\beta E_{J''}}}{3\sum_{J''}(2J''+1)e^{-\beta E_{J''}}+2 \times \frac{1}{2}\sum_{J''}(2J''+1)e^{-\beta E_{J''}}}\right] \quad (C.113)$$

Then we can obtain

$$N_{v''J''} = \frac{N_0}{V} \times 0.2554 \times \frac{e^{-\beta E_{v''}}}{\sum_{v''} e^{-\beta E_{v''}}} \times \frac{3}{4} \frac{(2J''+1)e^{-\beta E_{J''}}}{\sum_{J''} (2J''+1)e^{-\beta E_{J''}}}$$
(C.114)

where E_e is equal to zero for the ground electronic state. In the same way we can obtain Eqn.(2.41).

Appendix D

Identified and unused lines of Band 14' - 1''

·	·	able D.12: Band	1 14 - 1 promi	ne (19,81)	21
P(J)	$\nu \ cm^{-1}$	$N_{mv''J''}$	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
P(3)	17466.705	$2.6458 imes 10^{13}$	0.7206×10^{-4}	2.89×10^{-37}	2.35×10^{-2}
P(4)	17466.358	$3.3911 imes10^{13}$	$1.5938 imes10^{-4}$	2.88×10^{-37}	2.28×10^{-2}
P(5)	17465.965	4.1285×10^{13}	$2.2497 imes10^{-4}$	2.65×10^{-37}	2.22×10^{-2}
P(6)	17465.498	4.8563×10^{13}	2.5790×10^{-4}	2.42×10^{-37}	2.33×10^{-2}
P(7)	17464.969	5.5729×10^{13}	4.5523×10^{-4}	2.89×10^{-37}	2.66×10^{-2}
R(J)	$\nu \ cm^{-1}$	N _{mv" J"}	$\int k_{\nu} d\nu \ cm^{-2}$	$\mid R_e \mid^2$	$\Delta \nu \ cm^{-1}$
R(3)	17467.410	$2.6458 imes 10^{13}$	1.2148×10^{-4}	2.29×10^{-37}	2.24×10^{-2}
R(4)	17467.268	3.3911×10^{13}	1.6490×10^{-4}	2.50×10^{-37}	2.12×10^{-2}
R(5)	17467.064	4.1285×10^{13}	$1.7696 imes 10^{-4}$	2.24×10^{-37}	1.91×10^{-2}
R(6)	17466.796	$4.8653 imes 10^{13}$	3.0943×10^{-4}	2.89×10^{-37}	2.54×10^{-2}
R(7)	17466.477	5.5729×10^{13}	$2.9266 imes 10^{-4}$	2.88×10^{-37}	2.16×10^{-2}
R(8)	17466.096	6.2766×10^{13}	7.0570×10^{-4}	2.79×10^{-37}	$2.35 imes 10^{-2}$
R(9)	17465.655	6.9659×10^{13}	$5.8730 imes 10^{-4}$	2.70×10^{-37}	2.23×10^{-2}
R(10)	17465.152	$7.6392 imes 10^{13}$	3.9626×10^{-4}	2.89×10^{-37}	2.20×10^{-2}
R(11)	17464.591	8.2952×10^{13}	3.7230×10^{-4}	2.46×10^{-37}	2.14×10^{-2}

Table D.12: Band 14' - 1'' bromine (79,81)

Appendix D. Identified and unused lines of Band 14' - 1''

P(J)	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
P(1)	17474.510	7.3060×10^{12}	2.3747×10^{-4}	2.82×10^{-37}	$2.30 imes 10^{-2}$
P(4)	17473.655	$1.3058 imes 10^{13}$	3.8263×10^{-4}	2.11×10^{-37}	$2.07 imes 10^{-2}$
P(6)	17472.770	1.8698×10^{13}	$0.7201 imes 10^{-4}$	2.25×10^{-37}	1.46×10^{-2}
P(7)	17472.237	$3.5758 imes10^{13}$	1.8167×10^{-4}	$2.85 imes 10^{-37}$	2.01×10^{-2}
P(8)	17471.645	2.4162×10^{13}	1.0942×10^{-4}	2.60×10^{-37}	$2.25 imes 10^{-2}$
P(9)	17470.987	4.4689×10^{13}	1.8561×10^{-4}	$2.37 imes10^{-37}$	$2.27 imes 10^{-2}$
P(11)	17469.499	5.3206×10^{13}	2.3694×10^{-4}	$2.52 imes 10^{-37}$	2.12×10^{-2}
P(12)	17468.656	$3.4372 imes 10^{13}$	1.5725×10^{-4}	$2.58 imes 10^{-37}$	$2.17 imes10^{-2}$
P(13)	17467.756	6.1237×10^{13}	1.5741×10^{-4}	2.27×10^{-37}	2.07×10^{-2}
P(14)	17466.796	3.9029×10^{13}	$3.0943 imes 10^{-4}$	$2.89 imes10^{-37}$	2.39×10^{-2}
P(15)	17465.771	$6.8715 imes 10^{13}$	4.5367×10^{-4}	2.06×10^{-37}	2.47×10^{-2}
P(16)	17464.684	4.3337×10^{13}	1.9524×10^{-4}	$2.51 imes 10^{-37}$	$2.05 imes 10^{-2}$
R(J)	νcm^{-1}	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
R(4)	17474.546	1.3058×10^{13}	10.465×10^{-4}	2.82×10^{-37}	2.78×10^{-2}
R(5)	17474.359	1.3058×10^{13}	$1.5958 imes 10^{-4}$	2.65×10^{-37}	2.21×10^{-2}
R(7)	17473.761	2.5813×10^{13}	$2.5813 imes 10^{-4}$	2.12×10^{-37}	1.94×10^{-2}
R(8)	17473.368	$1.5832 imes 10^{13}$	1.5832×10^{-4}	3.00×10^{-37}	2.18×10^{-2}
R(9)	17472.926	3.8333×10^{13}	$3.8333 imes 10^{-4}$	2.38×10^{-37}	2.17×10^{-2}
R(11)	17471.841	$2.3285 imes 10^{13}$	$2.3285 imes 10^{-4}$	2.23×10^{-37}	1.94×10^{-2}
R(12)	17471.199	1.6754×10^{13}	$1.6754 imes 10^{-4}$	2.53×10^{-37}	2.42×10^{-2}
R(13)	17470.502	$2.6743 imes 10^{13}$	2.6743×10^{-4}	2.28×10^{-37}	1.96×10^{-2}
R(14)	17469.749	1.4127×10^{13}	1.4127×10^{-4}	2.22×10^{-37}	1.88×10^{-2}
R(15)	17468.925	3.0055×10^{13}	3.0055×10^{-4}	2.78×10^{-37}	2.03×10^{-2}
R(16)	17468.042	2.7618×10^{13}	2.7618×10^{-4}	2.65×10^{-37}	2.53×10^{-2}
R(17)	17467.095	3.6602×10^{13}	3.6602×10^{-4}	2.54×10^{-37}	2.09×10^{-2}
R(18)	17466.096	7.0570×10^{13}	7.0570×10^{-4}	2.65×10^{-37}	2.25×10^{-2}
R(19)	17465.032	4.6456×10^{13}	4.6454×10^{-4}	2.89×10^{-37}	2.46×10^{-2}

Table D.13: Band 14' - 1'' bromine (79,79)

Appendix D. Identified and unused lines of Band 14' - 1''

P(J)	$\cdot \nu \ cm^{-1}$	$N_{mv''J''}$	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
P(2)	17474.273	7.4295×10^{12}	1.0087×10^{-4}	9.34×10^{-37}	2.36×10^{-2}
P(3)	17473.990	1.6980×10^{13}	1.0253×10^{-4}	3.81×10^{-37}	$2.58 imes10^{-2}$
P(5)	.17473.234	$2.6494 imes 10^{13}$	1.7751×10^{-4}	3.98×10^{-37}	$2.80 imes 10^{-2}$
P(10)	17470.271	2.9402×10^{13}	2.9105×10^{-4}	$5.62 imes 10^{-37}$	$0.83 imes 10^{-2}$
R(J)	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
R(6)	17474.090	1.2210×10^{13}	1.2210×10^{-4}	3.28×10^{-37}	1.94×10^{-2}
R(10)	17472.412	2.4368×10^{13}	2.4368×10^{-4}	4.27×10^{-37}	2.09×10^{-2}

Table D.14: The unused lines from band 14' - 1'' bromine (79,79)

Table D.15: The unused lines from band 14' - 1'' bromine (79,81)

P(J)	$\nu \ cm^{-1}$	_N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
P(2)	17466.989	1.8943×10^{13}	0.9814×10^{-4}	$3.70 imes 10^{-37}$	2.86×10^{-2}
R(J)	$\nu \ cm^{-1}$	• N _{mv" J} "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
R(1)	17467.493	1.1383×10^{13}	2.7633×10^{-4}	0.65×10^{-37}	$2.94 imes 10^{-2}$
R(2)	17467.493	1.8943×10^{13}	2.7633×10^{-4}	0.65×10^{-37}	$2.94 imes10^{-2}$

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Appendix \mathbf{E}

Identified and unused lines of Band 17' - 2''

Table E.16: Band 17' - 2'' bromine (81,81)

P(J)	$\nu \ cm^{-1}$	$N_{mv''J''}$	$\int k_{ u} d u \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
P(1)	17465.821	$1.5504 imes 10^{12}$	1.3772×10^{-4}	2.06×10^{-37}	2.27×10^{-2}
P(3)	17465.312	$3.6068 imes 10^{12}$	$1.5765 imes 10^{-4}$	2.54×10^{-37}	1.92×10^{-2}
P(4)	17464.969	$2.7715 imes 10^{12}$	$4.5523 imes 10^{-4}$	2.89×10^{-37}	$2.59 imes10^{-2}$
P(5)	17464.554	$5.6241 imes 10^{12}$	2.6528×10^{-4}	2.01×10^{-37}	$2.19 imes 10^{-2}$
$\overline{R(J)}$	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{ u} d u \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
R(1)	17466.096	1.5504×10^{12}	7.0570×10^{-4}	2.65×10^{-37}	$2.25 imes 10^{-2}$
R(3)	17465.965	3.6038×10^{12}	$2.2497 imes 10^{-4}$	2.65×10^{-37}	$2.19 imes10^{-2}$
R(4)	17465.821	2.7715×10^{12}	1.3772×10^{-4}	2.06×10^{-37}	$2.27 imes10^{-2}$
R(6)	17465.312	3.9696×10^{12}	1.5765×10^{-4}	2.54×10^{-37}	1.92×10^{-2}
R(7)	17464.969	$7.5930 imes 10^{12}$	4.5523×10^{-4}	2.89×10^{-37}	$2.59 imes10^{-2}$
R(8)	17464.554	$5.1316 imes 10^{12}$	2.6528×10^{-4}	2.01×10^{-37}	$2.19 imes10^{-2}$

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Table E.17: Band 17' - 2'' bromine (79,79)

P(J)	νcm^{-1}	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
P(1)	17478.173	1.5369×10^{12}	0.9337×10^{-4}	2.62×10^{-37}	2.57×10^{-2}
P(2)	17477.944	1.5345×10^{12}	1.6993×10^{-4}	$2.66 imes10^{-37}$	$2.25 imes 10^{-2}$
P(4)	17477.285	2.7469×10^{12}	2.0088×10^{-4}	$2.19 imes 10^{-37}$	2.89×10^{-2}
P(5)	17476.860	5.5735×10^{12}	2.4222×10^{-4}	$2.65 imes10^{-37}$	2.31×10^{-2}
P(6)	17476.377	3.9335×10^{12}	2.9861×10^{-4}	$2.52 imes 10^{-37}$	$2.72 imes 10^{-2}$
P(7)	17475.815	7.5228×10^{12}	1.5628×10^{-4}	$2.06 imes10^{-37}$	1.79×10^{-2}
P(8)	17475.190	5.0834×10^{12}	4.0474×10^{-4}	2.74×10^{-37}	$3.03 imes10^{-2}$
P(9)	17474.510	9.4022×10^{12}	2.3747×10^{-4}	$2.82 imes 10^{-37}$	$2.30 imes10^{-2}$
P(10)	17473.761	6.1862×10^{12}	2.5813×10^{-4}	2.11×10^{-37}	$1.94 imes 10^{-2}$
P(11)	17472.956	1.1195×10^{13}	2.5975×10^{-4}	2.77×10^{-37}	$2.03 imes10^{-2}$
P(14)	17470.118	8.2130×10^{12}	1.3608×10^{-4}	$2.34 imes10^{-37}$	1.62×10^{-2}
P(15)	17469.035	1.4460×10^{13}	3.0989×10^{-4}	2.78×10^{-37}	2.06×10^{-2}
P(17)	17466.680	1.5907×10^{13}	3.5484×10^{-4}	$2.89 imes10^{-37}$	2.18×10^{-2}
P(18)	17465.402	9.9478×10^{12}	4.2071×10^{-4}	2.42×10^{-37}	$2.09 imes 10^{-2}$
R(J)	$\nu \ cm^{-1}$	N _{mv" J} "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
R(0)	17478.438	3.0762×10^{11}	0.5719×10^{-4}	2.66×10^{-37}	2.12×10^{-2}
R(2)	17478.438	$1.5345 imes 10^{12}$	0.5719×10^{-4}	2.66×10^{-37}	2.12×10^{-2}
R(4)	17478.173	2.7469×10^{12}	$0.9337 imes 10^{-4}$	2.62×10^{-37}	2.23×10^{-2}
R(5)	17477.944	$5.5735 imes 10^{12}$	1.6993×10^{-4}	2.66×10^{-37}	2.25×10^{-2}
R(7)	17477.285	7.5228×10^{12}	2.0088×10^{-4}	2.19×10^{-37}	2.81×10^{-2}
R(8)	17476.860	5.0843×10^{12}	2.4222×10^{-4}	2.65×10^{-37}	2.12×10^{-2}
R(9)	17476.377	9.4022×10^{12}	2.9861×10^{-4}	2.52×10^{-37}	2.68×10^{-2}
R(10)	17475.815	6.1862×10^{12}	1.5628×10^{-4}	2.06×10^{-37}	1.79×10^{-2}
R(11)	17475.190	$1.1195 imes 10^{13}$	4.0474×10^{-4}	2.74×10^{-37}	3.03×10^{-2}
R(12)	17474.510	$7.2323 imes 10^{12}$	2.3747×10^{-4}	2.82×10^{-37}	2.30×10^{-2}
R(14)	17472.926	8.2130×10^{12}	3.8333×10^{-4}	2.38×10^{-37}	2.17×10^{-2}
R(15)	17472.050	1.4460×10^{13}	5.6018×10^{-4}	2.62×10^{-37}	2.30×10^{-2}
R(16)	17471.094	9.1203×10^{12}	2.4579×10^{-4}	2.99×10^{-37}	2.06×10^{-2}
R(17)	17470.089	1.5907×10^{13}	3.3296×10^{-4}	2.34×10^{-37}	2.13×10^{-2}
R(18)	17469.002	9.9478×10^{12}	3.1130×10^{-4}	2.78×10^{-37}	2.32×10^{-2}
R(19)	17467.860	1.7216×10^{13}	3.7253×10^{-4}	2.65×10^{-37}	2.03×10^{-2}
R(20)	17466.645	1.0690×10^{13}	4.9965×10^{-4}	2.89×10^{-37}	2.02×10^{-2}
R(21)	17465.361	1.8379×10^{13}	2.4221×10^{-4}	2.47×10^{-37}	2.11×10^{-2}

Appendix E. Identified and unused lines of Band 17' - 2''

P(J)	$\nu \ cm^{-1}$	N _{mv" J"}	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
P(1)	17472.050	$2.4178 imes 10^{12}$	5.6018×10^{-4}	2.62×10^{-37}	$2.30 imes 10^{-2}$
P(2)	17471.819	4.0235×10^{12}	$2.7667 imes 10^{-4}$	2.50×10^{-37}	$1.99 imes 10^{-2}$
P(3)	17471.522	$5.6197 imes 10^{12}$	$3.5042 imes10^{-4}$	$2.54 imes10^{-37}$	$2.04 imes 10^{-2}$
P(4)	17471.166	$7.2029 imes 10^{12}$	4.0899×10^{-4}	2.49×10^{-37}	$2.12 imes10^{-2}$
P(5)	17470.745	$8.7694 imes 10^{12}$	$5.2775 imes10^{-4}$	2.76×10^{-37}	$2.14 imes 10^{-2}$
P(7)	17469.724	$1.1838 imes 10^{13}$	$5.6378 imes10^{-4}$	$2.22 imes10^{-37}$	$2.02 imes 10^{-2}$
P(8)	17469.106	$1.3333 imes 10^{13}$	$8.4040 imes 10^{-4}$	$2.78 imes10^{-37}$	$2.61 imes 10^{-2}$
P(9)	17468.438	$1.4798 imes 10^{13}$	7.3152×10^{-4}	$2.51 imes 10^{-37}$	$2.27 imes10^{-2}$
P(10)	17467.692	1.6229×10^{12}	8.3822×10^{-4}	2.27×10^{-37}	$2.49 imes 10^{-2}$
P(11)	17466.880	1.7623×10^{13}	$8.2927 imes 10^{-4}$	$2.45 imes 10^{-37}$	$2.51 imes 10^{-2}$
P(12)	17466.015	1.8977×10^{13}	$9.8095 imes 10^{-4}$	$2.65 imes 10^{-37}$	$2.74 imes10^{-2}$
P(13)	17465.080	2.0289×10^{13}	11.5934×10^{-4}	2.89×10^{-37}	$2.90 imes 10^{-2}$
$\mathbf{P}(\mathbf{I})$	$u cm^{-1}$	N	$\int h d\mu cm^{-2}$		$\Lambda \mu cm^{-1}$
10(3)		1 mv'' J''	J RUUD CIT	re	
R(3)	17472.201	$\frac{1}{mv''J''}$ 5.6197 × 10 ¹²	1.4712×10^{-4}	2.85×10^{-37}	$\frac{\Delta \nu \ cm}{1.83 \times 10^{-2}}$
$\begin{array}{c} R(3) \\ R(4) \end{array}$	17472.201 17472.050	$\frac{14_{mv} J''}{5.6197 \times 10^{12}}$ 7.2029×10^{12}	$\frac{1.4712 \times 10^{-4}}{5.6018 \times 10^{-4}}$	$ \frac{12.85 \times 10^{-37}}{2.62 \times 10^{-37}} $	$\frac{1.83 \times 10^{-2}}{2.30 \times 10^{-2}}$
$ \begin{array}{c} R(3) \\ R(4) \\ R(5) \end{array} $	17472.201 17472.050 17471.819	$\frac{11}{5.6197 \times 10^{12}}$ $\frac{5.6197 \times 10^{12}}{7.2029 \times 10^{12}}$ 8.7694×10^{12}	$\frac{1.4712 \times 10^{-4}}{5.6018 \times 10^{-4}}$ 2.7667 × 10 ⁻⁴	$\frac{11e}{2.85 \times 10^{-37}}$ $\frac{2.62 \times 10^{-37}}{2.50 \times 10^{-37}}$	$\frac{1.83 \times 10^{-2}}{2.30 \times 10^{-2}}$ $\frac{1.97 \times 10^{-2}}{1.97 \times 10^{-2}}$
$ \begin{array}{c} R(3) \\ R(3) \\ R(4) \\ R(5) \\ R(6) \end{array} $	17472.201 17472.050 17471.819 17471.522		$\begin{array}{c} 1.4712 \times 10^{-4} \\ 5.6018 \times 10^{-4} \\ 2.7667 \times 10^{-4} \\ 3.5042 \times 10^{-4} \end{array}$	$\begin{array}{c} 12e \\ \hline 2.85 \times 10^{-37} \\ \hline 2.62 \times 10^{-37} \\ \hline 2.50 \times 10^{-37} \\ \hline 2.54 \times 10^{-37} \end{array}$	$\frac{2.30 \times 10^{-2}}{2.30 \times 10^{-2}}$ $\frac{1.97 \times 10^{-2}}{2.04 \times 10^{-2}}$
$ \begin{array}{c} R(3) \\ R(3) \\ R(4) \\ R(5) \\ R(6) \\ R(7) \end{array} $	17472.201 17472.050 17471.819 17471.522 17471.166	$ \begin{array}{c} 17_{mv} J^{n} \\ 5.6197 \times 10^{12} \\ 7.2029 \times 10^{12} \\ 8.7694 \times 10^{12} \\ 1.0316 \times 10^{13} \\ 1.1838 \times 10^{13} \end{array} $	$\begin{array}{c} 1.4712 \times 10^{-4} \\ 5.6018 \times 10^{-4} \\ 2.7667 \times 10^{-4} \\ 3.5042 \times 10^{-4} \\ 4.0899 \times 10^{-4} \end{array}$	$\begin{array}{c} 11e \\ \hline 2.85 \times 10^{-37} \\ \hline 2.62 \times 10^{-37} \\ \hline 2.50 \times 10^{-37} \\ \hline 2.54 \times 10^{-37} \\ \hline 2.49 \times 10^{-37} \end{array}$	$\frac{1.83 \times 10^{-2}}{2.30 \times 10^{-2}}$ $\frac{1.97 \times 10^{-2}}{2.04 \times 10^{-2}}$ $\frac{2.12 \times 10^{-2}}{2.12 \times 10^{-2}}$
$ \begin{array}{r} R(3) \\ R(3) \\ R(4) \\ R(5) \\ R(6) \\ R(7) \\ R(8) \end{array} $	17472.201 17472.050 17471.819 17471.522 17471.166 17470.745	$\begin{array}{c} 17_{mv''J''}\\ 5.6197\times 10^{12}\\ 7.2029\times 10^{12}\\ 8.7694\times 10^{12}\\ 1.0316\times 10^{13}\\ 1.1838\times 10^{13}\\ 1.3333\times 10^{13} \end{array}$	$\begin{array}{c} 1.4712 \times 10^{-4} \\ 5.6018 \times 10^{-4} \\ 2.7667 \times 10^{-4} \\ 3.5042 \times 10^{-4} \\ 4.0899 \times 10^{-4} \\ 5.2775 \times 10^{-4} \end{array}$	$\begin{array}{c} 12e \\ \hline 2.85 \times 10^{-37} \\ 2.62 \times 10^{-37} \\ 2.50 \times 10^{-37} \\ 2.54 \times 10^{-37} \\ 2.49 \times 10^{-37} \\ 2.76 \times 10^{-37} \end{array}$	$\frac{1.83 \times 10^{-2}}{2.30 \times 10^{-2}}$ $\frac{1.97 \times 10^{-2}}{2.04 \times 10^{-2}}$ $\frac{2.12 \times 10^{-2}}{2.14 \times 10^{-2}}$
	17472.201 17472.050 17471.819 17471.522 17471.166 17470.745 17469.724	$\begin{array}{c} 17_{mv} J^{n} \\ 5.6197 \times 10^{12} \\ 7.2029 \times 10^{12} \\ 8.7694 \times 10^{12} \\ 1.0316 \times 10^{13} \\ 1.1838 \times 10^{13} \\ 1.3333 \times 10^{13} \\ 1.6229 \times 10^{13} \end{array}$	$\begin{array}{c} 1.4712 \times 10^{-4} \\ 5.6018 \times 10^{-4} \\ 2.7667 \times 10^{-4} \\ 3.5042 \times 10^{-4} \\ 4.0899 \times 10^{-4} \\ 5.2775 \times 10^{-4} \\ 5.6378 \times 10^{-4} \end{array}$	$\begin{array}{c} 11ce \\ \hline 2.85 \times 10^{-37} \\ \hline 2.62 \times 10^{-37} \\ \hline 2.50 \times 10^{-37} \\ \hline 2.54 \times 10^{-37} \\ \hline 2.49 \times 10^{-37} \\ \hline 2.76 \times 10^{-37} \\ \hline 2.22 \times 10^{-37} \end{array}$	$\frac{2.30 \times 10^{-2}}{1.83 \times 10^{-2}}$ $\frac{2.30 \times 10^{-2}}{1.97 \times 10^{-2}}$ $\frac{2.04 \times 10^{-2}}{2.12 \times 10^{-2}}$ $\frac{2.14 \times 10^{-2}}{2.02 \times 10^{-2}}$
	17472.201 17472.050 17471.819 17471.522 17471.166 17470.745 17469.724 17469.106	$\begin{array}{c} 17_{mv''J''}\\ 5.6197\times 10^{12}\\ 7.2029\times 10^{12}\\ 8.7694\times 10^{12}\\ 1.0316\times 10^{13}\\ 1.1838\times 10^{13}\\ 1.3333\times 10^{13}\\ 1.6229\times 10^{13}\\ 1.7623\times 10^{13} \end{array}$	$\begin{array}{c} 1.4712 \times 10^{-4} \\ 5.6018 \times 10^{-4} \\ 2.7667 \times 10^{-4} \\ 3.5042 \times 10^{-4} \\ 4.0899 \times 10^{-4} \\ 5.2775 \times 10^{-4} \\ 5.6378 \times 10^{-4} \\ 8.4040 \times 10^{-4} \end{array}$	$\begin{array}{r} 12.85 \times 10^{-37} \\ 2.85 \times 10^{-37} \\ 2.62 \times 10^{-37} \\ 2.50 \times 10^{-37} \\ 2.54 \times 10^{-37} \\ 2.49 \times 10^{-37} \\ 2.76 \times 10^{-37} \\ 2.22 \times 10^{-37} \\ 2.78 \times 10^{-37} \end{array}$	$\frac{2.30 \times 10^{-2}}{1.83 \times 10^{-2}}$ $\frac{1.83 \times 10^{-2}}{2.30 \times 10^{-2}}$ $\frac{1.97 \times 10^{-2}}{2.04 \times 10^{-2}}$ $\frac{2.12 \times 10^{-2}}{2.14 \times 10^{-2}}$ $\frac{2.02 \times 10^{-2}}{2.61 \times 10^{-2}}$
	$\begin{array}{c} 17472.201\\ 17472.050\\ 17471.819\\ 17471.522\\ 17471.166\\ 17470.745\\ 17469.724\\ 17469.106\\ 17468.438\end{array}$	$\begin{array}{c} 17_{mv''J''}\\ 5.6197\times 10^{12}\\ 7.2029\times 10^{12}\\ 8.7694\times 10^{12}\\ 1.0316\times 10^{13}\\ 1.1838\times 10^{13}\\ 1.3333\times 10^{13}\\ 1.6229\times 10^{13}\\ 1.7623\times 10^{13}\\ 1.8977\times 10^{13} \end{array}$	$\begin{array}{c} 1.4712 \times 10^{-4} \\ 5.6018 \times 10^{-4} \\ 2.7667 \times 10^{-4} \\ 3.5042 \times 10^{-4} \\ 4.0899 \times 10^{-4} \\ 5.2775 \times 10^{-4} \\ 5.6378 \times 10^{-4} \\ 8.4040 \times 10^{-4} \\ 7.3152 \times 10^{-4} \end{array}$	$\begin{array}{c} 12.85 \times 10^{-37} \\ 2.85 \times 10^{-37} \\ 2.52 \times 10^{-37} \\ 2.50 \times 10^{-37} \\ 2.54 \times 10^{-37} \\ 2.49 \times 10^{-37} \\ 2.76 \times 10^{-37} \\ 2.22 \times 10^{-37} \\ 2.78 \times 10^{-37} \\ 2.51 \times 10^{-37} \end{array}$	$\frac{2.50 \text{ cm}}{1.83 \times 10^{-2}}$ $\frac{1.83 \times 10^{-2}}{2.30 \times 10^{-2}}$ $\frac{1.97 \times 10^{-2}}{2.04 \times 10^{-2}}$ $\frac{2.12 \times 10^{-2}}{2.14 \times 10^{-2}}$ $\frac{2.02 \times 10^{-2}}{2.61 \times 10^{-2}}$ $\frac{2.61 \times 10^{-2}}{2.27 \times 10^{-2}}$
	$\begin{array}{c} 17472.201\\ 17472.050\\ 17471.819\\ 17471.522\\ 17471.522\\ 17471.166\\ 17470.745\\ 17469.724\\ 17469.106\\ 17468.438\\ 17467.692\end{array}$	$\begin{array}{c} 17_{mv} J^{n} \\ \hline 5.6197 \times 10^{12} \\ 7.2029 \times 10^{12} \\ 8.7694 \times 10^{12} \\ 1.0316 \times 10^{13} \\ 1.1838 \times 10^{13} \\ 1.3333 \times 10^{13} \\ 1.6229 \times 10^{13} \\ 1.7623 \times 10^{13} \\ 1.8977 \times 10^{13} \\ 2.0289 \times 10^{13} \end{array}$	$\begin{array}{c} 1.4712 \times 10^{-4} \\ 5.6018 \times 10^{-4} \\ 2.7667 \times 10^{-4} \\ 3.5042 \times 10^{-4} \\ 4.0899 \times 10^{-4} \\ 5.2775 \times 10^{-4} \\ 5.6378 \times 10^{-4} \\ 8.4040 \times 10^{-4} \\ 7.3152 \times 10^{-4} \\ 8.3822 \times 10^{-4} \end{array}$	$\begin{array}{c} 1.1c_{e} \\ \hline 2.85 \times 10^{-37} \\ 2.62 \times 10^{-37} \\ 2.50 \times 10^{-37} \\ 2.54 \times 10^{-37} \\ 2.49 \times 10^{-37} \\ 2.76 \times 10^{-37} \\ 2.22 \times 10^{-37} \\ 2.78 \times 10^{-37} \\ 2.51 \times 10^{-37} \\ 2.27 \times 10^{-37} \end{array}$	$\begin{array}{r} 1.83 \times 10^{-2} \\ 2.30 \times 10^{-2} \\ 1.97 \times 10^{-2} \\ 2.04 \times 10^{-2} \\ 2.12 \times 10^{-2} \\ 2.12 \times 10^{-2} \\ 2.14 \times 10^{-2} \\ 2.02 \times 10^{-2} \\ 2.61 \times 10^{-2} \\ 2.27 \times 10^{-2} \\ 2.49 \times 10^{-2} \end{array}$
	$\begin{array}{c} 17472.201\\ 17472.050\\ 17471.819\\ 17471.522\\ 17471.166\\ 17470.745\\ 17469.724\\ 17469.106\\ 17468.438\\ 17467.692\\ 17466.880\\ \end{array}$	$\begin{array}{c} 17_{mv''J''}\\ \overline{5.6197\times10^{12}}\\ 7.2029\times10^{12}\\ 8.7694\times10^{12}\\ 1.0316\times10^{13}\\ 1.1838\times10^{13}\\ 1.3333\times10^{13}\\ 1.6229\times10^{13}\\ 1.7623\times10^{13}\\ 1.8977\times10^{13}\\ 2.0289\times10^{13}\\ 2.1556\times10^{13}\\ \end{array}$	$\begin{array}{c} 1.4712 \times 10^{-4} \\ 5.6018 \times 10^{-4} \\ 2.7667 \times 10^{-4} \\ 3.5042 \times 10^{-4} \\ 4.0899 \times 10^{-4} \\ 5.2775 \times 10^{-4} \\ 5.6378 \times 10^{-4} \\ 8.4040 \times 10^{-4} \\ 7.3152 \times 10^{-4} \\ 8.3822 \times 10^{-4} \\ 8.2927 \times 10^{-4} \end{array}$	$\begin{array}{c} 11ce \\ \hline 2.85 \times 10^{-37} \\ \hline 2.62 \times 10^{-37} \\ \hline 2.50 \times 10^{-37} \\ \hline 2.54 \times 10^{-37} \\ \hline 2.54 \times 10^{-37} \\ \hline 2.76 \times 10^{-37} \\ \hline 2.78 \times 10^{-37} \\ \hline 2.78 \times 10^{-37} \\ \hline 2.51 \times 10^{-37} \\ \hline 2.27 \times 10^{-37} \\ \hline 2.45 \times 10^{-37} \end{array}$	$\begin{array}{r} \underline{1.83 \times 10^{-2}} \\ 1.83 \times 10^{-2} \\ 2.30 \times 10^{-2} \\ 1.97 \times 10^{-2} \\ 2.04 \times 10^{-2} \\ 2.12 \times 10^{-2} \\ 2.14 \times 10^{-2} \\ 2.02 \times 10^{-2} \\ 2.61 \times 10^{-2} \\ 2.27 \times 10^{-2} \\ 2.49 \times 10^{-2} \\ 2.51 \times 10^{-2} \end{array}$
$\begin{array}{c} R(3) \\ R(3) \\ R(4) \\ R(5) \\ R(6) \\ R(7) \\ R(8) \\ R(10) \\ R(11) \\ R(12) \\ R(13) \\ R(14) \\ R(15) \end{array}$	$\begin{array}{c} 17472.201\\ 17472.050\\ 17471.819\\ 17471.522\\ 17471.166\\ 17470.745\\ 17469.724\\ 17469.106\\ 17468.438\\ 17467.692\\ 17466.880\\ 17466.880\\ 17466.015\end{array}$	$\begin{array}{c} 17_{mv''J''}\\ \overline{5.6197\times10^{12}}\\ 7.2029\times10^{12}\\ 8.7694\times10^{12}\\ 1.0316\times10^{13}\\ 1.1838\times10^{13}\\ 1.3333\times10^{13}\\ 1.6229\times10^{13}\\ 1.7623\times10^{13}\\ 1.8977\times10^{13}\\ 2.0289\times10^{13}\\ 2.1556\times10^{13}\\ 2.2775\times10^{13}\\ \end{array}$	$\begin{array}{c} 1.4712 \times 10^{-4} \\ 5.6018 \times 10^{-4} \\ 2.7667 \times 10^{-4} \\ 3.5042 \times 10^{-4} \\ 4.0899 \times 10^{-4} \\ 5.2775 \times 10^{-4} \\ 5.6378 \times 10^{-4} \\ 8.4040 \times 10^{-4} \\ 7.3152 \times 10^{-4} \\ 8.3822 \times 10^{-4} \\ 8.2927 \times 10^{-4} \\ 9.8095 \times 10^{-4} \end{array}$	$\begin{array}{c} 12.85 \times 10^{-37} \\ 2.85 \times 10^{-37} \\ 2.62 \times 10^{-37} \\ 2.50 \times 10^{-37} \\ 2.54 \times 10^{-37} \\ 2.49 \times 10^{-37} \\ 2.76 \times 10^{-37} \\ 2.22 \times 10^{-37} \\ 2.78 \times 10^{-37} \\ 2.51 \times 10^{-37} \\ 2.27 \times 10^{-37} \\ 2.45 \times 10^{-37} \\ 2.65 \times 10^{-37} \end{array}$	$\begin{array}{r} 1.83 \times 10^{-2} \\ 2.30 \times 10^{-2} \\ 1.97 \times 10^{-2} \\ 2.04 \times 10^{-2} \\ 2.12 \times 10^{-2} \\ 2.14 \times 10^{-2} \\ 2.02 \times 10^{-2} \\ 2.61 \times 10^{-2} \\ 2.27 \times 10^{-2} \\ 2.49 \times 10^{-2} \\ 2.51 \times 10^{-2} \\ 2.74 \times 10^{-2} \end{array}$

Table E.18: Band 17' - 2'' bromine (79,81)

Appendix E. Identified and unused lines of Band 17' - 2''

P(J)	$\nu \ cm^{-1}$	$N_{mv''J''}$	$\int k_{ u} d u \ cm^{-2}$	$\mid R_{e} \mid^{2}$	$\Delta \nu \ cm^{-1}$
P(3)	17477.652	$3.5720 imes 10^{13}$	1.5972×10^{-4}	5.24×10^{-37}	2.89×10^{-2}
P(13)	17471.120	1.2886×10^{13}	3.5037×10^{-4}	$3.23 imes 10^{-37}$	2.57×10^{-2}
R(J)	$\nu \ cm^{-1}$	N _{mv" J} "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
R(1)	17478.461	1.5369×10^{12}	1.5994×10^{-4}	8.92×10^{-37}	2.61×10^{-2}
R(3)	17478.337	$3.5720 imes 10^{12}$	1.1779×10^{-4}	$3.30 imes 10^{-37}$	$2.39 imes 10^{-2}$
$\mathbf{R}(6)$	17477 652	3.0335×10^{12}	1.5628×10^{-4}	5.24×10^{-37}	2.80×10^{-2}

Table E.19: The unused lines from band 17' - 2'' bromine (79,79)

Table E.20: The unused lines from band 17' - 2'' bromine (79,81)

P(J)	$\nu \ cm^{-1}$	$N_{mv''J''}$	$\int k_{\nu} d\nu \ cm^{-2}$	$\mid R_e \mid^2$	$\Delta \nu \ cm^{-1}$
P(6)	1747.271	1.0316×10^{13}	2.9105×10^{-4}	1.34×10^{-37}	$2.11 imes 10^{-2}$
R(J)	$\nu \ cm^{-1}$	$N_{mv''J''}$	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
R(0)	17472.276	8.0657×10^{12}	11.584×10^{-4}	20.8×10^{-37}	$2.07 imes 10^{-2}$
R(1)	17472.330	2.4178×10^{12}	1.3005×10^{-4}	4.51×10^{-37}	2.16×10^{-2}
R(2)	17472.276	4.0235×10^{12}	11.584×10^{-4}	20.8×10^{-37}	$2.07 imes 10^{-2}$
R(9)	17470.271	1.4798×10^{13}	2.9105×10^{-4}	1.34×10^{-37}	$2.11 imes 10^{-2}$

Table E.21: The unused lines from band 17' - 2'' bromine (81,81)

P(J)	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$\mid R_e \mid^2$	$\Delta \nu \ cm^{-1}$
P(2)	17465.597	1.5480×10^{12}	2.0183×10^{-4}	3.09×10^{-37}	2.11×10^{-2}
R(J)	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
R(5)	17465.597	5.9624×10^{12}	2.0183×10^{-4}	3.09×10^{-37}	2.11×10^{-2}

Appendix F

Identified and unused lines of Band 18' - 2''

Table F.22: Band 18' - 2'' bromine (79,79)

P(J)	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_{e} ^{2}$	$\Delta \nu \ cm^{-1}$
P(53)	17477.072	1.7786×10^{13}	4.7254×10^{-4}	2.96×10^{-37}	$2.45 imes 10^{-2}$
P(54)	17473.334	1.0419×10^{13}	4.7261×10^{-4}	3.00×10^{-37}	2.41×10^{-2}
P(55)	17469.532	1.6935×10^{13}	3.6368×10^{-4}	2.40×10^{-37}	$1.99 imes 10^{-2}$
P(56)	17465.655	9.8985×10^{12}	5.8730×10^{-4}	$2.70 imes10^{-37}$	$2.25 imes 10^{-2}$
R(J)	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$\mid R_{e} \mid^{2}$	$\Delta \nu \ cm^{-1}$
R(56)	17476.356	9.8985×10^{12}	2.4532×10^{-4}	2.72×10^{-37}	2.09×10^{-2}
R(57)	17472.602	1.6054×10^{13}	3.4534×10^{-4}	$2.36 imes 10^{-37}$	2.09×10^{-2}
R(59)	17464.869	1.5152×10^{13}	3.2013×10^{-4}	$2.32 imes10^{-37}$	$1.88 imes 10^{-2}$

Table F.23: Band 18' - 2'' bromine (79,81)

P(J)	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
P(51)	17479.440	2.9630×10^{13}	7.1115×10^{-4}	2.62×10^{-37}	2.17×10^{-2}
P(52)	17475.897	2.9010×10^{13}	6.2008×10^{-4}	$2.06 imes 10^{-37}$	$2.02 imes 10^{-2}$
P(54)	17468.593	$2.7713 imes 10^{13}$	5.7247×10^{-4}	$2.31 imes10^{-37}$	1.88×10^{-2}
P(55)	17464.843	2.7041×10^{13}	5.7254×10^{-4}	2.37×10^{-37}	1.88×10^{-2}
R(J)	$\nu \ cm^{-1}$	N _{mv" J} "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
R(54)	17478.826	2.7713×10^{13}	5.5294×10^{-4}	2.19×10^{-37}	2.06×10^{-2}
R(55)	17475.257	2.7041×10^{13}	10.7176×10^{-4}	2.74×10^{-37}	2.51×10^{-2}
R(56)	17471.616	2.6356×10^{13}	6.9485×10^{-4}	2.89×10^{-37}	2.37×10^{-2}
R(57)	17467.919	2.5661×10^{13}	6.5901×10^{-4}	2.65×10^{-37}	2.21×10^{-2}
P(J)	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
--------------	-----------------	----------------------------------	-------------------------------	------------------------	------------------------
P(50)	17477.867	1.1775×10^{13}	2.2091×10^{-4}	2.14×10^{-37}	1.81×10^{-2}
P(52)	17470.934	1.1311×10^{13}	2.2259×10^{-4}	$2.25 imes10^{-37}$	2.22×10^{-2}
P(53)	17467.375	1.8845×10^{13}	3.6337×10^{-4}	$2.25 imes10^{-37}$	$1.98 imes 10^{-2}$
R(J)	$\nu \ cm^{-1}$	N _{mv" J} "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
R(53)	17477.315	$1.8445 imes 10^{13}$	$4.7498 imes 10^{-4}$	2.89×10^{-37}	1.79×10^{-2}
R(54)	17473.862	1.0816×10^{13}	$2.6044 imes 10^{-4}$	2.70×10^{-37}	1.88×10^{-2}
$R(55)^{-1}$	17470.360	1.7599×10^{13}	$3.4489 imes 10^{-4}$	$2.20 imes 10^{-37}$	$1.94 imes 10^{-2}$
R(56)	17466.783	1.0298×10^{13}	3.1334×10^{-4}	$2.89 imes10^{-37}$	$2.45 imes10^{-2}$

Table F.24: Band 18' - 2'' bromine (81,81)

Table F.25: The unused lines from band 18' - 2'' bromine (79,79)

R(J) .	νcm^{-1}	N _{mv} " _J "	$\int k_{ u} d u \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
R(58)	17468.766	9.3629×10^{12}	3.0098×10^{-4}	$3.53 imes 10^{-37}$	$2.35 imes 10^{-2}$

Table F.26: The unused lines from band 18' - 2'' bromine (79,81)

P(J)	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$\mid R_e \mid^2$	$\Delta \nu \ cm^{-1}$
P(53)	17472.276	$2.8370 imes 10^{13}$	11.5838×10^{-4}	20.8×10^{-37}	2.07×10^{-2}

Table F.27: The unused lines from band 18' - 2'' bromine (81,81)

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R(J)	$\nu \ cm^{-1}$	N _{mv" J} "	$\int k_{ u} d u \ cm^{-2}$	$\mid R_{e} \mid^{2}$	$\Delta \nu \ cm^{-1}$
R(51)	17474.434	$1.9245 imes 10^{13}$	5.2880×10^{-4}	3.14×10^{-37}	$2.22 imes 10^{-2}$

Appendix G

Identified and unused lines of Band 19' - 2''

Table G.28: Band 19' - 2'' bromine (79,79)

P(J)	$\nu \ cm^{-1}$	$N_{mv''J''}$	$\int k_{ u} d u \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
P(74)	17475.310	5.1682×10^{12}	0.3988×10^{-4}	2.74×10^{-37}	2.27×10^{-2}
P(75)	17469.938	8.2301×10^{12}	2.0805×10^{-4}	$2.80 imes 10^{-37}$	$2.31 imes 10^{-2}$
P(76)	17464.554	4.7136×10^{12}	2.6528×10^{-4}	2.01×10^{-37}	2.19×10^{-2}
R(J)	$\nu \ cm^{-1}$	N _{mv" J} "	$\int k_{ u} d u \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
R(76)	17478.640	4.7136×10^{12}	1.8104×10^{-4}	2.67×10^{-37}	2.32×10^{-2}
R(77)	17473.368	7.4919×10^{12}	$1.5832 imes10^{-4}$	3.00×10^{-37}	2.18×10^{-2}
R(78)	17467.982	4.2828×10^{12}	0.9802×10^{-4}	2.65×10^{-37}	$2.34 imes10^{-2}$

Table G.29: Band 19' - 2'' bromine (79,81)

P(J)	$\nu \ cm^{-1}$	$N_{mv''J''}$	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
P(73)	17477.024	1.4541×10^{13}	2.8446×10^{-4}	2.16×10^{-37}	2.03×10^{-2}
P(74)	17471.862	1.3917×10^{13}	3.1012×10^{-4}	2.46×10^{-37}	1.94×10^{-2}
P(75)	17466.607	1.3307×10^{13}	$3.0955 imes 10^{-4}$	$2.89 imes 10^{-37}$	2.00×10^{-2}
[R(J)]	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
R(76)	17475.257	1.2711×10^{13}	10.7176×10^{-4}	2.74×10^{-37}	2.51×10^{-2}
R(77)	17470.058	1.2131×10^{13}	2.4787×10^{-4}	2.34×10^{-37}	1.91×10^{-2}
R(78)	17464.769	1.1566×10^{13}	6.0178×10^{-4}	2.21×10^{-37}	1.91×10^{-2}

Appendix H

Identified and unused lines of Band 15' - 1''

Table H.30: Band 15' - 1'' bromine (79,79)

P(J)	$\nu \ cm^{-1}$	N _{mv" J"}	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_{e} ^{2}$	$\Delta \nu \ cm^{-1}$
P(57)	17476.913	7.5921×10^{13}	4.6382×10^{-4}	2.61×10^{-37}	$2.34 imes \overline{10^{-2}}$
P(58)	17473.141	4.4271×10^{13}	$2.5729 imes 10^{-4}$	$2.48 imes 10^{-37}$	$1.94 imes10^{-2}$
P(59)	17469.309	3.9268×10^{13}	2.3394×10^{-4}	$2.34 imes 10^{-37}$	$2.31 imes 10^{-2}$
P(60)	17465.411	4.1680×10^{13}	2.4221×10^{-4}	$2.42 imes 10^{-37}$	$2.09 imes 10^{-2}$
R(J)	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_{e} ^{2}$	$\Delta \nu \ cm^{-1}$
R(61)	17473.645	6.7295×10^{13}	3.8263×10^{-4}	2.10×10^{-37}	2.07×10^{-2}
R(63)	17465.929	6.2957×10^{13}	3.0085×10^{-4}	2.65×10^{-37}	2.23×10^{-2}

Table H.31: Band 15' - 1'' bromine (79,81)

P(J)	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
P(55)	17478.132	1.2671×10^{14}	6.4400×10^{-4}	2.27×10^{-37}	1.97×10^{-2}
P(56)	17474.530	1.2348×10^{14}	10.465×10^{-4}	2.82×10^{-37}	2.78×10^{-2}
P(57)	17470.882	1.2020×10^{14}	6.3559×10^{-4}	2.36×10^{-37}	$2.19 imes 10^{-2}$
P(58)	17467.161	1.1689×10^{14}	6.8468×10^{-4}	2.62×10^{-37}	2.20×10^{-2}
R(J)	$\nu \ cm^{-1}$	N _{mv" J} "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
R(58)	17478.691	1.1689×10^{14}	6.4681×10^{-4}	2.67×10^{-37}	$2.19 imes 10^{-2}$
R(59)	17475.099	1.1354×10^{14}	6.0241×10^{-4}	2.33×10^{-37}	1.97×10^{-2}
R(60)	17471.445	1.1017×10^{14}	5.5828×10^{-4}	2.23×10^{-37}	2.04×10^{-2}
R(61)	17467.732	1.0679×10^{14}	5.9345×10^{-4}	2.27×10^{-37}	$2.28 imes 10^{-2}$

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P(J)	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
P(53)	17478.874	8.5633×10^{13}	5.1914×10^{-4}	$2.71 imes 10^{-37}$	$2.36 imes 10^{-2}$
P(54)	17475.459	5.0208×10^{13}	2.7060×10^{-4}	2.41×10^{-37}	$2.22 imes 10^{-2}$
P(55)	17471.981	8.1681×10^{13}	4.0085×10^{-4}	$2.19 imes10^{-37}$	$2.08 imes10^{-2}$
P(56)	17468.441	4.7785×10^{13}	2.4417×10^{-4}	2.28×10^{-37}	$2.17 imes 10^{-2}$
P(57)	17464.839	7.7571×10^{13}	6.0178×10^{-4}	2.21×10^{-37}	1.91×10^{-2}
R(J)	$\nu \ cm^{-1}$	N _{mv" J} "	$\int k_{\nu} d\nu \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
R(56)	17479.455	4.7785×10^{13}	2.1641×10^{-4}	2.62×10^{-37}	$1.90 imes 10^{-2}$
R(58)	17472.572	4.5283×10^{13}	2.0538×10^{-4}	2.00×10^{-37}	$2.07 imes10^{-2}$
R(59)	17469.037	7.3353×10^{13}	3.7690×10^{-4}	2.78×10^{-37}	2.26×10^{-2}
R(60)	17465.438	4.2731×10^{13}	5.8411×10^{-4}	2.42×10^{-37}	2.11×10^{-2}

Table H.32: Band 15' - 1'' bromine (81,81)

Table H.33: The unused lines from band 15' - 1'' bromine (79,79)

1	R(J)	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{ u} d u \ cm^{-2}$	$ R_e ^2$	$\Delta \nu \ cm^{-1}$
	R(60)	17477.434	4.1680×10^{13}	4.3797×10^{-4}	4.41×10^{-37}	4.41×10^{-2}
	R(62)	17469.834	3.9074×10^{13}	1.6549×10^{-4}	1.78×10^{-37}	1.78×10^{-2}

Table H.34: The unused lines from band 15' - 1'' bromine (81,81)

R(J)	$\nu \ cm^{-1}$	N _{mv} " _J "	$\int k_{\nu} d\nu \ cm^{-2}$	$\mid R_e \mid^2$	$\Delta \nu \ cm^{-1}$
R(57)	17476.045	7.7571×10^{13}	1.5676×10^{-4}	$0.89 imes10^{-37}$	1.78×10^{-2}

State	Isotope	Band	F.C.F.
	$(79,79)Br_2$	14' - 1''	0.00509
	$(79, 81)Br_2$	14' - 1''	0.00408
	$(79,79)Br_2$	15' - 1''	0.00650
;	$(79, 81)Br_2$	15' - 1''	0.00621
	$(81, 81)Br_2$	15' - 1''	0.00594
$B^3\Pi_{o^+u}$	$(79,79)Br_2$	17' - 2''	0.02405
	$(79, 81)Br_2$	17' - 2''	0.02378
	$(81, 81)Br_2$	17' - 2''	0.02324
	$(79,79)Br_2$	18' - 2''	0.02487
· · ·	$(79, 81)Br_2$	18' - 2''	0.02478
•	$(81,81)Br_2$	18' - 2''	0.02429
	$(79,79)Br_2$	19' - 2''	0.02504
	$(79,81)Br_2$	19' - 2''	0.02511

Table H.35: The F.C.F. used for calculating $\mid R_{e} \mid^{2}$

Table H.36: The F.C.F.(^(79,79) Br_2) used for calculating τ_{rad}

Band	F.C.F.	Band	F.C.F.	Band	F.C.F.
14'-0"	0.00060	17'-0"	0.00144	15'-0"	0.00083
14'-1"	0.00509	17'-1"	0.00951	15'-1"	0.00650
14'-2"	0.01775	17'-2"	0.02405	15'-2"	0.02040
14'-3"	0.03145	17'-3"	0.02640	15'-3" [`]	0.03111
14'-4"	0.02639	`17'-4"	0.00812	15'-4"	0.01995
14'-5"	0.00543	17'-5"	0.00107	15'-6"	0.00126
14'-6"	0.00264	17'-6"	0.01531	15'-7"	0.00731
14'-7"	0.01859	17'-7"	0.01233	15'-8"	0.01958
14'-8"	0.01447	17'-8"	0.000016	15'-9"	0.00727
14'-9"	0.00018	17'-9"	0.01058	15'-10"	0.00133
14'-10"	0.01026	17'-10"	0.01235	15'-11"	0.01537

Isotope	Band	F.C.F.	Band	F.C.F.
	18'-0"	0.00180	19'-0"	0.00220
	18'-1"	0.00.99	19'-1"	0.01238
	18'-2"	0.02487	19'-2"	0.02504
	18'-3"	0.02273	19 '- 3"	0.01876
	18'-4"	0.00400	19'-4"	0.00137
$^{(79,79)}Br_2$	18'-5"	0.00358	19'-5"	0.00660
	18'-6"	0.01651	19'-6"	0.01571
	18'-7"	0.00726	19'-7"	0.00316
	18'-8"	0.00106	19'-8"	0.00391
	18'-9"	0.01339	19'-9"	0.01348
	18'-10"	0.00712	19'-10"	0.00263

Table H.37: The F.C.F. used for calculating τ_{rad}

Table H.38: The F.C.F.($^{(81,81)}Br_2$) used for calculating τ_{rad}

Band	F.C.F.	Band	F.C.F.	Band	F.C.F.
18'-0"	0.00164	17'-0"	0.00130	15'-0"	0.00074
18'-1"	0.01030	17'-1"	0.00884	15'-1"	0.00594
18'-2"	0.02429	17'-2"	0.02324	15'-2"	0.01931
18'-3"	0.02378	17'-3"	0.02712	15'-3"	0.03094
18'-4"	0.00525	17'-4"	0.00975	15'-4"	0.02173
18'-5"	0.00253	17'-5"	0.00048	15'-6"	0.00223
18'-6"	0.01608	17'-6"	0.01418	15'-7"	0.00565
18'-7"	0.00877	17'-7"	0.01384	15'-8"	0.01940
18'-8"	0.00041	17'-8"	0.00030	15'-9"	0.00927
18'-9"	0.01250	.17?-9"	0.00897	15'-10"	0.00048
18'-10"	0.00811	17'-10"	0.01326	15'-11"	0.01402

Band	F.C.F.	Band	F.C.F.	Band	F.C.F.
14'-0"	0.00056	17'-0"	0.00138	15'-0"	0.00079
14'-1"	0.00482	17'-1"	0.00924	15'-1"	0.00621
14'-2"	0.01714	17'-2"	0.02378	15'-2"	0.01985
14'-3"	0.03106	17'-3"	0.02684	15'-3"	0.03102
14'-4"	0.02715	17'-4"	0.00899	15'-4"	0.02091
14'-5"	0.00640	17'-5"	0.00071	15'-5"	0.00178
14'-6"	0.00198	17'-6"	0.01446	15'-6"	0.00635
14'-7"	0.01790	17'-7"	0.01314	15'-7"	0.01952
14'-8"	0.01551	17'-8"	0.00013	15'-8."	0.00835
14'-9"	0.00046	17'-9"	0.00976	15'-9"	0.00083
14'-10"	0.00914	17'-10"	0.01309	15'-10"	0.01472
14'-11"	0.01736	17'-11"	0.00045	15'-11"	0.01145
14'-12"	0.00327	17'-12"	0.00817	15'-12"	0.000001
14'-13"	0.00415	17'-13"	0.01255	15'-13"	0.01126
14'-14"	0.01662	17'-14"	0.00055	15'-14"	0.01296
14'-15"	0.00640	17'-15"	0.00766	15'-15"	0.00029
14'-16"	0.00155	17'-16"	0.01201	15'-16"	0.00896
14'-17"	0.01514	17'-17"	0.00044	15'-17"	0.01385
14'-18"	0.00930	17'-18"	0.00787	15'-18"	0.00092
14'-19"	0.00028	17'-19"	0.01164	15'-19"	0.00728
14'-20"	0.01324	17'-20"	0.00028	15'-20"	0.01451

Table H.39: The F.C.F.($^{(79,81)}Br_2$) used for calculating τ_{rad}

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Table H.40: The F.C.F. used for calculating τ_{rad}

Isotope	Band	FCF	Band	FCF
15000pc	Dunu	1.0.1.	101 01	1.0.1.
	18'-0"	0.00175	19'-0".	0.00215
	18'-1"	0.01076	19'-1"	0.01220
	18'-2"	0.02478	19'-2"	0.02511
	18'-3"	0.02334	19'-3"	0.01942
	18'-4"	0.00463	19'-4"	0.00174
	18'-5"	0.00298	19'-5"	0.00593
	18'-6"	0.01624	19'-6"	0.01578
$(79,81)Br_2$	18'-7"	0.00809	19'-7"	0.00378
	18'-8"	0.00068	19'-8"	0.00326
	18-9"	0.01297	19'-9"	0.01354
	18'-10"	0.00802	19'-10"	0.00331
1	18'-11"	0.00051	19'-11" -	0.00348
	18'-12"	0.01207	19'-12"	0.01254
	18'-13"	0.00715	19'-13"	0.00220

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