PULSED MOLECULAR BEAM CAVITY MICROWAVE FOURIER

TRANSFORM SPECTROSCOPY OF SOME FUNDAMENTAL VAN DER WAALS

DIMERS AND TRIMERS

ΒY

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ABSTRACT

The pure rotational spectra of several van der Waals dimers and trimers, namely $Ar-Cl_2$, Ne-Kr, Ne-Xe, Ar-Xe, Kr-Xe, Ne_2 -Kr and Ne_2 -Xe, as well as Ar_2 -OCS and Ar_2 -CO₂, have been investigated using a pulsed molecular beam cavity microwave Fourier transform spectrometer.

 $Ar-Cl_2$ has been found to have a T-shaped geometry dominated by pairwise additive forces, in contrast to the previously studied linear complex Ar-ClF. An effective van der Waals bond distance has been obtained, as well as an average vibrational angle for Cl_2 . This study has not only confirmed the structure obtained from electronic spectroscopy, but has also provided a reliable estimate of the ³⁵Cl nuclear quadrupole coupling constant in the free chlorine molecule.

In the microwave investigation of four mixed rare gas dimers, the newest available mixed rare gas pair potentials have been adjusted to obtain the equilibrium distances (r_e) between the rare gas atoms. The results have been compared with those obtained from isotopic data. It has been found that the present literature r_e values for these dimers had been underestimated in the order of 1~2%. The quadrupole coupling constants of ⁸³Kr and ¹³¹Xe have been determined for several different species containing these nuclei. The magnitudes of these constants are in the order of several hundreds of kHz, which are surprisingly large. The induced dipole moments are estimated to be in the order of 0.01 D.

Transitions of four isotopomers of ${}^{20}\text{Ne}_2$ -Kr and of six isotopomers of ${}^{20}\text{Ne}_2$ -Xe, all with C_{2v} symmetry, as well as two mixed isotopomers of ${}^{20}\text{Ne}{}^{22}\text{Ne}$ -Kr, have been measured. A recent theoretical model derived for such floppy systems has been used to obtain structural parameters. The structures, harmonic force constants, ${}^{83}\text{Kr}$ and ${}^{131}\text{Xe}$ nuclear quadrupole coupling constants and dipole moments have been compared with the corresponding parameters of the dimers. Possible nonpairwise additive contributions to these properties have been deduced from deviations of the experimental values from those obtained from corresponding dimers assuming pairwise additivity.

The complexes Ar_2 -OCS and Ar_2 -CO₂ have been found to have distorted tetrahedral geometries (C_s and C_{2V} symmetry, respectively), with the linear molecule lying in the symmetry plane. Harmonic force field analyses have been performed for Ar_2 -OCS and Ar_2 -CO₂. The structures and force constants obtained indicate a dominance of pairwise additivity. The basic geometric trend in Ar_2 -molecule trimers is discussed.

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CHAPTER 1

Introduction

This thesis is concerned with the measurement and analysis of microwave pure rotational spectra of weakly bound van der Waals complexes. The spectra of the complexes have been measured using a cavity pulsed molecular beam microwave Fourier transform (MWFT) spectrometer. The underlying aim is to provide information on the weak interactions between the atoms and the molecules comprising these complexes.

Weak intermolecular interactions have received considerable attention in recent years and their study is a field of growing experimental and theoretical activity [1,2]. Such weak interactions are responsible for various physical and biological phenomena, ranging from gas imperfections, and condensation and solidification of matter [3], to the unique folded structures of polypeptide chains in proteins [4] in much more sophisticated in vivo molecular systems. Furthermore, computer simulation of molecular dynamics, widely used in bio-science and chemistry [5], is a rapidly advancing field. Such simulations are important to increase our knowledge of the nature of complex chemical and biochemical processes as well as of complex molecules, especially for systems which are not amenable to direct measurements. However, the success of the simulation approach relies on our knowledge of weak

intermolecular interactions and on the correctness of the potentials used.

Speculation concerning the origin and the form of intermolecular interactions goes back to as early as the beginning of the twentieth century [6]. But it was not until the establishment of the principles of quantum mechanics that a basic understanding of the nature of intermolecular forces was developed in the 1930s [3]. It took another 40 years for a reasonably precise description of the forces, i.e. potential energy curves, to be obtained for even the simplest systems, namely pairs of rare gas atoms [7].

Weak intermolecular interactions, in general, include both long-range attractive forces, such as electrostatic forces (between permanent multipoles), induction and dispersion forces, and short-range repulsive forces [3]. The hydrogen bond, as a special case, is now generally accepted as being due mainly to electrostatic interactions with significant overlap effects, after many years of controversy [8]. It may seem surprising at first, yet is important to note, that the dispersion energy usually makes the major contribution to the attractive energy, with the only exception being for small, highly polar molecules such as water, where it is the hydrogen bond which makes the major contribution [9]. The induction energy on the other hand, is almost always small, unless one or more of the interacting species is charged [9].

A decade ago, information about the potential energy surfaces of van der Waals complexes was dominated by results from "bulk" phase experiments such as second virial coefficients, gas transport properties, and energies of crystallization of rare gases, and by results from molecular beam scattering experiments [3]. Because properties of dense systems are influenced by multi-body interactions, approximations had to be made to extract information about the binary systems from these "bulk" experiments. This was difficult, because current knowledge about many-body nonpairwise additive contributions [10] is far from satisfactory [11]. On the other hand, although molecular beam scattering experiments seemed to show promise for success in determining potential energy surfaces, these experiments are in general very difficult for heavier systems, and the majority of experiments has been done on very light systems such as He, H₂ and Ne [12,13].

Recent developments in high resolution spectroscopy in the microwave (MW), infrared (IR) and far infrared (FIR) regions, combined with the use of seeded molecular beams, have led to a breakthrough in the experimental study of weak intermolecular interactions [14,15,16]. One advantage is that such studies provide detailed information about intrinsic properties of the *isolated* gas phase complexes, such as van der Waals dimers,

trimers, and larger clusters.* Perturbations caused by solvent and lattice interactions, which are unavoidable in dense systems, are absent. This makes it possible to use spectroscopic data directly, to construct the potential energy surfaces and to compare the experimental data with theoretical calculations.

The recent rapid progress in this field, resulting to a large degree from cooperation between experimentalists and theoreticians, is reflected by the fact that the number of publications related to van der Waals complexes has doubled every 2.1 years since 1980 [15]. The experimental work in the MW and IR ranges prior to 1988 has been summarized by Novick, Leopold and Klemperer [17], followed by a review by Klemperer and Yaron on the current problems and the future prospects of the experimental aspects of this field [18]. High resolution infrared spectroscopy of weakly bound complexes has been reviewed by Nesbitt [15]. The corresponding theoretical work has been reviewed by Buckingham, Fowler, and Hutson [19] and by Hutson [20]. Most recently, some prospects for far infrared probing of van der Waals complexes have been reviewed by Saykally and Blake [16].

^{*} It should be noted that binary (e.g. Ar-HCl) and ternary (e.g. Ar_2 -HCl) systems are sometimes referred to as "dimers" and "trimers" in this thesis, as is commonly done in publications of this field.

Current knowledge of potential energy surfaces of interatomic and intermolecular interactions in *dimers* is growing rapidly, even though we are still far away from the ultimate goal of predicting the properties of any system simply by solving the Schrödinger equation. For example, homonuclear rare gas dimer potentials are fairly precisely known: any properties of these systems can be derived from their potential energy curves with an uncertainty of up to only a few percent [21]. For more complicated systems, atom-diatom interactions are the best understood. For example, Ar-HCl has been extensively studied using high resolution microwave [22], far infrared [23] and near infrared [24] spectroscopy to provide sufficient data for a full dimensional potential energy surface to be determined [25]. The potential energy surface for Ar-HCl has been repeatedly revised [26] and improved [25] to become one of the best quantitatively determined surfaces. It has survived some rigorous tests, mainly imposed by new far infrared measurements, although the part of the potential energy surface concerning the secondary minimum is still not quantitatively well represented [16]. Detailed information on dimer potential energy surfaces dwindles dramatically, however, from rare gas dimer systems to larger molecular systems. For example, for slightly larger binary systems such as Ar-H₂O and Ar-NH₃, only qualitative details of the potential energy surfaces are

well established [16].

The current goal in this field is to understand not only binary interactions, but also three and more-body interactions [3]. Knowledge of many-body interactions is essential for understanding properties of condensed phase systems in terms of pairwise additive binary potentials, by considering three and more-body interactions as a perturbation [3]. The possibility of spectroscopic determination of many-body contributions to cluster properties depends on the small discrepancies between the experimentally measured properties from those predicted using a pairwise additive calculations. Clearly, in order to attribute the small discrepancies to many-body effects, not only binary interaction potentials must be known to a very high degree of accuracy, but also pairwise additive calculations on larger systems need to be as rigorous as possible; furthermore, accurate quantitative experimental data on *isolated* trimers and larger clusters, provided by high resolution spectroscopy, are unequivocally necessary.

It was only five years ago that high resolution spectroscopy was first applied to larger van der Waals clusters such as trimers and tetramers [17]. Pioneering work on microwave rotational spectroscopy of larger clusters was carried out by Gutowsky and co-workers [27], followed by the recent near IR and FIR investigations on such systems by Nesbitt and co-workers [28], and by

Saykally and co-workers [29]. One of the experimentally and theoretically best studied trimer systems so far is Ar2-HCl. A series of FIR investigations by Elrod et al. [29], along with a microwave study [27], has provided much spectroscopic information. In a parallel theoretical treatment, Cooper and Hutson [30] pointed out the possibility of three-body nonpairwise additive contributions, and attempted to calculate some of these contributions theoretically. However, they encountered several problems. First, intensive computing is needed for the pairwise calculation using a full-dimensional treatment [30], since the cheaper adiabatic separation [31] has been found to be inadequate for Ar₂-HCl. Secondly, the theory dealing with many-body interactions has been developed mostly for atomic systems [32] and has not yet been well established for molecular systems [30]. Therefore approximations were needed in the case of Ar,-HCl [30].

Theoreticians have shown considerable interest for several decades in simpler and more fundamental systems such as dimers and trimers containing only rare gas atoms [33], as well as atom-homonuclear diatom complexes [34]. The problem with using these species to investigate interatomic and intermolecular forces has been a lack of experimental spectroscopic data, largely because the required transition moments are nearly prohibitively small.

This thesis presents data which overcome part of this problem, in the form of microwave rotational spectra of several very fundamental systems. These systems include both van der Waals dimers and trimers, namely $Ar-Cl_2$, Ne-Kr, Ne-Xe, Ar-Xe, Kr-Xe, Ne_2-Kr, Ne_2-Xe, Ar_2-OCS and Ar_2-CO_2 , which have been investigated using a cavity pulsed molecular beam MWFT spectrometer. None of these complexes had been previously studied in the microwave region; no high resolution spectra of any kind had been investigated previously for the four trimers. Most of these complexes have extremely low electric dipole moments, making them a challenging experimental problem in microwave spectroscopy.

Discussion of these complexes is presented in Chapters 4-7. Although the complexes in each individual chapter are somewhat independent, with the specific interesting points discussed in the introduction of each chapter, they are also connected in a general way. Chapter 4 describes the microwave investigation of the low dipole moment atom-homonuclear diatom dimer Ar-Cl₂. The geometry of Ar-Cl₂ has been found to be T-shaped dominated by pairwise additivity, which is in contrast to the previously studied linear complex Ar-ClF [35]. It is presented as the first complex in this thesis because the experimental experience from the study of this dimer was essential to the later investigation of other low dipole moment complexes, particularly those containing only rare

gas atoms.

The following three chapters present a series of investigations of complexes ranging from the simplest rare gas dimers (Ne-Kr, Ne-Xe, Ar-Xe and Kr-Xe) to two rare gas trimers (Ne2-Kr and Ne2-Xe), and eventually to more complicated trimers containing molecular subunits (Ar₂-OCS and Ar₂-CO₂). Chapter 5 focuses on the properties of the mixed rare gas dimers, especially their equilibrium internuclear distances, as well as such properties as the quadrupole coupling constants of ⁸³Kr and ¹³¹Xe nuclei and the induced dipole moments. It was found that the literature equilibrium distances for these dimers, which had been obtained from "bulk" properties, had been underestimated in the order of 1~2%. Such differences, although small, would have significant impact in any subsequent many-body nonpairwise additive study, where a nonpairwise additive contribution is usually a very small fraction of the pairwise contribution.

The microwave spectroscopy of the mixed rare gas van der Waals trimers Ne_2 -Kr and Ne_2 -Xe is described in Chapter 6. The geometries of these two trimers have been established using various isotopic data. Information about their structures and dipole moments, as well as nuclear quadrupole coupling constants of ⁸³Kr and ¹³¹Xe have been obtained. This study provides high resolution data, which are essential in the determination of the

three-body nonpairwise additive effects.

Chapter 7 describes the spectra of a new series of rare gas-small molecule van der Waals trimers, namely Ar_2 -OCS and Ar_2 -CO₂. The basic geometric trend in Ar_2 -molecule trimers is discussed. This work provides more complicated and challenging problems for future theoretical calculations.

Each study involved a large amount of spectral measurement and analysis. To assist the reader in locating these results, the tables in this thesis are presented at the end of each chapter. It should be noted, however, that the figures are placed in the text near the point where they are first cited.

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CHAPTER 2

Theory

This chapter summarizes briefly some of the basic theory used to analyze the spectra and to obtain the molecular parameters reported in this thesis. Although this theory has not been developed as part of the thesis research, it is presented to familiarize the reader with the notation used in the following chapters.

First, some theory relevant to the assignment and analysis of pure rotational spectra is outlined. The topics include: (1) the semirigid rotor model; (2) nuclear quadrupole hyperfine structure; (3) structural information from rotational constants; (4) harmonic force field analysis. They are treated in detail in several text books [1,2]. Although these treatments have been developed for "normal" chemically bonded systems, they have also been applied to van der Waals complexes in the majority of recent publications [3].

Secondly, some basic theoretical aspects of pulsed excitation experiments are also briefly summarized in this chapter.

Theoretical aspects of the dynamics of van der Waals complexes in terms of their intermolecular potential energy surfaces are a rapidly developing field [4]. Some of the most recent theoretical results will be compared with the experimental results presented in the following

chapters. However, because the theories underlying those calculations are not tightly connected with the thesis work presented here, and are out of the scope of this work, they will not be summarized here. The reader is referred to some introductory books on this field [5] and to some review articles [6].

2.1 Energy levels of asymmetric rotors

For a rigid rotor in its principal inertial axes system, the Hamiltonian for the rotational energy levels can be written as:

$$\mathcal{H}_{R} - A \boldsymbol{P}_{a}^{2} + B \boldsymbol{P}_{b}^{2} + C \boldsymbol{P}_{c}^{2}$$
(2.1)

where P_{a} , P_{b} and P_{c} are the components of the total rotational angular momentum vector P with respect to the molecule fixed axes. A, B and C are the rotational constants, which are related to the principal moments of inertia I_{g} by G (A, B or C)=h/($8\pi^{2}I_{g}$) with g=a, b or c. Here a, b and c are the principal inertial axes, chosen so that A>B>C. The rotational constants are in frequency units.

Rigid rotors are generally classified into several different types:

| (1) | linear molecules | $I_a=0, I_b=I_c (A \rightarrow \infty, B=C);$ |
|-----|------------------|---|
| (2) | spherical tops | $I_a = I_b = I_c$ (A=B=C); |

| (3) | prolate symmetric tops | $I_a < I_b = I_c$ | (A>B=C); |
|-----|------------------------|---|----------|
| (4) | oblate symmetric tops | $I_a = I_b < I_c$ | (A=B>C); |
| (5) | asymmetric tops | I _a <i<sub>b<i<sub>c</i<sub></i<sub> | (A>B>C); |

The range of B values between A and C corresponds to various conditions of asymmetry, which can be denoted by asymmetry parameters. For example, Ray's asymmetry parameter, κ , is defined as [7]:

$$\kappa = \frac{2B - A - C}{A - C}$$
(2.2)

ranging from -1 to 1, corresponding to the prolate and oblate symmetric top limits, respectively.

By solving the Schrödinger equation, one can obtain the corresponding rotational energy levels of a rigid rotor. For example, a linear rigid rotor has rotational energies $E_R=BJ(J+1)$; while prolate symmetric tops correspond to $E_R=BJ(J+1)+(A-B)K^2$ and oblate symmetric tops to $E_R=BJ(J+1)+(C-B)K^2$ [8]. Here J and K are quantum numbers, with J denoting the total rotational angular momentum, and K representing the projection of J onto the molecular axis; K can take integer values from -J to J. Any state of an isolated rigid symmetric top can be described by the quantum numbers J and K, and the corresponding wavefunction may be denoted by |J,K> in bra-ket notation. There is a third quantum number, M_J , representing the component of J along the space fixed Z axis; it has no effect on rotational energies in the absence of external fields.

However, for an asymmetric top, such closed form expressions for rotational energy levels no longer exist [8]. An asymmetry splits the levels $|J,\pm K\rangle$, which are degenerate for symmetric tops. Although the total angular momentum P is a constant of motion and J is still a "good" quantum number which can be used to specify the state of the rotor, K is no longer a "good" quantum number and cannot specify the rotational state very well. Instead $|J, K_a, K_c >$ or $|J, \tau >$ are used to denote the wavefunctions of asymmetric rotors, with K_a and K_c being the |K| values in the limiting prolate and oblate symmetric top cases, and $\tau = K_a - K_c$. The common notation is to designate the levels as $J_{Ka,Kc}$ (e.g. $1_{0,1}$, $7_{3,5}$, …). For an asymmetric top, the energies of rotational levels can be obtained by directly diagonalizing the rigid rotor energy matrix expressed in a basis set of symmetric top wavefunctions |J,K>. The non-zero matrix elements, in the I^r representation [9], which is usually chosen for prolate asymmetric tops, are:

$$\langle J, K | \mathcal{H}_{R} | J, K \rangle = \frac{1}{2} (B+C) J (J+1) + [A - \frac{1}{2} (B+C)] K^{2}$$
 (2.3)

$$\langle J, K \pm 2 | \mathcal{H}_{R} | J, K \rangle = \frac{1}{4} (B-C) \{ [J(J+1) - K(K\pm 1)] \times [J(J+1) - (K\pm 1)(K\pm 2)] \}^{\frac{1}{2}}$$
 (2.4)

For very flexible systems such as the van der Waals complexes studied in this thesis, the simple rigid rotor model cannot accurately describe even low J transitions. Extra terms such as quartic and sextic centrifugal distortion terms [10,11] are needed for an adequate analysis of the rotational spectra of these systems. One of the most commonly used rotational Hamiltonians, including both quartic and sextic distortion terms, in Watson's A-reduction, I^r representation can be written as [11]:

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_{R} + \mathcal{H}_{D} + \mathcal{H}_{D'} \\ \mathcal{H}_{R} &= A P_{a}^{2} + B P_{b}^{2} + C P_{c}^{2} \\ \mathcal{H}_{D} &= -\Delta_{J} P^{4} - \Delta_{JK} P^{2} P_{a}^{2} - \Delta_{K} P_{a}^{4} - 2\delta_{J} P^{2} (P_{b}^{2} - P_{c}^{2}) \\ &= \delta_{K} \{ [P_{a}^{2} (P_{b}^{2} - P_{c}^{2}) + (P_{b}^{2} - P_{c}^{2}) P_{a}^{2}] \} \end{aligned}$$
(2.5)
$$\begin{aligned} \mathcal{H}_{D'} &= H_{J} P^{6} + H_{JK} P^{4} P_{a}^{2} + H_{KJ} P^{2} P_{a}^{4} + H_{K} P_{a}^{6} + h_{J} P^{4} (P_{b}^{2} - P_{c}^{2}) \\ &= 2^{2} (P_{b}^{2} - P_{c}^{2}) - (P_{a}^{2} - P_{c}^{2}) - (P_{b}^{2} - P_{c}^{2}) - (P_{b}^{2} - P_{c}^{2}) \end{aligned}$$

$$+ h_{JK} \mathbf{P}^{2} [\mathbf{P}_{a}^{2} (\mathbf{P}_{b}^{2} - \mathbf{P}_{c}^{2}) + (\mathbf{P}_{b}^{2} - \mathbf{P}_{c}^{2}) \mathbf{P}_{a}^{2}]$$

$$+ h_{K} [\mathbf{P}_{a}^{4} (\mathbf{P}_{b}^{2} - \mathbf{P}_{c}^{2}) + (\mathbf{P}_{b}^{2} - \mathbf{P}_{c}^{2}) \mathbf{P}_{a}^{4}]$$

The matrix elements of \mathfrak{H}_{D} and \mathfrak{H}_{D} , can be evaluated in a rigid symmetric top basis in a similar fashion as those of \mathfrak{H}_{R} . The non-zero elements are, in the I^r representation [11]:

$$\langle \mathbf{J}, \mathbf{K} | \mathbf{\mathcal{H}}_{\mathrm{D}} + \mathbf{\mathcal{H}}_{\mathrm{D}'} | \mathbf{J}, \mathbf{K} \rangle = -\Delta_{\mathrm{J}} \mathbf{J}^{2} (\mathbf{J}+1)^{2} - \Delta_{\mathrm{JK}} \mathbf{J} (\mathbf{J}+1) \mathbf{K}^{2} - \Delta_{\mathrm{K}} \mathbf{K}^{4} + H_{\mathrm{J}} \mathbf{J}^{3} (\mathbf{J}+1)^{3} + H_{\mathrm{JK}} \mathbf{J}^{2} (\mathbf{J}+1)^{2} \mathbf{K}^{2} + H_{\mathrm{KJ}} \mathbf{J} (\mathbf{J}+1) \mathbf{K}^{4} + H_{\mathrm{K}} \mathbf{K}^{6}$$

$$\langle \mathbf{J}, \mathbf{K} \pm 2 | \mathbf{\mathcal{H}}_{\mathrm{D}} + \mathbf{\mathcal{H}}_{\mathrm{D}'} | \mathbf{J}, \mathbf{K} \rangle = \{ -\delta_{\mathrm{J}} \mathbf{J} (\mathbf{J}+1) - \frac{1}{2} \delta_{\mathrm{K}} [(\mathbf{K} \pm 2)^{2} + \mathbf{K}^{2}] + h_{\mathrm{J}} \mathbf{J}^{2} (\mathbf{J}+1)^{2} + \frac{1}{2} h_{\mathrm{JK}} (\mathbf{J}+1) [(\mathbf{K} \pm 2)^{2} + \mathbf{K}^{2}] + \frac{1}{2} h_{\mathrm{K}} [(\mathbf{K} \pm 2)^{4} + \mathbf{K}^{4}] \}$$

$$(2.6)$$

× {
$$[J(J+1) - K(K\pm 1)] [J(J+1) - (K\pm 1) (K\pm 2)] \}^{\frac{1}{2}}$$
(2.7)

A complete diagonalization to obtain the semirigid rotor energy levels can easily be done on a personal computer. Several such programs have been used in this thesis work, and their sources have been documented in each specific case.

Transitions between the rotational energy levels $|J, K_a, K_c \rangle$ and $|J', K_a', K_c' \rangle$ require the presence of an electric dipole moment. For any rotor, these transitions are governed by the selection rules $\Delta J=0$, ± 1 . Furthermore, for an asymmetric rotor, the dipole moment may in general lie in any arbitrary direction with respect to the principal inertial axes. Additional selection rules connected with its nonzero components along the three axes result:

a-type transitions: $K_a, K_c-K_a^{!}, K_c^{!} = ee-eo$, oo-oe; b-type transitions: $K_a, K_c-K_a^{!}, K_c^{!} = ee-oo$, eo-oe; c-type transitions: $K_a, K_c-K_a^{!}, K_c^{!} = ee-oe$, oo-eo. with e and o denoting even and odd quantum numbers,

lac ac

respectively.

2.2 Nuclear quadrupole hyperfine structure

A nucleus with a spin I greater than 1/2 possesses a nuclear electric quadrupole moment eQ, which can interact with the electric charge distribution surrounding the nucleus. The interaction energy will be zero in case of a spherically symmetric electric charge distribution around the nucleus, for example in case of an isolated rare gas atom, since there is no preferred orientation for the quadrupolar nucleus. However, when such a spherical symmetric charge distribution is distorted upon chemically bonding with other atoms, or through weak van der Waals interactions, different energies connected with different orientations of the quadrupolar nucleus result.

Quantum mechanically, such phenomena can be described as the coupling between the rotational angular momentum J with the nuclear spin angular momentum I to give a total angular momentum F: F=J+I, where the quantum number F ranges from J+I to |J-I|. Each rotational energy level is split into 2I+1 (if J \geq I) or 2J+1 (if J \leq I) hyperfine levels. Transitions between these hyperfine levels are governed by the additional selection rule $\Delta F=0, \pm 1$. This results in a splitting of a rotational transition into a hyperfine pattern. The Hamiltonian describing such interaction can be written as the scalar product of two second rank tensors, the electric nuclear quadrupole moment Q and the electric field gradient ∇E at the site of the quadrupolar nucleus [12]:

$$\mathcal{H}_{Q} - -\frac{1}{6} \mathbf{Q} : \nabla \mathbf{E} - \frac{1}{6} \sum_{i,j=x,y,z} Q_{ij} V_{ij}$$
(2.8)

where $V_{ij} = -\nabla E_{ij}$. For a rotating molecule, this can be rearranged to give as the classical interaction energy [12]:

$$E_{\text{quad}} = \frac{1}{4} eQ \left(\frac{\partial^2 V}{\partial Z^2} \right)_o \qquad (2.9)$$

where eQ is the quadrupole moment of the nucleus defined by $\int \rho (3Z^2 - r^2) d\tau$, where ρ is the charge density of the nucleus, and $(\partial^2 \nabla / \partial Z^2)_o$ is the field gradient along a space-fixed Z axis at the nucleus. The classical energy expression is transformed to quantum mechanics *via* the Wigner-Eckart theorem [13]. The matrix elements of the quadrupolar Hamiltonian \mathcal{H}_o are written in terms of the basis set $|J,i,I,F,M_F\rangle$ with i denoting any inner quantum numbers such as K_a, K_c or τ . For linear or symmetric top molecules, both the diagonal matrix elements $\langle J,K,M_J=J|\mathcal{H}_o|J,K,M_J=J\rangle$ [14] and the off-diagonal matrix elements $\langle J,K,M_J=J|\mathcal{H}_o|J+2,K,M_J=J\rangle$ [15], can be evaluated explicitly and can be expressed in a closed form [12]. Matrix elements off diagonal in K exist for symmetric tops, but will not be discussed here. For the more general case of asymmetric rotors, the non-vanishing matrix elements of \mathfrak{H}_{0} have been evaluated by Bragg [16]:

with $V_{ZZ}=(\partial^2 V/\partial Z^2)_o$. $M_J=J$ indicates the maximum projection of **J** along a *space*-fixed axis. C_o , C_1 and C_2 are constants and are functions of I, J and F. Since the matrix is Hermitian, the matrix elements for J'=J-1 and J'=J-2 may also be obtained from these expressions.

 V_{ZZ} is the ZZ-component of the field gradient expressed in terms of *space*-fixed axes. This quantity can be related to the *molecule*-fixed components V_{gg} , along the principal inertial axes with g,g'=a,b,c:

$$V_{ZZ} = \sum_{\substack{g,g'-\\a,b,c}} V_{gg'} \phi_{Zg} \phi_{Zg'}$$

= $V_{aa} \phi_{Za}^{2} + V_{bb} \phi_{Zb}^{2} + V_{cc} \phi_{Zc}^{2} + 2V_{ab} \phi_{Za} \phi_{Zb}$
+ $2V_{ac} \phi_{Za} \phi_{Zc} + 2V_{bc} \phi_{Zb} \phi_{Zc}$ (2.11)
where ϕ_{Zg} and $\phi_{Zg'}$ are the direction cosines which relate the Z axis of the space fixed system to the a,b and c axes of the molecule fixed system; $V_{gg'}$ are the field gradients with reference to the principal inertial axes, and are to a high order of approximation, independent of molecular rotational state.

Conventionally, the nuclear quadrupole coupling constants are designated by $\chi_{gg'}$ with $\chi_{gg'}=eQV_{gg'}$. It should be noted that for the three diagonal terms $\chi_{gg'}$, Laplace's equation holds, and $\chi_{aa}+\chi_{bb}+\chi_{cc}=0$. Thus there are only two independent variables; the final constants for this part are usually expressed in terms of χ_{aa} and $(\chi_{bb}-\chi_{cc})$.

The first order perturbation values of the quadrupole coupling constants can be evaluated in the basis set of the unperturbed rotor $|J,i,M_{j}\rangle$. As a result, the off-diagonal elements, involving $\phi_{Zg}\phi_{Zg'}$ (g≠g') are identically zero, leaving the quadrupole matrix diagonal with only χ_{gg} in the diagonal terms [12]. The hyperfine splitting thus generated is called a "first order pattern".

However, deviations from first order behaviour have been observed in some cases, for example for a nucleus with a large nuclear quadrupole moment Q. Furthermore, with the much higher resolution (FWHH~7kHz [17]) and sensitivity of MWFT spectrometers, compared with those of conventional Stark modulated instruments (FWHH typically ~100kHz), even small deviations from "first order patterns" for a moderate eQ nucleus can easily be detected and need to be accounted for [Chapter 4]. One approach is to use higher order perturbation theory [12]. Another approach is to include all terms in the matrix elements and to employ a complete diagonalization procedure for a matrix which is diagonal only in F and M_F . The second approach has been used in this thesis work using Dr.H.M.Pickett's SPCAT and SPFIT programs [18].

Symmetry considerations can be used to decide which terms of the matrix elements are non-vanishing. Nonvanishing contributions to \mathcal{H}_{q} will appear whenever the direct product of the symmetries of $|J, K_{a}, K_{c} >$, $|J', K_{a}', K_{c}' >$, ϕ_{2g} and $\phi_{2g'}$ belong to the representation A of the Four-group, D_{2} , whose character table is the following:

| D ₂ | E | C ₂ a | C ₂ ^b | C ₂ c | K _a K _c |
|----------------|---|------------------|-----------------------------|------------------|-------------------------------|
| A | 1 | 1 | 1 | 1 | ee |
| B _a | 1 | 1 | -1 | -1 | eo |
| В _ь | 1 | -1 | 1 | -1 | 00 |
| B _c | 1 | -1 | -1 | 1 | oe |

For an asymmetric rotor, the non-zero elements are related to the parities of K_a and K_c as follows:

non-vanishing terms in

 $\begin{array}{cccc} \chi_{aa}, \ \chi_{bb}, \ \chi_{cc} & ee-ee, \ oo-oo, \ eo-eo, \ oe-oe \\ \chi_{ab} & ee-oe, \ eo-oo \\ \chi_{ac} & ee-oo, \ eo-oe \\ \chi_{bc} & ee-eo, \ oe-oo \end{array}$

It can be seen from the above that off-diagonal elements in τ (or K_a, K_c) will appear for symmetry reasons, with additional selection rule: $\Delta F=0$ and $\Delta J=0$, ± 1 , ± 2 .

There are many cases where there are more than one quadrupolar nucleus in a molecule or a complex. For example, Ar-Cl₂, studied in this thesis (Chapter 4), has two quadrupolar chlorine nuclei. In this case, two coupling schemes are possible:

(1) $\mathbf{F}_1 = \mathbf{J} + \mathbf{I}_1$; $\mathbf{F} = \mathbf{F}_1 + \mathbf{I}_2$; with \mathbf{F}_1 taking integers or half integers from $\mathbf{J} + \mathbf{I}_1$ to $|\mathbf{J} - \mathbf{I}_1|$, and F taking integers or half integers from $\mathbf{F}_1 + \mathbf{I}_2$ to $|\mathbf{F}_1 - \mathbf{I}_2|$;

or (2) $I=I_1+I_2$; F=J+I; with I ranging from I_1+I_2 to $|I_1-I_2|$, and F from J+I to |J-I|.

Since a complete diagonalization program was employed in this work, the final result is the same for these two coupling schemes. The latter one has some advantage for identical nuclei, such as in case of $Ar-Cl_2$ described in Chapter 4, since it allows one to consider the symmetry of the nuclear spin wavefunctions. The problem for any number of coupling nuclei was studied in detail by

K_aK_c-K'K'

Thaddeus et al. [19], who expressed the matrix elements of \mathcal{H}_{q} in terms of 6j Wigner coefficients [20], which are tabulated [21].

2.3 Structural information from rotational spectra

Microwave spectroscopy is one of the most widely used methods to provide accurate structural information of small to medium sized molecules in the gas phase. However, there are limitations. For example, it is usually necessary to observe spectra of several isotopomers in order to determine complete molecular geometries. Also, molecular vibrational effects are often difficult to account for in the determination of structural parameters.

In general, four types of geometrical parameters, designated r_o , r_s , r_{av} (or r_z) and r_e , are most often encountered in microwave spectroscopy. These are the effective ground vibrational state, substitution, ground state average, and equilibrium structures, respectively, and have different physical meanings. Detailed discussion on how to extract structural information from microwave spectra for chemically bonded systems can be found in Ref.[2]. There have also been several reviews on the relationships between the different structural parameters [22].

However, it should be pointed out that for the very weakly bonded and flexible van der Waals complexes investigated in this thesis work such structural concepts do not always apply in a straightforward fashion. This is because of the very low dissociation energies, which are in general about 100 times smaller than those of normal chemical bonds, and because of the very large vibrational amplitudes involved [5]. The structures derived by applying some conventional microwave structural approximations should therefore be treated with caution. The details are discussed in later chapters separately for each individual complex studied here. It should also be pointed out that van der Waals complexes are considered dynamic entities, which are perhaps more appropriately characterized by their potential energy surfaces rather than by application of conventional structural concepts [23]. Determination of potential energy surfaces, however, would require additional data about vibrational transitions which are not yet available for the systems studied here.

The following considerations apply to most chemically bonded systems.

In a rigid rotor approximation, the principal moments of inertia are defined as: where I_a , I_b and I_c are the principal moments of inertia as defined before; m_i is the mass of the *i*th atom; a_i , b_i

$$I_{a} = \sum_{i} m_{i} (b_{i}^{2} + c_{i}^{2})$$

$$I_{b} = \sum_{i} m_{i} (c_{i}^{2} + a_{i}^{2})$$

$$I_{c} = \sum_{i} m_{i} (a_{i}^{2} + b_{i}^{2})$$
(2.12)

and c_i are the coordinates of the *i*th atom along the principal moment of inertia axes.

One way to extract structural information is to utilise directly the rotational constants obtained from rotational spectra in the ground vibrational state. The structure thus obtained is called an effective, or r_o , structure. For a simple diatomic molecule, there is enough information to calculate the structure for each isotopomer. However, for more complicated molecules, extra isotopic data are usually necessary to determine the structure. In these cases, a least squares procedure can be used to fit the r_o structural parameters to the observed principal moments of inertia of a sufficient number of isotopic species [24]. Such a procedure neglects zero-point vibrational effects by assuming that the r_o parameters are the same for different isotopic species.

Neglect of zero-point vibrational effects severely limits the accuracy of the r_o structural parameters obtained. For example, for a planar molecule, the inertial defect is defined as: where v denotes the specific vibrational state. Δ_o would

$$\Delta_{v} = I_{c}^{v} - I_{b}^{v} - I_{a}^{v} \qquad (2.13)$$

be automatically zero if the molecule were rigid. But this is not the case for a real molecule. Δ_0 is usually a small positive value ranging from 0.05 to 0.2 amu Å² for a planar molecule in its ground vibrational state [25]. Although this residual is relatively small compared to the moments of inertia, it can cause variations in the bond lengths as large as 0.01 Å when different pairs of principal moments of inertia are used [24]. This discrepancy would be expected to be even larger in the case of van der Waals complexes, such as in the case of Ne₂-Kr (described in Chapter 6), where Δ_0 is in the order of 6.8 amu Å².

The contributions to Δ can be written as [26]:

$$\Delta = \Delta_{\rm vib} + \Delta_{\rm cent} + \Delta_{\rm elec}$$
(2.14)

where Δ_{vib} , Δ_{cent} , and Δ_{elec} are contributions of vibration, centrifugal distortion and electronic effects to the inertial defect Δ . For a normal molecule Δ_{vib} is usually the largest contribution. It has been shown that for a planar molecule, Δ_{vib} comes solely from the harmonic parts of the vibrations [27], and can be calculated from a harmonic force field analysis [26]. The degree to which Δ_o can be predicted by a particular harmonic force field is sometimes used as a measure of the quality of the force field analysis.

Another type of structural parameter often used in microwave spectroscopy is the so called substitution, or r_s , structure obtainable using Kraitchman's equations [28]. In this method, the coordinate of a certain atom is determined by the changes in the principal moments of inertia upon isotopic substitution at this atom. The formulae for the determination of substitution coordinates in a general asymmetric top molecule are tabulated in Chapter 7, where they have been applied to the case of Ar_2 -OCS.

The r_s structure is considered to have some advantage over the r_o structure since the vibrational contributions to the principal moments of inertia are largely cancelled [29]. In practice, one difficulty is to synthesize the isotopic species with isotopic substitution at a specific atom. However, with the great sensitivity improvement of MWFT spectrometers over the earlier Stark cell spectrometer, spectra of increased numbers of substituted isotopomers can be observed in their natural abundances [30]. Some atoms, e.g. F, have only one stable isotopic species. In this case, the first moment equation (the centre of mass condition) is used to locate it. However, the r_s procedure has notorious problems in dealing with atoms close to the principal inertial axes. In these cases, vibrational effects are

significantly magnified and the coordinates of such atoms cannot be obtained reliably [31], without considering corrections for isotopic shrinkage [32].

Although the above two structures are most often encountered in the literature, they suffer from having no specific physical meaning. One of the physically better defined parameters is the ground state average, r_{av} (or r_z) structure. r_{av} can be calculated in the same fashion as r_o by replacing I_o with I_{av} . The average rotational constants are obtained by removing the harmonic part of the vibrational contributions to the vibration-rotation constant α_i , calculated from a harmonic force field analysis from the effective rotational constants [33]:

$$G_{av} = G_o + \sum_{i=1}^{3N-6} \frac{d_i \alpha_i}{2}$$
 (harmonic); $G = A, B, C.$ (2.15)

 G_{av} and G_o denote the ground state average rotational constants and effective rotational constants, respectively; α_i is the vibration-rotation interaction constant and d_i is the degeneracy of the *i*th normal mode.

The equilibrium, or r_e , structure defines the coordinates of a molecule at the hypothetical vibrationless state (i.e. at the potential minimum). It is normally obtained by measuring the rotational constants for a sufficient number of isotopomers of a molecule in its ground vibrational state and in at least one excited state of each normal mode. The equilibrium rotational constants are obtained by applying the equation [24]:

$$G_n = G_e - \sum_{i=1}^{3N-6} \alpha_i (v_i + \frac{d_i}{2}) + \cdots$$
 (2.16)

where G_n is the rotational constant in the *n*th vibrational state; α_i now includes both anharmonic and harmonic contributions; v_i are the vibrational quantum numbers for the 3N-6 normal modes which specify the *n*th vibrational state; d_i has been defined previously. For anything more than a triatomic molecule, the number of required measurements is normally prohibitively high.

If an r_{av} structure is obtainable, then one can use the following equation derived by Kuchitsu and co-workers [34,35] to obtain an approximation for the equilibrium structure:

$$r_{av} = r_e + \frac{3}{2}au^2 - K$$
 (2.17)

where u^2 is the zero-point, mean-square amplitude of the bond in question and K the corresponding mean-square perpendicular amplitude correction. These quantities can be evaluated from a harmonic force field [36]. The Morse anharmonicity parameter *a* may be estimated from similar diatomic molecules. The derivative of the above equation can also be used to estimate isotopic changes in the bond lengths with isotopic substitution [34,35]:

$$\delta r_{av} = \frac{3}{2} a \, \delta u^2 - \delta K \qquad (2.18)$$

This equation is used in determining r_{av} using several isotopomers, because values for r_{av} are isotopomer dependent.

2.4 Harmonic force field analysis

A harmonic force field analysis is of interest to obtain an r_{av} structure. The quartic centrifugal distortion constants from the analysis of the rotational spectra can be used in such an analysis. The quartic distortion constants are related to the τ 's of Wilson and Howard [10]. For Watson's A-reduction constants in the I^r representation, the τ 's are obtained from [11]:

$$\tau_{aaaa} = -4 (\Delta_{J} + \Delta_{JK} + \Delta_{K})$$

$$\tau_{bbbb} = -4 (\Delta_{J} + 2\delta_{J})$$

$$\tau_{cccc} = -4 (\Delta_{J} - 2\delta_{J})$$

$$\tau_{aabb} + 2\tau_{abab} + \tau_{aacc} + \tau_{bcbc} = -4 (3\Delta_{J} + \Delta_{JK})$$

$$C\tau_{aabb} + A\tau_{bbcc} + B\tau_{ccaa} + 2C\tau_{abab} =$$

$$-4 [(A + B + C)\Delta_{J} + \frac{1}{2} (B + C)\Delta_{JK} - (B - C) (\delta_{J} + \delta_{K})]$$

(2.19)

These τ 's are related to the elements of the inverse harmonic force constant matrix [37]. In the approximation of a harmonic force field and small vibrational amplitudes, one can write [37]:

$$\tau_{\alpha\beta\gamma\delta} = -\left[\frac{1}{2}\left(I_{\alpha\alpha}I_{\beta\beta}I_{\gamma\gamma}I_{\delta\delta}\right)\right]\sum_{i,j}\left(J_{\alpha\beta}^{i}\right)_{o}\left(f^{-1}\right)_{ij}\left(J_{\gamma\delta}^{j}\right)_{o}$$
(2.20)

For adaptation to the units commonly used in microwave spectroscopy, the above equation can be rewritten [38]:

$$\tau_{\alpha\beta\gamma\delta} = -\frac{A\Delta}{I_{\beta\beta}I_{\gamma\gamma}} 2h \times 10^{17} \sum_{i,j} (J^{i}_{\alpha\beta})_{\circ} (f^{-1})_{ij} (J^{j}_{\gamma\delta})_{\circ} (2.21)$$

with h in erg sec. A, Δ are the rotational constants in MHz; I_{BB} and $I_{\gamma\gamma}$ are the equilibrium principal moments of inertia in amu Å²; and $(J^{i}_{\alpha B})_{o}$ and $(J^{j}_{\gamma \delta})_{o}$ are derivatives of the inertia tensor with respect to the *i*th internal coordinate evaluated at the equilibrium configuration, in amu Å and amu Å² rad⁻¹ for a stretch and a bend, respectively; $(f^{-1})_{ij}$ are elements of the inverse force constant matrix, with f in mdyn Å⁻¹, mdyn Å rad⁻² and mdyn rad⁻¹ for a stretch, a bend, and a stretch bend interaction; the τ 's thus obtained are in MHz.

 $(J_{\alpha\beta}^{i})_{o}$ can be evaluated using Polo's vectors \mathbf{e}_{i} [39]. If $\mathbf{e}_{i}=(\varrho_{i1}^{(\alpha)}, \varrho_{i1}^{(\beta)}, \varrho_{i2}^{(\gamma)}, \varrho_{i2}^{(\alpha)}, \ldots, \varrho_{iN}^{(\gamma)})$ is any set of Cartesian displacements in the principal inertial axes which produce a unit increment δR_{i} in the *i*th internal coordinate and leave the other 3N-7 internal coordinates unchanged, then [39]:

$$J_{\alpha\alpha}^{i} = 2 \sum_{k} m_{k} \{ \beta_{k} \varrho_{ik}^{(\beta)} + \gamma_{k} \varrho_{ik}^{(\gamma)} \}$$

$$J_{\alpha\beta}^{i} = -2 \{ \sum_{h} m_{h} \alpha_{h}^{2} \sum_{k} m_{k} \beta_{k} \varrho_{ik}^{(\alpha)} + \sum_{h} m_{h} \beta_{h}^{2} \sum_{k} m_{k} \alpha_{k} \varrho_{ik}^{(\beta)} \} / I_{\gamma\gamma}$$
(2.22)

Here the *k*th atom has mass m_k and equilibrium coordinates α_k , β_k , γ_k ; $I_{\gamma\gamma}$ is an equilibrium moment of inertia.

Strictly speaking, only equilibrium values should be used in such a force field analysis. However, equilibrium geometries are very rarely available, and approximations have to be made by using r instead of r values in the analyses. A fitting program is available to fit the force constants to the corresponding vibration frequencies and the quartic centrifugal distortion constants. For a moderately large molecule, the inversion of Eq.(2.21) to allow the determination of a molecular force field from the microwave data is in general not possible, because the number of force constants usually exceeds the number of determinable centrifugal distortion constants. Instead, the quartic distortion constants are used together with known vibrational frequency information to refine the harmonic force field of the molecule. For a complex, it has been shown that the vibrations of the rigidly bonded subunits make a negligible contribution to the centrifugal distortion constants since the van der Waals modes are much lower in energy compared the vibrations of covalent bonds [40]. This assumption helps to simplify a harmonic force field analysis for complexes, although for such flexible systems, the degree of validity of a harmonic force field is still under discussion [41].

2.5 Theoretical description of pulsed

excitation experiments

This section is concerned with the interaction of an ensemble of molecular dipoles with a microwave pulse, and with the transient effects which arise immediately after a sudden radiation-induced change in the system. In such experiments, the radiation power levels not only cause rapidly oscillating superposition states, but also considerably change the thermal equilibrium populations of the stationary states [42]. In an experiment, a macroscopic dipole moment is created by a microwave pulse of appropriate strength and duration. This dipole moment evolves in time and emits microwave radiation at the molecular transition frequencies. The intensity of the emitted microwave radiation decreases in time as the macroscopic dipole moment decreases, as a result of increasing disorder or relaxation due to molecular collisions and other effects.

These phenomena can be described by analogy with the Bloch equations used in nuclear magnetic resonance (NMR) [40]. Details of the derivation have been given by Flygare [42], Shoemaker [43], and Dreizler and co-workers [44,45]. Only some important results and some simple derivations are discussed here in order to acquaint the reader with some phrases and notation used in the following chapters of this thesis.

An appropriate frame of description is provided by time dependent Schrödinger theory in a density matrix formalism [44]. The complete time dependent Hamiltonian \mathcal{H} can be expressed as: $\mathcal{H}=\mathcal{H}_{0}+\mathcal{H}_{1}$, where \mathcal{H}_{0} is the time independent Hamiltonian describing the stationary states of the system, and \mathcal{H}_{1} describes the time dependent perturbation introduced by the interaction with a microwave field. For a two-level particle, the space (q) and time (t) dependent wave function can be written as:

$$\Psi_{v}(q,t) = c_{va}(t)\phi_{a}(q) + c_{vb}(t)\phi_{b}(q)$$
(2.23)

where v denotes the vth particle; $c_{va}(t)$ and $c_{vb}(t)$ are complex time-dependent coefficients; $\phi_a(q)$ and $\phi_b(q)$ are the solutions of the time independent Schrödinger equation with the Hamiltonian \mathcal{H}_a of a two-level particle:

$$\mathcal{H}_{o}\phi_{i}(q) = E_{i}\phi_{i}(q); \quad i=a,b \quad (2.24)$$

The perturbation Hamiltonian for the interaction with an external field is: $\Re_1 = -\mu \cdot \mathbf{E}(t)$, with $\mathbf{E}(t) = \varepsilon \cos(\omega t - \varphi)$, the external microwave field. Here μ is the molecular dipole moment operator, with the matrix elements $\mu_{aa} = \mu_{bb} = 0$ and $\mu_{ab} = \mu_{ba} \neq 0$, corresponding to an electric dipole allowed transition between states (a) and (b); ε is the external microwave field amplitude; ω is the angular microwave radiation frequency, not necessarily resonant with the

rotational transition frequency $\omega_{ab}^{o} = (E_{b} - E_{a})/\hbar$; φ is an arbitrary phase factor. The matrix elements of \mathcal{H} in the basis set $\{\phi_{i}\}$ are:

 $H_{aa}=E_{a}$, $H_{bb}=E_{b}$, and $H_{ab}=H_{ba}=-\mu_{ab}\varepsilon\cos(\omega t-\phi)$.

The expectation value $\langle A \rangle$ of an operator A of the vth particle in the state $\Psi_{v}(q,t)$ can be written as:

$$\langle A \rangle = \langle \Psi_{v}(q,t) | A | \Psi_{v}(q,t) \rangle$$

=
$$\sum_{n-a,b} \sum_{m-a,b} c_{vm}^{*}(t) c_{vn}(t) A_{mn}$$
 (2.25)

with $A_{mn} = \langle \phi_m | A | \phi_n \rangle$. Now if one considers an ensemble of N particles, the mean expectation value of the same operator A is:

The density matrix $\varrho(t)$ of an ensemble of N particles is given by its elements:

$$\varrho_{nm} = \frac{1}{N} \sum_{\nu=1}^{N} c_{\nu m}^{*}(t) c_{\nu n}(t) \qquad m, n = a, b$$
(2.27)

and can be further separated into two parts, namely the amplitude and phase factors:

$$\varrho_{nm} - \{ \frac{1}{N} \sum_{\nu=1}^{N} |c_{\nu m}(t)| \cdot |c_{\nu n}(t)| \} \cdot \{ \frac{1}{N} \sum_{\nu=1}^{N} \exp[i(\gamma_{\nu n}(t) - \gamma_{\nu m}(t))] \}$$
(2.28)

At thermal equilibrium, the density matrix is diagonal since the phase relation between individual particles is random. The diagonal elements describe the population distributions of the stationary states. However, when the particles interact with external coherent radiation, a phase coherence between the wavefunctions of the individual particles is created and the off-diagonal elements are no longer necessarily zero. From the above equations, the quantity $\langle A \rangle_{av}$ can also be written in a simple matrix expression: $\langle A \rangle_{av} = Tr\{A \cdot \varrho\}$, where Trindicates the trace of the matrix. For example, the induced macroscopic dipole moment P of the ensemble of N particles can be expressed as $P = N \cdot Tr\{\mu \cdot \varrho\}$.

The time dependence of $\varrho(t)$ is described by

$$i\hbar \frac{\partial \varrho}{\partial t} - [\mathcal{H}, \varrho] - \mathcal{H} \varrho - \varrho \mathcal{H}$$
(2.29)

where \mathcal{H} is the matrix representation of the Hamilton operator in the $\phi_i(q)$ basis. By substituting the matrix expressions of \mathcal{H} and $\varrho(t)$ into Eq.(2.29), a set of linear differential equations for the elements of the density matrix results:

$$\dot{\varrho}_{aa} = i x_{ab} \cos(\omega t - \varphi) (\varrho_{ba} - \varrho_{ab}) \dot{\varrho}_{bb} = -i x_{ab} \cos(\omega t - \varphi) (\varrho_{ba} - \varrho_{ab}) \dot{\varrho}_{ab} = i \omega_{o} \varrho_{ab} + i x_{ab} \cos(\omega t - \varphi) (\varrho_{bb} - \varrho_{aa})$$

$$\dot{\varrho}_{ba} = -i \omega_{o} \varrho_{ba} + i x_{ab} \cos(\omega t - \varphi) (\varrho_{aa} - \varrho_{bb}) - \dot{\varrho}_{ab}^{*}$$

$$(2.30)$$

where $x_{ab} = \epsilon \cdot \mu_{ab}/\hbar$, by analogy to the Rabi frequencies in NMR spectroscopy. By introducing a new set of matrix elements $\tilde{\varrho}_{nm}$ (n,m=a,b):

$$\begin{aligned} \varrho_{aa} &= \tilde{\varrho}_{aa} \\ \varrho_{bb} &= \tilde{\varrho}_{bb} \\ \varrho_{ab} &= \tilde{\varrho}_{ab} \exp\left[i\left(\omega t - \varphi\right)\right] \\ \varrho_{ba} &= \tilde{\varrho}_{ba} \exp\left[-i\left(\omega t - \varphi\right)\right] \end{aligned} \tag{2.31}$$

and by neglecting terms in 2ω (the "rotating wave approximation" [46]), Eq.(2.30) can be transformed into the simpler form:

$$\begin{split} \tilde{\varrho}_{aa} &= i x_{ab} \left(\tilde{\varrho}_{ba} - \tilde{\varrho}_{ab} \right) \\ \tilde{\varrho}_{bb} &= i x_{ab} \left(\tilde{\varrho}_{ab} - \tilde{\varrho}_{ba} \right) \\ \tilde{\varrho}_{ab} &= i \left(\omega_{o} - \omega \right) \tilde{\varrho}_{ab} + i x_{ab} \left(\varrho_{bb} - \varrho_{aa} \right) \\ \tilde{\varrho}_{ba} &= -i \left(\omega_{o} - \omega \right) \tilde{\varrho}_{ba} - i x_{ab} \left(\varrho_{bb} - \varrho_{aa} \right) \end{split}$$

$$\end{split}$$

$$\end{split}$$

$$\end{split}$$

In order to keep the notation simple for later discussion, the following real variables connected with the above quantities are introduced:

$$u_{ab} = \tilde{\varrho}_{ab} + \tilde{\varrho}_{ba}$$

$$v_{ab} = i (\tilde{\varrho}_{ba} - \tilde{\varrho}_{ab})$$

$$w_{ab} = \tilde{\varrho}_{aa} - \tilde{\varrho}_{bb}$$

$$s_{ab} = \tilde{\varrho}_{aa} + \tilde{\varrho}_{bb}$$

(2.33)

where u_{ab} and v_{ab} are connected with the polarization P by the following relationship which can be derived from Eqs.(2.31) and (2.33):

$$P = N \mu_{ab} [u_{ab}(t) \cos(\omega t - \varphi) - v_{ab}(t) \sin(\omega t - \varphi)]$$
(2.34)

 u_{ab} is called the real part of the macroscopic polarization P, which is in-phase with the microwave perturbation, and v_{ab} the imaginary part of P, which is 90° out-of-phase. $w_{ab}=\Delta N/N$, where ΔN is the population difference, and s_{ab} is the sum of population probabilities, which is a constant in the two level system and needs no longer to be considered. Eq.(2.32) can now be written in a simple form as Bloch Equations:

$$\dot{u}_{ab} = -\Delta \omega v_{ab}$$

$$\dot{v}_{ab} = \Delta \omega u_{ab} - x_{ab} w_{ab}$$
 (2.35)
$$\dot{w}_{ab} = x_{ab} v_{ab}$$

with $\Delta \omega {=} \omega_{ab}^{o} {-} \omega$. ω_{ab}^{o} and ω are defined as before.

The Bloch equations will now be applied to a description of a pulse excitation experiment. The experiment will be described in two phases: the excitation and the observation periods. The initial condition is such that the polarization is zero i.e. $u_{ab}(t_i)=v_{ab}(t_i)=0$ and that the population difference is ΔN_o i.e. $w_{ab}(t_i)=-\Delta N_o/N$. Under the assumption of a near resonant, strong, short excitation pulse $\Delta \omega < x_{ab}$, $\Delta \omega$ can be neglected in Eq.(2.35):

$$\dot{u}_{ab} = 0$$

 $\dot{v}_{ab} = -x_{ab} W_{ab}$ (2.36)
 $\dot{w}_{ab} = -x_{ab} V_{ab}$

The solution is:

$$u_{ab}(t) - u_{ab}(t_{i}) = 0$$

$$v_{ab}(t) - w_{ab}(t_{i}) \sin(x_{ab}\tau_{e})$$

$$w_{ab}(t) - w_{ab}(t_{i}) \cos(x_{ab}\tau_{e})$$

(2.37)

with $\tau_e = t - t_i$ denoting the microwave excitation pulse length. The condition of a " $\pi/2$ pulse" is fulfilled when:

$$x_{ab}\tau_{e} = \frac{\pi}{2}$$

$$\mu_{ab} \cdot \varepsilon \cdot \tau_{e} = \frac{\pi}{2}\hbar$$
(2.38)

and it corresponds to a maximum macroscopic polarization. The maximum signal is connected to $\Delta N(t_{\pi/2})=0$.

The observation period starts at the completion of the " $\pi/2$ pulse"; its initial conditions are: $u_{ab}(t_{\pi/2}) = w_{ab}(t_{\pi/2}) = 0$ and $v_{ab}(t_{\pi/2}) = -\Delta N_o/N$. Since the microwave pulse is switched off, i.e. the system no longer interacts with the radiation field, all terms involving x_{ab} can be dropped. Eq.(2.35) becomes:

$$\dot{u}_{ab} - \Delta \omega v_{ab}$$

$$\dot{v}_{ab} - \Delta \omega u_{ab}$$
 (2.39)
$$\dot{w}_{ab} - 0$$

with the solution:

$$\begin{aligned} u_{ab}(t) &= +w(t_i)\sin(\Delta\omega t) \\ v_{ab}(t) &= -w(t_i)\cos(\Delta\omega t) \\ w_{ab}(t) &= 0 \end{aligned} \tag{2.40}$$

The variables u_{ab} and v_{ab} oscillate with the off-resonant frequency $\Delta \omega$. The observed polarization becomes:

$$P(t) - N \mu_{ab} w(t_i) \sin(\omega_{ab}^{\circ} t - \varphi)$$
 (2.41)

and oscillates with the rotational transition frequency ω_{ab}^{o} . Notice that P is proportional to μ_{ab} .

Eq.(2.39) pictures the situation after a pulse without considering the relaxation effects. In a real case, ΔN (i.e. w_{ab}) relaxes to ΔN_o ($\Delta N_o/N$), and P (i.e. u_{ab} and v_{ab}) to zero with relaxation times T_1 and T_2 , respectively. The exponential terms $exp(-t/T_1)$ and $exp(-t/T_2)$ are then introduced to describe phenomenologically the relaxation of the particular quantities to their equilibrium values.

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CHAPTER 3

Experimental Methods

The pulsed molecular beam cavity microwave Fourier transform spectrometer used in this work is similar to that of the original design of Balle and Flygare [1]. The combination of the Fourier transform technique and pulsed molecular expansions has sparked a small revolution in microwave spectroscopy, and has improved the sensitivity, resolution and precision of the measurement of transition frequencies by orders of magnitude. Since its appearance in 1981 [1], this type of spectrometer has been widely used in the study of transient species [2-5] such as weakly bound van der Waals complexes, ions, radicals, and unstable molecules. Today, there are about a dozen microwave groups worldwide using these instruments.

The advantages of the pulsed excitation Fourier transform technique over a conventional Stark modulation experiment, have been discussed in detail by Flygare [6] and by Dreizler [7]. First, the signal-to-noise (S/N) improvement achieved by the pulsed excitation Fourier transform technique, compared to a Stark cell experiment is estimated to be more than an order of magnitude [6]. This great improvement can be rationalized as follows. In a pulsed experiment, a number of transitions within a given excitation bandwidth can be excited simultaneously. The time domain signal contains, besides noise, information about all these transitions. A Fourier transform then yields a display of the transitions in the frequency domain. In a Stark cell experiment, on the other hand, at any instant of time, only one point of the frequency spectrum under investigation is recovered. Because microwave spectra in general are not very dense, much of the sweeping time is spent in recording the base line between the spectral lines.

Secondly, a pinhole jet expansion is the most commonly used method to introduce sample into the microwave cavity in this type of spectrometer. The molecular beam thus generated can have extremely low translational (well below 1K) and rotational (~1K to 2K) temperatures as well as low vibrational temperatures [8], which vary according to the sample mixture, nozzle structure and backing pressure. This significantly reduces the number of quantum states being populated, and squeezes the broad Boltzmann distribution at room temperature into a very sharp distribution with only the few lowest lying states being populated. This not only simplifies the spectra greatly, but also enhances the intensities of lower lying rotational transitions.

Thirdly, the pulsed technique has an advantage in the case of molecules with very small dipole moment μ . The observed signal is proportional to μ , once the " $\pi/2$ pulse" [Chapter 2] condition is achieved, as compared to the square of the dipole moment in the case of Stark cell experiments [6]. The pulse technique thus allows detection of transitions with very low transition moments.

The resolution is also greatly enhanced compared to conventional Stark modulated spectroscopy, because of the absence of several line broadening mechanisms. The lines are essentially free of pressure and wall collision broadening since a molecular jet expansion is used. Also modulation broadening is absent because there is no modulation; and power broadening is absent since signals are observed in emission. The full line width at half height (FWHH) in the present case was typically ~7 kHz.

However, it is in general not possible to obtain reliable intensity information with such spectrometers. The actual intensity observed is affected by several factors such as the off-resonance from the excitation frequency, microwave pulse length and cavity mode.

Although the basic design of the spectrometer has been given by Balle and Flygare [1], with the subsequent modifications described elsewhere [9,10], a brief description of the instrument used is given here. The emphasis is on the experimental conditions, which had to be carefully chosen and optimized for the weak van der Waals complexes studied in this thesis.

3.1 Pulsed molecular beam cavity microwave Fourier transform spectrometer:



Fig.3.1 Schematic circuit diagram of the pulsed molecular beam cavity Fourier transform spectrometer

The numbers 1,2,3,4, here represent a train of pulses which control the experiment. The details are illustrated in Fig.3.2.

A schematic circuit diagram of the spectrometer is given in Figure 3.1. Following this diagram, the spectrometer is divided into five main parts: (1) microwave radiation source and generation of microwave pulses; (2) Fabry-Perot resonator and molecular beam source; (3) signal detection system; (4) data acquisition system (computer data processing); (5) experimental control.

3.1.1 Microwave radiation source and generation of microwave pulses

The microwave source used is a HP 8341A synthesized sweeper which is controlled via an IEEE-bus with a 286 personal computer. With use of a single sideband modulator the upper sideband 20 MHz from the carrier frequency v_{MW} is obtained. The microwave radiation is modulated by two fast microwave PIN diode switches to generate the excitation pulses. Because the switches reflect the microwave power when closed, isolators are used to reduce the influence on the signal source. The microwave pulse is then fed through a circulator into the cavity via a simple "wire hook" antenna (of length $\sim\lambda/4$).

The microwave radiation power from the HP synthesizer is 13.0 dBm (20 mw). A considerable amount of power (~18 dB) is lost before the microwave radiation is coupled into the cavity. For the measurement of low dipole moment complexes with μ in the order of or less

than 0.1 D, more power is needed in order to achieve the " $\pi/2$ pulse" condition [Chapter 2]. The microwave excitation pulses in these cases are amplified with solid state power amplifiers with a specified maximum microwave output power of 30 dBm (1000 mW) in the frequency range of 8-18 GHz, and 27 dBm (500 mW) in the range 4-8 GHz. The present operating frequency region of the spectrometer is from 4.0 GHz to 24.0 GHz

3.1.2 Fabry-Perot resonator and pulsed

molecular beam source

The heart of the spectrometer is a Fabry-Perot cavity, where the molecules interact with the microwave radiation. It is situated in a stainless steel vacuum chamber and consists of two spherical aluminum mirrors with diameters of 28 cm and radii of curvature of 38.4 cm. The separation of the mirrors is in the range of 30 cm. One of the mirrors is movable, allowing manual tuning of the cavity with a micrometer screw; the other mirror is held at a fixed position. The mirrors are supported by three 3/4-inch diameter aluminum rods which are fastened to the wall of the vacuum chamber. Three teflon rings riding on the rods are attached to the movable mirror to allow smooth linear motion for adjusting the mirror separation. The cavity is tuned into resonance with the microwave excitation frequency by feeding a frequency sweep into the cavity and monitoring

the microwave power in transmission. The tuning mirror is then moved with a micrometer screw until a cavity mode appears at the excitation frequency. For example, a frequency step of 100 kHz at 10 GHz and 30 cm mirror separation requires the cavity to be tuned by ~3 μ m.

The quality factor of the cavity is ~10,000: the bandwidth of the cavity (FWHH) is about 1 MHz at a frequency of 10 GHz. This comparatively broadbanded microwave cavity makes searching for unknown lines less tedious than in the case of higher Q cavities [11] because a single experiment can cover a wider frequency range. The excitation frequency can be changed in steps of up to 1 MHz in order to scan a wide frequency region.

Another important parameter is the beam waist radius ω_o , corresponding to the radial distance from the centre of the cavity to the 1/e field strength point. It can be related to the geometric parameters of the cavity by the following equation [12]:

$$\omega_{o} = \left\{ \frac{\lambda}{2\pi} \left[d \left(2R - d \right) \right]^{\frac{1}{2}} \right\}^{\frac{1}{2}}$$
(3.1)

where d is the distance between mirrors, R is the radius of curvature and λ is the radiation wave length. The resulting value for ω_{0} is 4.2 cm at λ =3.0 cm (10 GHz).

Two different types of commercially available nozzles have been used as the molecular beam source:

Bosch fuel injector nozzles with an orifice diameter of 1 mm and General Valve series 9 nozzles with 0.8 mm orifices. In the normal operation mode, a nozzle is placed parallel to the input-output radiation axis, mounted near the centre of one of the mirrors.

3.1.3 Signal detection system and data acquisition system

The radiation signal emitted by the excited molecules is picked up by the same antenna that was used to broadcast the excitation pulse, and then fed through a circulator to couple out of the cavity. The signal, which contains the frequencies corresponding to rotational transitions, is amplified by a high quality low-noise microwave amplifier. High quality amplifiers and mixers in the detection circuit, especially a microwave amplifier with a very low noise figure, seem to be crucial for the high sensitivity of the spectrometer.

Since further data processing, like analog-to-digital (A/D) conversion, is much easier in the radio frequency range than in the microwave frequency range, the microwave signal is downconverted to in two steps to frequencies ~5 MHz. The data then undergo analog-to-digital conversion and are stored with a commercially available 'plug-in' transient recorder board (obtained from Dr. Strauss GMBH) for the personal computer. This board features a programmable preamplifier, an 8-bit A/D-converter and a memory depth of 32k 8-bit words. The board can be operated at sample rates of up to 25 MHz. In our instrument 4k data points at 50, 100 or 150 ns sample intervals are transferred to the computer, where the signal averaging of successive experiments is done.

3.1.4. Experiment control

A home built programmable pulse generator creates the TTL pulses for controlling the sample injection nozzle and the microwave PIN diode switches and provides the trigger signal for the start of the data acquisition. The timing of the pulse sequences is qualitatively shown in Figure 3.2. It is essential for signal averaging that the master clock of the pulse sequence generator and the 5 MHz intermediate frequency after the second downconverting step be phase synchronous. The timing of the experiment is based on the internal 10 MHz reference oscillator of the HP synthesized sweeper.

In a given experiment, the microwave cavity is first tuned into resonance with the excitation frequency. A burst of sample gas is then injected into the cavity between the aluminum mirrors. After a short delay, a microwave pulse, usually in the order of 1 to 10 μ s, is coupled into the cavity via the antenna, and a standing wave pattern results. The microwave radiation interacts with the molecular dipoles of the molecules. A short time (in the order of 10 μ s) after the pulse is turned off,



Fig.3.2 Control pulse sequence for one experiment cycle.

the microwave switch to the detection circuit is opened. This third PIN diode switch protects the sensitive detection circuit from the strong microwave pulse during the excitation period. The molecular emission signal, coupled out of this cavity, is further amplified, downconverted and then stored in a personal computer as a time domain signal. The cavity background signal, obtained by applying only a MW-pulse and no molecular pulse, is subtracted in each experiment. A Fourier transform then yields the frequency spectrum.

The repetition rate of the experiments was restricted to ca. 1 Hz by the pumping speed of the diffusion pump.

3.2 Optimization of the experimental conditions

The pulsed nozzle is commonly mounted at a position where the axis of the molecular beam is perpendicular to the input-output microwave radiation axis [13]. This arrangement was also used during the development stage of the spectrometer used here. A parallel nozzle configuration was originally mentioned by Balle and Flygare back in 1981 [1]. The first test experiment was published by Grabow and Stahl [10] in 1990. This parallel arrangement results in a longer observation time for the coherent emission, compared to the perpendicular set up



Fig.3.3 Hyperfine components due to ⁷⁹Br and ¹⁴N nuclear quadrupole coupling of rotational transition $3_{0,3}-2_{0,2}$ of ⁷⁹BrCH₂C=N. (a) measured with the parallel nozzle position, 10 experimental cycles. Each component is doubled by the Doppler effect. (b) measured with the perpendicular nozzle position, 800 experimental cycles.
and therefore in a higher sensitivity and a higher resolution. A great improvement of sensitivity and resolution was also found in this thesis work by changing the nozzle from the perpendicular to the parallel position. An example is illustrated in Figure 3.3. The spectrum shown is a 0.5 MHz section of hyperfine splitting due to both ^{79}Br and ^{14}N , of the $3_{0.3}-2_{0.2}$ rotational transition of $^{79}BrCH_2C=N$. It can be seen that the spectrum obtained with the parallel nozzle position not only has a better S/N ratio but also narrower line widths. Furthermore, it has been obtained with only 10 experimental cycles, compared to 800 cycles with the perpendicular nozzle position. Each line is split into a doublet due to the Doppler effect [14]. The line frequencies are calculated by taking the average of the two Doppler components. It should be noted that the excitation frequencies applied in these two experiments are different, resulting in different intensity patterns.

One of the original concerns about mounting a nozzle in one of mirrors was possible interference with the microwave radiation. However, the diameters of the holes in the mirror are in the order of 0.5 cm, which is smaller than the microwave wavelength (7.5 cm at 4GHz and 1.7 cm at 18 GHz), and no perturbations have been detected. Another question was the position of the nozzle in the mirror. As was mentioned before, two types of commercial nozzles have been used as the molecular beam source: Bosch fuel injectors and General Valve (GV) Series 9 nozzles. It was interesting to note that the GV nozzles were more sensitive to the position in the mirror than the Bosch nozzles. A severe intensity decrease (an order of magnitude) has been observed by moving the GV nozzle from its current position (3cm off centre) by only 2cm in either direction, close to or further away from the centre. A similar effect was not observed for the Bosch nozzles. This seems to suggest that the sample generated by the GV nozzle is more confined, thus more sensitive to the microwave field strengths at different positions, while that from the Bosch nozzle is more of a cloud shape.

Furthermore, it was found that the GV nozzle was mechanically more reliable compared to the Bosch fuel injector. The GV nozzle can also work against high backing pressures (~5 to 6 atm), which is essential for achieving the very low translational and rotational temperatures needed to stabilize some very weakly bound van der Waals complexes such as the mixed rare gas dimers and trimers studied in this work. The high backing pressure would, on the other hand, affect the performance of the Bosch nozzles.

One of the most important problems was how to prepare a sufficient amount of the transient species in order to permit the observation of a microwave spectrum. In a static gas mixture of Ar and HF at a pressure of 1

Torr at room temperature only one molecule in 10° of the molecules is bound as a complex with a very short life time [8]. This number is greatly increased in the jet expansion [8]. The high number of collisions inside the nozzle orifice provides a high yield of complexes, which are subsequently stabilized through the extremely low translational and rotational temperature achieved in the jet expansion.

A further question was how to enhance the yield of the complex to be investigated. The molecular beam expansion used is a very complex dynamical process and is far from being understood in every detail [15]. The optimization of the expansion condition is therefore a tedious, time consuming procedure with many variables like the nature of the carrier gas, sample composition, backing pressure, opening time of the nozzle, modification of the nozzle, and tubing material of sample system, to be considered. The importance of this optimization procedure cannot be overemphasized; it was crucial for the detection of any of the complexes reported in this thesis. Most of the parameters have to be adjusted empirically. The choice of carrier (backing) gas, however, warrants some special consideration.

The most commonly used carrier gases for beam experiments are Ar, Ne and He. Helium is the atom with the smallest polarizability in this series and is therefore least likely to form clusters, either with

itself or other substances. It has been established that the rotational temperature in a He beam is usually higher than in an Ar beam, and higher energetic isomers are quite often observed, for example in infrared experiments [16]. A possible explanation is that He is very light and moves very fast, so that the formation of clusters might block the beam, which would result in a higher beam temperature. Attempts were made to use He as carrier gas to observe some complexes such as Ne-Xe/Kr, but no signal could be observed. This is possibly because of the very low dissociation energy of these very weakly bound complexes and because of a relatively higher rotational temperature in the He beam.

Ar, on the other hand, is the most commonly used carrier gas for economic reasons. However, the use of Ar as carrier gas resulted in some cases in only very weak lines, even in the case of Ar-containing van der Waals complexes such as $Ar-N_2$ [17] or Ar-CO [18]. The explanation is that Ar, in contrast to He, has a strong tendency to form clusters among itself, resulting in a much lower yield of the desired complexes.

The properties of Ne are somewhat between those of He and Ar, and it was found that use of Ne as a carrier gas significantly improved the S/N ratio in the case of the van der Waals complexes studied in this thesis.

The ratio of the mixture plays an important role for the rotational temperature achieved after the beam

expansion. For example, while 1~2% of F_2CS in 0.5 atm Ar is quite suitable for measuring lower J transitions such as $1_{0,1}-0_{0,0}$, it is not possible to observe higher J transitions such as $7_{1,3}-6_{2,4}$. On the other hand, a mixture with 30% F_2CS nicely improved the sensitivity for $7_{1,3}-6_{2,4}$; the observed intensity for $1_{0,1}-0_{0,0}$ decreased, indicating a much higher rotational temperature [19]. This can also serve as an extra piece of information for assignment purposes.

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CHAPTER 4

Rotational Spectrum of Ar-Cl,

4.1 Introduction

Van der Waals complexes between an atom and a homonuclear diatomic molecule, such as Ar-Cl₂, are among the simplest possible which can undergo large amplitude motions due to both stretching and bending. The binding forces here are very weak, and are mainly due to dispersion forces; only a minor role is played by the induction part arising from the molecular electric quadrupole moment of the diatomic monomer [1].

There is special interest in the $Ar-Cl_2$ van der Waals dimer. Since it was established that two different forms of rare gas-halogen complexes exist, a great deal of attention has been paid to these systems. One form is linear, which can be ascribed to an "incipient charge transfer" [2,3] from the rare gas atom to the halogen. Examples are Ar-ClF [2] and Kr-ClF [3]. The other has a T-shaped equilibrium structure which is consistent with the atom-atom additive van der Waals model [4]. Examples are the He- [5], Ne- [6] and $Ar-Cl_2$ [7] complexes. The difference provides a challenge for both experimentalists and theoreticians to try to explain its origin in detail.

A recent theoretical investigation [8] has suggested that a linear conformer of Ar-Cl₂ should also exist, close in energy to the T-shaped one. There is also recent evidence for the existence of both T-shaped and linear $Ar-I_2$, provided by the optical spectrum of this complex [10], where the observed continuum fluorescence has been interpreted as being due to a linear $Ar-I_2$ form. It was thus of considerable interest to search for the pure rotational spectra of both T-shaped and linear $Ar-Cl_2$ complexes.

There is further reason to investigate the microwave spectrum of $Ar-Cl_2$. Over the last twenty years, Ar-ClF [2] and Kr-ClF [3] have been the only two rare gas-halogen complexes studied by microwave spectroscopy, and the only two rare gas-halogen complexes found to be linear. All other rare gas-halogen complexes studied by electronic spectroscopy, such as $Ar-Cl_2$ [7], Ne-IBr [10], have been found to be T-shaped. A further puzzle came when electronic spectroscopy failed to reveal spectra of Ar-ClF and Kr-ClF, possibly because of unfavourable Frank-Condon factors [7].

The anticipated difficulties in observing the rotational spectrum of $Ar-Cl_2$ were twofold. The dipole moment for $Ar-Cl_2$, which is essential for the observation of a pure rotational spectrum, is due entirely to the weak van der Waals interaction between Ar and Cl_2 . The asymmetric top (in case of T-shaped $Ar-Cl_2$) spectrum is irregular and is difficult to search for. However, $Ar-N_2$ [11] and $Kr-N_2$ [12] have been recently measured with a

high S/N ratio. This success stimulated the search for the microwave spectrum of Ar-Cl₂ with the hope of solving this puzzle.

In this chapter, a microwave spectroscopic investigation of the T-shaped $Ar-Cl_2$ complex is described. Accurate rotational constants and quartic centrifugal distortion constants have been determined and have been used to estimate the structure of $Ar-Cl_2$, as well as its harmonic force field. These results are compared with the structure obtained from electronic spectroscopy [7] and with the van der Waals frequencies from the theoretical study [8]. In addition, it has also been possible to resolve the hyperfine structure due to the quadrupole coupling of the Cl nuclei. The quadrupole coupling constants in both $Ar-^{35}Cl_2$ and $Ar-^{35}Cl^{37}Cl$ have been determined, from which an estimate of the previously unmeasured Cl nuclear quadrupole coupling constant for the free diatomic chlorine molecule has been obtained.

4.2 Search and spectrum assignment

The $Ar-Cl_2$ complex was formed by the expansion of a gas mixture consisting of 0.4% Cl_2 and 0.8% Ar in Ne at a backing pressure of 5.0 atm. Because of the anticipated low dipole moment of the $Ar-Cl_2$ complex (μ <0.01 Debye [7]), the solid state amplifier was used to

increase the MW excitation pulse power.

To make an initial prediction of the rotational spectrum of $Ar^{-35}Cl_2$, the complex was taken to be T-shaped, with Ar on the *a*-inertial axis. Rotational constants were calculated using the geometric parameters derived from the electronic spectrum [7] and were in turn used to predict the frequencies of the anticipated *a*-type transitions. Because the chlorine nucleus has a spin 3/2, all rotational transitions were expected to show nuclear quadrupole hyperfine structure. Since no accurate nuclear quadrupole coupling constants for free Cl_2 were previously available, a value of 115 MHz estimated from the rotational spectrum of HF-Cl₂ [13] was used to predict the hyperfine patterns.

In the expected T-shaped equilibrium structure of $Ar^{-35}Cl_2$ the two chlorine nuclei are equivalent. The two equivalent fermions require the total wavefunction to be antisymmetric with respect to a C_2 operation. With symmetric electronic and vibrational functions, the product of the rotational and nuclear spin functions has to be antisymmetric. The coupling scheme used is: I=I_1+I_2, F=J+I, where I₁ and I₂ are the individual chlorine nuclear spins. The quantum number I can take the values 0,1,2,3. As a result, rotational levels with $K_a=0$ have antisymmetric nuclear spin functions with I= 0 and 2, and $K_a=1$ rotational levels have symmetric spin

functions with I= 1 and 3. The spin statistical weights of $K_a=0$ and $K_a=1$ transitions are in the ratio 6:10.

The initial search was carried out for the $3_{0,3}-2_{0,2}$ transition, as it has the lowest lying rotational energy level accessible within the specified frequency range of the power amplifier and a relatively simple hyperfine pattern, namely a symmetric triplet in a first order approximation. From the experience with Ar-N₂ [11] and $Kr-N_2$ [12], the line intensities were expected to be fairly high. The first line found, however, at 7903.06 MHz, was rather weak. It was checked by removing Ar or Cl, and was confirmed to be due to Ar+Cl,. Using the predicted hyperfine patterns, two weaker satellite lines could be located after a very careful search, thus confirming the assignment of the $3_{0,3}-2_{0,2}$ transition of $Ar-^{35}Cl_2$. Three other transitions, $2_{0,2}-1_{0,2}$, $4_{0,4}-3_{0,3}$ and $5_{0.5}-4_{0.4}$, were soon found and their assignments were again confirmed with their hyperfine triplets.

Because spin conversion between spin functions of different symmetries in $Ar-{}^{35}Cl_2$ is not allowed in the beam expansion, molecules in energy level stacks with $K_a=0$ and $K_a=1$ cool separately. Levels with $K_a=1$ are metastable, and it is possible to observe $K_a=1$ transitions with similar intensity as in corresponding $K_a=0$ transitions, even though these levels are higher in energy by ~0.2 cm⁻¹. Six such transitions were found, one of which, $3_{1,3}-2_{1,2}$, is depicted in Fig.4.1 to illustrate the signal-to-noise ratio and resolution achieved.

Searches were also carried out for the mixed isotopomer, $Ar-^{35}Cl^{37}Cl$, (37% natural abundance) using the structure calculated for the main isotopomer, $Ar-^{35}Cl_2$ (57%). This time, although three $K_a=0$ transitions were easily found, only a few components from the two lowest $K_a=1$ rotational transitions could be observed, since the chlorine nuclei were no longer equivalent and separate cooling for the two different K_a stacks no longer occurred.

All measured frequencies for $Ar-{}^{35}Cl_2$ and $Ar-{}^{37}Cl^{35}Cl$ are listed with their assignments in Table 4.1.

4.3 Analysis of the argon-chlorine dimer spectrum

The Hamiltonian used to account for the observed spectrum is given by: $\mathcal{H}=\mathcal{H}_{R}+\mathcal{H}_{q}$, where \mathcal{H}_{R} is the semirigid rotor Hamiltonian, including rotational constants and quartic centrifugal distortion constants. The quadrupole Hamiltonian \mathcal{H}_{q} includes nuclear quadrupole coupling due to two chlorine nuclei: $\mathcal{H}_{q}=\mathcal{H}_{q}(1)+\mathcal{H}_{q}(2)$. The programs SPCAT and SPFIT [14], which employ complete diagonalization of the Hamiltonian matrix, were used. The programs were applied in the coupling scheme: $\mathbf{F}_{1}=\mathbf{J}+\mathbf{I}_{1}$, $\mathbf{F}_{2}=\mathbf{F}_{1}+\mathbf{I}_{2}$. However, the quantum numbers in Table 4.1 are given in the





Each doublet (due to Doppler splitting) has been recorded separately using 200 to 400 averaging cycles. The polarization frequency was always near resonant to the observed line. The Doppler splitting in this region is ~41 kHz. coupling scheme $I=I_1+I_2$, F=J+I, which is more appropriate for a molecule with two equivalent or near equivalent nuclei.

A global least squares analysis was used to fit the measured frequencies simultaneously to the rotational constants, centrifugal distortion constants of Watson's A-reduction Hamiltonian in I^r representation [15], and nuclear quadrupole coupling constants. Since only $\Delta K_a{=}0$ transitions were observed, not all distortion constants could be obtained from the spectra, and an iterative procedure was used. In the first fit for $Ar-^{35}Cl_{2}$ the constants Δ_{κ} and δ_{κ} were set to zero, and the only distortion constants included were Δ_{j} , Δ_{jK} and δ_{j} . These were sufficient to evaluate the harmonic force field (as described in the next section), from which values for Δ_r and δ_{κ} were estimated and fixed in the next fit. This iterative procedure converged rapidly and the inclusion of Δ_{κ} and δ_{κ} improved the fit slightly. The results are in Table 4.2. Although only a-type transitions were observed, the A rotational constant could be determined fairly accurately, because of the relatively high degree of asymmetry in the complex (κ =-0.921). For Ar-³⁵Cl³⁷Cl, since many fewer transitions were observed, all the quartic distortion constants were fixed at values derived from the force field analysis of the most abundant isotopomer.

The differences between measured frequencies and the frequencies calculated from the derived constants are also in Table 4.1 for $Ar-^{35}Cl_{2}$ and $Ar-^{37}Cl^{35}Cl_{2}$. The standard deviation of the fit for $Ar-{}^{35}Cl_2$ is about 2.3 kHz, while that for $Ar-^{35}Cl^{37}Cl$ is about 1.3 kHz. The differences between observed and calculated frequencies of Ar-35Cl, show small systematic deviations in the transitions $2_{1,2}-1_{1,1}$ and $2_{1,1}-1_{1,0}$: the same hyperfine components (I,F= 3,4-3,4 and 3,4-3,3) in both transitions show similar differences, considerably larger than the measurement uncertainty. Inclusion of the off diagonal element $\chi_{_{ab}}$ or spin rotation interaction did not remove these deviations. Similar but more pronounced effects have been observed for Ar-N, [11], Kr-N, [12], and Ar-HCN [16] and Kr-HCN [17], where the nuclear quadrupole coupling constants seem to be functions of rotational states. However, the effect for Ar-35Cl, is small and no further attempt was made to account for these deviations.

4.4 Estimation of the ³⁵Cl nuclear guadrupole coupling constant in the free chlorine molecule

The Cl quadrupole coupling constants χ_{gg} of Ar-Cl₂ along the *g*-principal inertial axes can be related to χ_o , the value for free Cl₂, through the following equation,

$$\chi_{gg} = \frac{\chi_o}{2} \langle 3\cos^2\theta_{gg} - 1 \rangle \qquad (4.1)$$

where θ_{gg} is the instantaneous angle between the Cl-Cl bond and the g-axis. Evaluation of θ_{gg} requires prior knowledge of χ_o , the ³⁵Cl coupling constant in free Cl₂. Since it had not been previously evaluated, however, it was determined using χ_{cc} of Ar-³⁵Cl₂, because the out-of-plane component χ_{cc} is free of van der Waals vibrational averaging ($\cos\theta_{cc}=0$). The value of χ_o thus obtained is -111.7902(38) MHz.

This determination of $\chi_{_{O}}$ assumes that there is no severe perturbation of the electronic structure of the subunits on complex formation. In some complexes, such as linear HF-Cl₂ [13], this is not entirely the case. The field gradients at the Cl nuclei differ by about 3%; in this case the coupling constants for the inner and the outer ³⁵Cl nuclei are -111.530(17) MHz and -108.161(17) MHz, respectively. However, previous studies on the rare gas-small molecule complexes have not yet shown such large perturbations in the field gradients of the small molecules on complex formation. In T-shaped Ar-ClCN [18], for example, it was found that the perturbation along the c-axis is only ~0.15% at the Cl nucleus. Assuming a similar effect in Ar-Cl,, the estimated $\chi_{_{\rm O}}$ in free diatomic $\text{Cl}_{_2}$ should be accurate to within ~100 kHz.

From the above equation an average value for the angle θ_{aa} , defined by $\arccos < \cos^2 \theta_{aa} >^{\frac{1}{2}}$ can be calculated. The result is 85.40(1)°. This represents an average deviation of ~4.6° from the T-shaped configuration, arising essentially from an internal rotation of the Cl₂ unit about its centre of mass. This value is to be compared with 21.7° in Ar-N₂ [11] and 21.3° in Kr-N₂ [12]; evidently Ar-Cl₂ is much more rigid than these two complexes. This observation is consistent with the much lower centrifugal distortion constants in Ar-Cl₂ than in the N₂ complexes.

The χ_{cc} values for the ³⁵Cl nuclei in both isotopomers agree within twice the standard deviation. Also, the ratio of the χ_{cc} values of ³⁵Cl and ³⁷Cl in the mixed isotopomer is 1.2681(6), which agrees with the ratio of the quadrupole moments of the two nuclei 1.2688773(15) [19]. It is unusual to be able to determine this ratio by measurement on ³⁵Cl and ³⁷Cl in a single isotopomer.

4.5 Harmonic force field analysis and structure

The distortion constants which could be determined from the spectrum made it possible to perform a harmonic force field analysis on $Ar-Cl_2$. There are only three vibrational modes, namely the Cl-Cl stretch (v_1) and the van der Waals stretch (v_2) , both of A_1 symmetry, and the van der Waals bend (v_3) , of B_2 symmetry. The two van der Waals modes describe, respectively, the change in distance between the Ar and Cl_2 subunits, and an essential internal rotation of Cl_2 about its centre of mass. The modes can be approximately characterized by the symmetry coordinates in Table 4.3. The B_2 mode is treated formally as an asymmetric ClArCl stretch, without losing its essential internal rotation character.

The measured distortion constants of $Ar^{-35}Cl_2$ were fit by least squares to the diagonal force constants f_{22} and f_{33} . The Cl-Cl stretching constant, f_{11} , was held at 3.2882 mdyn Å⁻¹, estimated from the Cl₂ vibration frequency [20], with the interaction constant, f_{12} , set to zero. The fitting was done in two iterations, in conjunction with the fits to the microwave spectrum, as described in section 4.3. The results of the final force field fit are in Table 4.3. Evidently the force constants are well determined, and reproduce the distortion constants well. The wavenumbers of the van der Waals modes, estimated from the force constants, are also in Table 4.3.

The inertial defects Δ were estimated using the derived force field. The values obtained are 2.395 amu Å² and 2.424 amu Å² for Ar-³⁵Cl₂ and Ar-³⁵Cl³⁷Cl, respectively. These are in moderate agreement with the experimental

values in Table 4.2. An alternative approach is to assume that Δ arises mainly from the low-lying van der Waals bending mode, and to use the formula of Herschbach and Laurie [22] to estimate the wavenumbers of this mode. The equation is $\Delta \approx 4 K/\omega_3$, where K=16.85763 amu Å² cm⁻¹, for Δ in amu Å² and ω_3 in cm⁻¹. The result for Ar-³⁵Cl₂ is ω_3 =26.6 cm⁻¹, which is rather less than 29.9 cm⁻¹, obtained in the force field analysis. This conclusion is very similar to those obtained for several other complexes, including Ar-OCS [23,24], Ar-CO₂ [25] and Ar-ClCN [18], where the approximate method consistently underestimated the bending wavenumbers compared to those from a force field analysis.

The equivalence of the two ³⁵Cl sites in $Ar^{-35}Cl_2$ has been confirmed by the details of the hyperfine structure in the rotational transitions and by the fact that the $K_a=0$ and $K_a=1$ stacks cooled separately in the molecular expansion, as shown by the similar intensities of the corresponding transitions. Consequently, with the angle θ between the Cl-Cl bond and the *a*-axis fixed at 90°, there remained only one parameter to be determined, namely the van der Waals distance R between the Ar atom and the centre of mass of the Cl_2 subunit. The C rotational constant here is independent of the average vibrational angle, since $I_{cc}=\mu R^2+I_o$, where μ is the reduced mass of $Ar-Cl_2$ and I_o is the moment of inertia of free Cl_2 . In similar cases such as in Ar-OCS [23,24] and Ar-CO₂ [25], it has been shown that the C rotational constant is the one least influenced by vibrational effects. From the C rotational constant values of 3.7190 Å and 3.7184 Å were calculated for $Ar-{}^{35}Cl_2$ and $Ar-{}^{35}Cl^{37}Cl$, respectively. The value 3.72±0.1 Å from electronic spectroscopy [7] is in excellent agreement with the one presented here.

4.6 Comments on the argon-halogen dimers and experimental observations

From the MW spectrum it has been found that the Ar-Cl₂ complex is T-shaped and can be fairly well described by a semirigid rotor model. The possibility of the existence of a linear conformer was discussed by Tao and Klemperer in their recent *ab initio* study of Ar-ClF and Ar-Cl₂ [8]. In a later *ab initio* calculation with a larger basis set, Tao and Klemperer [26] found that the linear conformer should be the higher energy conformer. Following their prediction a search was carried out for this conformer, but without success. Because of the uncertainty in the predicted structural parameters of the linear conformer and the very low line intensities of the T-shaped Ar-Cl₂, no definite conclusion could be drawn from the search. It is very likely that there is a very low probability for structural degeneracy at the very low rotational temperature (<5 K) achieved by the supersonic jet expansion. In this sense, the observation of T-shaped Ar-Cl₂ would rule out the existence of a linear conformer with lower zero point energy, which is in agreement with the later *ab initio* calculation.

The experimental and theoretical parameters of Ar-Cl₂ are compared in Table 4.4 to those of Ar-ClF. While the *ab initio* studies [8,26] and the realistic model intermolecular potential energy surface [27] produced only slightly higher or lower van der Waals stretch frequencies compared to the value from the force field for $Ar-Cl_2$, both calculations overestimate the flexibility of the van der Waals bending motion. This is shown by the much lower predicted bending frequencies.

The chlorine quadrupole coupling constant estimated for the free molecule fits into the trend χ (free molecule)=-111.7902 MHz > χ (atom)=-109.746 MHz [28] > χ (crystal)=-108.95 MHz [29], that was previously observed for iodine and bromine [13].

The surprisingly low intensity of the transitions observed, as compared to the case of e.g. $Ar-N_2$ [11], is worth some consideration. The slightly higher number of hyperfine components in the rotational transitions of $Ar-Cl_2$ cannot exclusively account for this. Three factors could cause the weak lines. These are a small dipole moment, a low abundance of the complex in the molecular

expansion, and a high temperature. The last point can be ruled out, however, since a considerable decrease in line intensity has been observed in going from lower to higher J transitions, thus verifying a low rotational temperature. The length of the applied MW excitation pulses, optimized for maximum polarization of the molecular sample, indicated that the dipole moment is slightly higher than that of Ar-N₂ (~0.01 D) [11]. A relatively low abundance of Ar-Cl₂ might be caused by the formation of Cl₂ dimers and larger clusters in the expansion. The intensity of the transitions decreased if the chlorine percentage in the sample (0.4% Cl₂, 0.8% Ar in Ne) was only slightly raised. This picture is supported also by the higher boiling point of chlorine, as compared to nitrogen, indicating relatively strong van der Waals forces between the Cl₂ molecules.

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|----|----|---|---|---|---|
|----|----|---|---|---|---|

Observed Frequencies of $\text{Ar-}^{35}\text{Cl}_2$ and $\text{Ar-}^{35}\text{Cl}^{37}\text{Cl}$

| Transition | | | | | | | Observed | Obs |
|------------------------------------|---------|------------|----|---|-----|---------------------------------|-----------|-------|
| $J'_{K_a'K_c'} - J''_{K_a'K}$ | 11 C | ! ' | F' | - | I" | F" | (MHz) | (kHz) |
| | | | | | _ | 35 ~ 2 | | |
| | | | | | Ar· | - ³⁵ C1 ₂ | | |
| $2_{0,2} - 1_{0,1}$ | 2 | 2 | - | 0 | 1 | | 5284.8003 | -0.3 |
| | 2 | 4 | - | 2 | 3 | | 5281.2187 | 1.6 |
| | 0 | 2 | - | 2 | 1 | | 5277.6249 | -1.2 |
| | | | | | | | | |
| $2_{1,1} - 1_{1,0}$ | 3 | 4 | - | 3 | 4 | | 5560.9627 | -8.4 |
| | 3 | 3 | - | 1 | 2 | | 5554.1780 | -1.1 |
| | 1 | 3 | - | 3 | 2 | | 5544.0945 | 0.4 |
| | 3 | 4 | - | 3 | 3 | | 5538.6083 | 3.3 |
| | 3 | 5 | - | 3 | 4 | | 5521.3749 | -0.7 |
| | | | | | | | | |
| 2 _{1,2} -1 _{1,1} | 3 | 4 | | 3 | 3 | | 5066.0652 | 4.1 |
| | 3 | 3 | - | 1 | 2 | | 5046.9235 | -0.8 |
| | 3 | 5 | - | 3 | 4 | | 5041.5892 | -0.5 |
| | 3 | 4 | - | 3 | 4 | | 5021.7926 | -8.7 |
| | 1 | 3 | - | 1 | 3 | | 5008.4428 | 1.2 |
| | | | | | | | | |
| $3_{0,3} - 2_{0,2}$ | 2 | 3 | _ | 2 | 2 | | 7904.8239 | -1.0 |
| | 2 | 4 | - | 2 | 3 | | 7903.0635 | 0.5 |
| | 2 | 5 | - | 2 | 4 | | 7903.0635 | 1.5 |
| | 0 | 3 | - | 0 | 2 | | 7901.2865 | 0.3 |

Table 4.1 (continued)

| Trans | siti | Observed Frequency | Obs | | |
|-------------------------------------|------|-----------------------|--------|------------|-------|
| "K'aK' ~ J"" | K" | I' F' - | · I" F | " (MHz) | (kHz) |
| $3_{1,1} - 2_{1,2}$ | 3 | 5 - 3 | 4 | 7566.8362 | 3.1 |
| | 1 | 2 - 1 | 1 | 7565.6719 | 0.5 |
| | 3 | 4 - 3 | 3 | 7565.0001 | -0.4 |
| | 3 | 6 - 3 | 5 | 7561.3425 | 1.0 |
| | 1 | 4 - 1 | 3 | 7559.6287 | 0.2 |
| | 1 | 3 - 1 | 2 | 7557.3367 | 0.9 |
| | | | | | |
| $3_{1,2} - 2_{1,1}$ | 3 | 4 - 3 | 3 | 8297.9554 | 0.3 |
| | 1 | 4 - 1 | 3 | 8295.5233 | 1.1 |
| | 1 | 2 - 1 | 1 | 8291.6951 | 0.8 |
| | 1 | 3 - 1 | 2 | 8291.5650 | 2.5 |
| | 3 | 5 - 3 | 4 | 8288.9675 | 1.6 |
| | 3 | 6 - 3 | 5 | 8287.4075 | 1.4 |
| | | | | | |
| $4_{0,4} - 3_{0,3}$ | 2 | 4 - 2 | 3 | 10504.5169 | -0.9 |
| | 2 | 5 - 2 | 4 | 10502.6732 | 0.5 |
| | 2 | 6 - 2 | 5 | 10502.6732 | 1.5 |
| | 0 | 4 - 0 | 3 | 10500.8139 | 0.6 |
| | | | | | |
| 4 _{1,4} - 3 _{1,3} | 3 | 6 - 3 | 5 | 10075.7144 | -0.6 |
| | 3 | 5 - 3 | 4 | 10075.1238 | -0.6 |
| | 3 | 7 - 3 | 6 | 10073.8349 | 1.0 |
| | 1 | 5 - 1 | 4 | 10073.2055 | -1.4 |

| $Trans J'_{K_a'K_c'} - J''_{K_a'K_c'}$ | iti I | on :'F'- | I" F" | Observed Frequency (MHz) | Obs Calc. (kHz) |
|--|----------|-------------|-------|--------------------------------|-----------------------|
| $4_{1,3} - 3_{1,2}$ | 1 | 5 - 1 | 4 | 11047.8160 | -1.2 |
| .,,. | 3 | 5 - 3 | 4 | 11047.3538 | -1.6 |
| | 3 | 7 - 3 | 6 | 11043.7242 | 0.0 |
| | 3 | 6 - 3 | 5 | 11043.0576 | 0.4 |
| | | | | | |
| $5_{0,5} - 4_{0,4}$ | 2 | 5 - 2 | 4 | 13075.5617 | 0.6 |
| | 2 | 6 - 2 | 5 | 13073.4716 | -0.6 |
| | 2 | 7 - 2 | 6 | 13073.4716 | 0.4 |
| | 0 | 5 - 0 | 4 | 13071.3164 | -0.5 |

Table 4.1 (continued)

Ar-³⁵Cl³⁷Cl

| $2_{0,2} - 1_{0,1}$ | 3 | 4 - 3 | 4 | 5237.0880 | 0.7 |
|---------------------|---|-------|---|-----------|------|
| | 3 | 3 - 1 | 2 | 5226.9762 | -0.4 |
| | 2 | 3 - 2 | 2 | 5222.4106 | -1.6 |
| | 2 | 4 - 2 | 3 | 5222.1248 | -1.3 |
| | 3 | 5 - 3 | 4 | 5220.5347 | -1.8 |
| | 3 | 4 - 3 | 3 | 5217.3670 | -2.3 |
| | | | | | |
| $2_{1,1} - 1_{1,0}$ | 4 | 3 - 3 | 3 | 5480.4015 | -0.4 |
| | 4 | 2 - 3 | 2 | 5473.6246 | 0.8 |
| | 5 | 3 - 4 | 3 | 5464.7621 | 2.2 |

| Transition | | | | | | Observed | Obs | |
|------------------------------|----|----|----|---|----|----------|------------|-------|
| $J'_{K_a'K_c'} - J''_{K_a'}$ | K" | I' | F' | - | I" | F" | (MHz) | (kHz) |
| | | | | _ | | | | |
| $2_{1,2} - 1_{1,1}$ | 4 | 2 | - | 3 | 2 | | 4984.8948 | 2.1 |
| | 5 | 3 | - | 4 | 3 | | 4982.1541 | 0.4 |
| $3_{0.3} - 2_{0.2}$ | 1 | 4 | - | 1 | 3 | | 7815.3355 | -1.0 |
| -,,- | 2 | 3 | - | 2 | 2 | | 7815.2765 | 0.6 |
| | 2 | 4 | - | 2 | 3 | | 7814.0443 | 0.8 |
| | 2 | 5 | - | 2 | 4 | | 7813.7577 | 0.1 |
| | 3 | 6 | - | 3 | 5 | | 7813.4824 | -0.5 |
| | 3 | 4 | - | 3 | 3 | | 7813.1372 | 0.1 |
| | 0 | 3 | - | 0 | 2 | | 7812.1597 | 0.4 |
| | 3 | 5 | - | 3 | 4 | | 7810.8633 | -0.4 |
| $4_{04} - 3_{03}$ | 1 | 4 | _ | 1 | 3 | | 10384.2970 | 1.1 |
| ·)· · ·)· | 2 | 4 | - | 2 | 3 | | 10383.8730 | -0.7 |
| | 1 | 5 | - | 1 | 4 | | 10382.8805 | -0.9 |
| | 3 | 7 | - | 3 | 6 | | 10382.8289 | 1.3 |
| | 2 | 6 | - | 2 | 5 | | 10382.3182 | 0.2 |
| | 3 | 5 | - | 3 | 4 | | 10380.4238 | -0.2 |
| | 3 | 6 | - | 3 | 5 | | 10380.2508 | 0.1 |

Table 4.2

Spectroscopic Constants of $Ar-^{35}Cl_2$ and $Ar-^{35}Cl^{37}Cl$

| Parameter | Ar- ³⁵ Cl ₂ | Ar- ³⁵ Cl ³⁷ Cl |
|--|-----------------------------------|---------------------------------------|
| Rotational cons | stants_/MHzª | |
| A | 7373.50(12) | 7173.929(34) |
| В | 1444.08802(23) | 1429.91722(19) |
| с | 1200.31288(20) | 1185.11335(19) |
| <u>Centrifugal dis</u> | stortion constants / | <u>kHz^a</u> |
| Δ _J | 8.2522(47) | 8.048 ^b |
| Δ _{JK} | 108.21(14) | 105.4 ^b |
| Δ _κ | -111.1 ^b | -107.8 ^b |
| δ _J | 1.4155(36) | 1.407 ^b |
| δ _κ | 73.69 ^b | 71.69 ^b |
| ³⁵ Cl and ³⁷ Cl nu | <u>clear quadrupole cou</u> | pling constants /MHz |
| χ_{aa} (³⁵ Cl) | 54.8180(16) | 54.8407(27) |
| χ _{bb} (³⁵ Cl) | -110.7131(19) | -110.706(20) |
| χ _{cc} (³⁵ Cl) | 55.8951(19) | 55.866(20) |
| χ_{aa} (³⁷ Cl) | - | 43.2111(29) |
| χ _{bb} (³⁷ Cl) | - | -87.267(12) |
| χ _{cc} (³⁷ Cl) | - | 44.056(12) |
| Inertial defect | . /amu Å ² | |
| Δ _o | 2.5354(11) | 2.5604(3) |
| Standard deviat | ion /kHz | |
| σ | 2.3 | 1.1 |

^a I^r representation, Watson's A-reduction Hamiltonian was used [16].

^b Fixed at the values obtained from the force field analysis.

Table 4.3

The structure and harmonic force field of $Ar^{-35}Cl_2$

Structural parameters: $r(Cl(1)-Cl(2))=r=1.991 Å^{a}$ r(Ar-c.m. of Cl₂)=R=3.7190 Å $r(Ar-Cl(1)) = r_1 = 3.8499 \text{ Å}$ $r(Ar-Cl(2)) = r_2 = 3.8499 \text{ Å}$ Symmetry coordinates: $A_1: S_1 = \Delta r$ S₂=∆R B₁: S₃=(1/2)^{- $\frac{1}{2}$} ($\Delta r_1 - \Delta r_2$) Harmonic force constants and vibrational frequencies: $f_{11}=f(Cl_2) \pmod{\text{\AA}^{-1}}$ 3.2882 $f_{22}=f_s \pmod{\text{\AA}^{-1}}$ 0.01782 ω_{cm}^{-1} 34.5 $f_{33}=f_b \pmod{\text{\AA}^{-1}}$ 0.01651 $\omega_{\rm b}$ (cm⁻¹) 29.9

<u>Comparison of Observed and Calculated</u> <u>centrifugal distortion constants (kHz):</u>

| | Observed ^b | Calculated ^c |
|-----------------|-----------------------|-------------------------|
| Δ _J | 8.2522(47) | 8.251 |
| Δ _{JK} | 108.21(14) | 108.2 |
| Δ _κ | -111.1 (fixed) | -111.1 |
| δ _၂ | 1.4155(36) | 1.422 |
| δ _κ | 73.69 (fixed) | 73.69 |
| | | |

^a Ref. 21.

^b The values are those in Table 4.2.

^c Calculated from the derived force constants.

| Parameter | | Ar- ³⁵ Cl ₂ | | Ar- ³⁵ ClF | | |
|---------------------------------------|-----------|-----------------------------------|----------|-----------------------|--------|--|
| | Exp. | Theo. | Theo. | Exp. | Theo. | |
| Structure type | T-shaped | T-shaped | T-shaped | linear | linear | |
| R(Ar-Cl)/ Å | 3.8499 | 3.9 | 3.97 | 3.33 | 3.38 | |
| Bond energy/ cm ⁻¹ | 188±1ª | 197.9 | 180.8 | 230 | 233.5 | |
| k _s / mdyn Å ⁻¹ | 0.01782 | - | - | 0.0301 | - | |
| $\omega_{\rm s}$ / cm ⁻¹ | 34.5 | 33.1 | 41 | 47.2 | 51.4 | |
| k _b ∕ mdyn Å ^{−1} | 0.01651 | - | - | 0.0215 | - | |
| $\omega_{\rm b}$ / cm ⁻¹ | 29.9 | 20.7 | 12 | 41.0 | 48.6 | |
| θ° | 4.6 | - | - | 11.1 | - | |
| References | This work | 26 | 27 | 2 | 8 | |

Table 4.4 Comparison of the properties of Ar-Cl₂ with those of Ar-ClF.

^a Ref. 7

CHAPTER 5

Pure Rotational Spectra of the Mixed Rare Gas

<u>van der Waals Dimers</u>

5.1 Introduction

Rare gas (RG) pair potentials were among the first van der Waals potentials studied, since the van der Waals interactions between two rare gas atoms are the simplest type possible and exhibit no angular dependence of the pair potentials. Since the 1970s some major advances have been made in the determination of rare gas pair potentials, as more precise experimental and theoretical information as well as new techniques of analysis have become available [1,2]. Research involving the rare gas pair potentials is an active field. This is shown by the continuing close interaction between experimentalists and theoreticians, for these pair potentials have been repeatedly revised whenever new experimental data have become available [3].

The homonuclear dimers in particular have been extensively studied, and accurate interaction potentials have been derived [4]. Results from spectroscopic investigations have been especially valuable, when combined with data from 'bulk' and scattering experiments [2]. Absorption and laser induced fluorescence spectra [5,6] obtained in the vacuum ultraviolet (VUV) region were of comparatively high resolution, and vibrational and rotational structures could be resolved. They have led in some cases to fairly accurate rotational and centrifugal distortion constants for several vibrational levels in the ground and excited electronic states, as well as to equilibrium bond lengths and harmonic vibration frequencies.

The situation is far less satisfactory in the case of the heteronuclear RG dimers. The newest available potentials for He-Ne, He-Ar, He-Kr, He-Xe [7], Ne-Ar [8], Ne-Kr, Ne-Xe [9], Ar-Kr [10], and Ar-Xe, Kr-Xe [11] are based on scattering and 'bulk' experimental data only, and even this is not very accurate, because homonuclear interactions must also be accounted for [2]. VUV absorption spectra have been obtained for Xe- and Kr-RG mixtures [12], but no conclusive assignment of the observed bands could be made. Collision induced absorption (CIA) spectra, which probe the repulsive wall of the potential curve near the collision diameter of RG mixtures, have yielded information about the induced dipole moments of RG-RG' collision pairs [13].

On the other hand, information from high resolution infrared and microwave spectroscopy has proven to be very useful for the investigation of many van der Waals molecules [14]. For example, information about the interaction potential energy surfaces, especially near their minima, can be extracted from microwave

(rotational) spectra of such systems [15]. Furthermore, information can be obtained about the molecular electric charge distribution through the determination of electric dipole moments and, if quadrupolar nuclei (e.g. 131 Xe, 83 Kr, 21 Ne) are involved, of nuclear quadrupole coupling constants. These parameters may then be test cases for sophisticated *ab initio* calculations.

However, high resolution IR and MW spectroscopies have never previously been applied to the heteronuclear RG dimer systems, although these spectroscopies are in principle possible for the systems mentioned, because of their small, but nonvanishing, induced dipole moments. The search for the rotational spectra of these systems faces some serious unknowns, such as the yield of the complexes, the rough magnitude of the dipole moments, and drawbacks, such as the large uncertainty in the frequencies.

The success with some very low dipole moment van der Waals complexes, such as $Ar-N_2$ [16], $Kr-N_2$ [17], and especially $Ar-Cl_2$ [Chapter 4], have shown that the method of pulsed molecular beam MW Fourier Transform (FT) spectroscopy is particularly powerful when only a small transition dipole moment is involved. Furthermore, from the study of $Ar-Cl_2$, as discussed in Chapter 4 of this thesis, it seemed that the abundance of the species of interest is more critical for an observation than the

magnitude of the dipole moment. In addition, another part of this thesis work, namely the investigations of the van der Waals trimers Ar_2 -OCS and Ar_2 -CO₂ [Chapter 7], with Ar_2 subunits, has suggested that there is an abundance of rare gas dimers in the molecular expansion. These results suggested that microwave spectroscopic investigation of RG dimers might be feasible. Rotational and vibrational transition frequencies of all possible heteronuclear RG dimers have recently been predicted [18], based on the newest available potentials, and these were expected to provide valuable starting points for spectroscopic searches.

In this chapter the measurements of rotational transitions of various isotopomers of the RG dimers Ne-Kr, Ne-Xe, Ar-Xe and Kr-Xe with low values of J (up to J=9) are described. The analyses have yielded rotational constants, along with quartic and, in some cases, sextic centrifugal distortion constants. The experimental frequencies and constants are compared to those predicted from the newest mixed rare gas potentials. Furthermore, some parameters in the potentials, e.g. the equilibrium distances r_e and (or) the dissociation energies ϵ , have been manually adjusted in order to bring the experimental data and the predictions based on the potentials into agreement. The high resolution capability of MWFT spectroscopy has made it possible to resolve the nuclear
hyperfine structure of rotational transitions of isotopomers containing quadrupolar RG nuclei, and to derive the nuclear quadrupole coupling constants of these nuclei. Values for the electric dipole moments have been estimated for all four dimers from the MW excitation pulse lengths, optimized for maximum signal strength (" $\pi/2$ condition" [19], see Chapter 2).

5.2 Experimental considerations

In the present work the following gas mixtures were used: (i) for Ne-Kr: 1.5% Kr in Ne; (ii) for Ne-Xe: 1% Xe in Ne; (iii) for Ar-Xe: 2% Ar and 1% Xe in Ne; (iv) for Kr-Xe: 1.5% Kr and 1% Xe in Ne. The backing pressures were up to 5 atm. All gases were of research grade purity, purchased from Linde, Canada. The MW power amplifier was used here because of the very low dipole moments anticipated for all these dimers.

Since the molecular electric multipole moments of the isolated dimers usually play a minor role in the attractive forces [20], the yields of rare gas dimers formed in the molecular expansion were probably similar to those of van der Waals complexes containing polar subunits.

For well separated lines, the frequency information is obtained after Fourier transformation, using a three point interpolation formalism. On the other hand, where lines were closely spaced (as was found for complexes containing ⁸³Kr and ¹³¹Xe in the present work), the displayed spectra were often slightly distorted. In this case accurate frequencies were obtained by direct analysis of the time-domain signals [21].

5.3 Search and spectral assignments

5.3.1 Search and spectral assignment of Ne-Kr

The prediction from Ref.18 provided the starting point for the search. It was done in 0.2 MHz increments for the excitation frequency, using a pulse length of 2 μ s and 10 averaging cycles at each frequency.

There are several possible isotopic combinations in Ne-Kr, since Ne has two major isotopes 20 Ne (90.92%) and 22 Ne (8.28%); and Kr has five: 84 Kr (56.90%), 86 Kr (17.37%), 82 Kr (11.56%), 83 Kr (11.55%), and 80 Kr (2.27%). The first transition was found at 8188.6913 MHz and was later assigned to the complex 22 Ne- 86 Kr by comparing isotopic data and intensity. It could be seen easily with one experimental cycle. Following this, it was relatively straightforward to find transitions at other values of J, as well as lines of other isotopomers. The intensities of the lines decreased dramatically with increasing J values, indicating an extremely low rotational temperature achieved in the expansion. Altogether spectra of nine isotopomers have been observed, with J values ranging from 0 to 4, constrained by the frequency range of the microwave power amplifier (4-18 GHz) or by the line intensities. The complicated nuclear quadrupole hyperfine structures due to 83 Kr (nuclear spin 9/2) have been resolved for 20 Ne- 83 Kr. Only one transition, namely J=2-1, has been observed for 21 Ne- 84 Kr because of its extremely low natural abundance (~0.1%); no hyperfine splitting due to 21 Ne (I=3/2) could be observed.

All measured rotational transition frequencies and their assignments are given in Table 5.1. The measured frequencies of the hyperfine components of $^{20}Ne^{-83}Kr$ are in Table 5.2; for this isotopomer the frequencies in Table 5.1 are those of the hypothetical unsplit lines.

Fits of the rotational constants and quartic and sextic centrifugal distortion constants to the measured frequencies gave the spectroscopic constants in Table 5.3, which reproduce the experimental frequencies to within 1 kHz (see Table 5.1). The quadrupole coupling constant for ²⁰Ne-⁸³Kr was obtained from a fit of this constant and the hypothetical unsplit line frequencies to the observed hyperfine components. The standard deviation

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of this fit was again within the measurement accuracy (see Δv in Table 5.2); the constant is given in Table 5.13.

The J=2-1 rotational transition of 20 Ne- 83 Kr is depicted in Fig. 5.1, showing its resolved hyperfine components. The illustration is a composite one, obtained from three experiments. This was necessary because an experiment at a certain frequency is relatively narrow banded, covering roughly 200 kHz around the excitation frequency for this particular transition. For some weak components such as components 7/2-9/2 in Fig. 5.1, the excitation bandwidths are even narrower. This is the result of the quality factor Q=10000 of the MW cavity and the fairly long MW excitation pulse length of 2 μ s.

5.3.2. Ne-Xe spectra and assignments

Essentially the same search procedure was used for Ne-Xe as for Ne-Kr. Xe has even more major isotopes than Kr: 128 Xe (2%), 129 Xe (26%), 130 Xe (4%), 131 Xe (21%), 132 Xe (27%), 134 Xe (10%), and 136 Xe (9%). This time the search was started for the J=2-1 transition and the line of 20 Ne- 128 Xe at 7326.1225 MHz was the first one found. Subsequently spectra of ten other isotopomers were assigned. Four transitions, ranging from J=2-1 to J=5-4, could be measured for most of the isotopomers, and the



Fig.5.1. Hyperfine pattern of the J=2-1 rotational transition of 20 Ne- 83 Kr.

The spectrum is a composite one, obtained from three experiments with different excitation frequencies. 200 averaging cycles were used. Each hyperfine component is split into a Doppler doublet because the molecular expansion is injected parallel to the cavity axis. measured frequencies are given in Table 5.4. The frequencies of the hyperfine components due to the quadrupolar ¹³¹Xe nucleus in ²⁰Ne-¹³¹Xe and ²²Ne-¹³¹Xe are in Table 5.5; for these two isotopomers the frequencies in Table 5.4 are those of the hypothetical unsplit lines. The derived rotational and centrifugal distortion constants are in Table 5.6, while the quadrupole coupling constants obtained are in Table 5.13. Again, the spectroscopic constants obtained here reproduce the experimental frequencies well, as can be seen from Δv in Tables 5.4 and 5.5.

Spectra of isotopomers containing the quadrupolar ²¹Ne nucleus (0.21% natural abundance) were too weak to be observed.

The hyperfine splitting of J=2-1 rotational transition of $^{20}Ne^{-131}Xe$ is depicted in Fig.5.2. The illustration is again a composite one, obtained from three experiments.

5.3.3 Ar-Xe spectra and assignment

Essentially the same search procedure was used for Ar-Xe as for Ne-Kr. The first transition was found at 7702.13 MHz and was assigned to the complex $Ar-^{131}Xe$, because of its ¹³¹Xe nuclear quadrupole hyperfine pattern. Altogether spectra of seven isotopomers have been observed, with J values ranging from 2 to 9. The effects



Fig.5.2. Hyperfine pattern of the J=2-1 rotational transition of 20 Ne- 131 Xe.

The spectrum is a composite one, obtained from three experiments with different excitation frequencies. For the F"-F'=3/2-1/2 component 400 averaging cycles were used; 20 cycles were needed for the strongest components.

of spin rotation coupling in the case of the ¹²⁹Xe isotopomer (spin 1/2) were too small to be observed. No attempt was made to measure transitions of isotopomers containing ³⁶Ar because of the very low intensity expected.

All rotational transition frequencies are given in Table 5.7. The measured frequencies of the hyperfine components of $Ar-^{131}Xe$ are in Table 5.8; for this isotopomer the frequencies in Table 5.7 are those of the hypothetical unsplit lines. The derived rotational constants and quartic and sextic centrifugal distortion constants are in Table 5.9. The quadrupole coupling constant for $Ar-^{131}Xe$ is given in Table 5.13. The fits are of similar quality as those of Ne-Kr and Ne-Xe.

5.3.4 Kr-Xe spectra and assignments

Although Kr-Xe was anticipated to be the most stable of the complexes among these four mixed rare gas dimers, it was considered the most unfavourable case. Both rare gases occur as several isotopes, each with considerable natural abundance. The lowest transition within the operating range of the spectrometer was J=4-3, near 4.4 GHz, well below the specified operating range of the then available power amplifier (8-18 GHz). The J=5-4transition at roughly 5.5 GHz was expected for search purposes to be the best compromise between available MW power and population. The search was started slightly below the frequency estimated from the predictions in Ref.18, following the trend observed in the other three dimers. The first line found was at 5496.05 MHz; it was assigned to 84 Kr- 132 Xe. Measurements for further isotopomers were straightforward. The measured frequencies for five different isotopomers are given in Table 5.10, together with the values of the deviations Δv , obtained from the rotational and centrifugal distortion constants in Table 5.12. The fits are of similar quality to those of the other three dimers.

The measured frequencies of the quadrupole hyperfine patterns of 84 Kr- 131 Xe are in Table 5.11. The derived quadrupole coupling constant in Table 5.13 is the least precise of those reported here. The reason is that only two transitions with relatively high J quantum numbers could be measured. Furthermore the sign of the quadrupole coupling constant could not be unambiguously determined because only two hyperfine components could be resolved for each rotational transition. The sign in Table 5.11 was inferred from the intensity ratios of the doublets and from the signs determined for the other two complexes containing 131 Xe.

No attempt was made to observe quadrupole hyperfine structure due to ⁸³Kr. The intensity of isotopomers containing ⁸³Kr was expected to be much too small because

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of its low natural abundance (11.5%), its relatively high nuclear spin (I=9/2) and the relatively high J of the lowest accessible transition (J=4-3).

5.4 Estimation of the induced dipole moments of the mixed rare gas dimers

Rough estimates for the dipole moments of the dimers were obtained using the dependence of the signal strength on the duration of the MW excitation pulse. The product of transition dipole moment and MW excitation pulse length is a constant at a given field strength for the condition of maximum signal strength, i.e. $\pi/2$ condition" [19, see also Chapter 2]:

$$\mu_{ab} \cdot \varepsilon \cdot \tau_{e} = \frac{\pi}{2}\hbar \tag{5.1}$$

The permanent dipole moment μ of a linear molecule is connected with the transition dipole moment μ_{ab} by [22]:

$$\mu = \left(\frac{2J+1}{J+1}\right)^{\frac{1}{2}} \mu_{ab}$$
 (5.2)

with J denoting the higher level in a transition.

The spectrometer was calibrated by finding the " $\pi/2$ condition" for the 2_{0,2}-1_{0,1} transition of Ar-CO₂ at 7317.288 MHz [23] using its known dipole moment of

0.06793(20) D [24]. The method was checked using Ne-CO₂, by measuring the ratio of the optimized microwave pulse lengths of Ne-CO₂ and Ar-CO₂. The value obtained for Ne-CO₂ is 0.026 D, in good agreement with the known value μ =0.0244(13) D [25] measured with the Stark effect.

The J=2-1 transition of 22 Ne- 86 Kr at 8188.6913 MHz, the J=2-1 transition of 20 Ne- 132 Xe at 7296.9286 MHz, and the J=4-3 transition of Ar- 129 Xe at 7729.7703 MHz are quite close in frequency to the Ar-CO₂ calibration transition and were used to estimate the induced dipole moments in Ne-Kr, Ne-Xe and Ar-Xe, respectively. The estimated values of the dipole moments are given in Table 5.14. Their uncertainties are difficult to evaluate. The values of the dipole moments obtained are believed to be of the correct order of magnitude.

Unfortunately, applying the above estimation method was much more difficult in the case of Kr-Xe than in the other three cases. The J=7-6 transition, which is the closest in frequency to the calibration transition of $Ar-CO_2$, was too weak for a reasonable intensity investigation because the J=6 energy level had too low a population. Instead, the J=5-4 transition of ⁸⁴Kr-¹²⁹Xe at 5545.3940 kHz was used. The result in Table 5.14 is much less reliable than for the other two complexes.

5.5 Interpretation of the spectroscopic constants

5.5.1 Estimations of the equilibrium distances from the isotopic data

With the rotational constants obtained, two types of distances, namely the ground state effective (r) and the substitution (r,) distances have been calculated. For Ne-Kr, Ne-Xe, and Kr-Xe, in which isotopic substitutions were made at both nuclei, complete r_s structures have been obtained. The resulting values, obtained using ²⁰Ne-⁸⁴Kr, ²⁰Ne-¹³²Xe and ⁸⁴Kr-¹³²Xe as the "parent" species, are given in Table 5.15. These distances were cross checked using several different isotopic combinations, and were found to be the same within 0.001 Å, irrespective of the isotopomers used. For Ar-Xe, where isotopic substitutions could be made only at Xe, the Ar nucleus was located using the first moment condition. This procedure was checked by using the same procedure for the other three complexes: the resulting distances were within 0.001 Å of the true r values. The resulting "r_s" distance for 40 Ar- 132 Xe is given in Table 5.15. Table 5.15 also contains the r values for the isotopomers given above, along with the r_o values for the isotopomers which have the biggest r value changes with respect to their "parent" species.

However, one important parameter used to

characterize the potential energy curve is the equilibrium distance r_e . Even though all the measured spectra were of the complexes in their ground vibrational states, it has nevertheless been possible to obtain values of the equilibrium (r_e) distances, because spectra of so many isotopomers have been observed. It was shown by Costain [26] that for diatomic molecules, the r_s distances are, to a good approximation, the averages of the ground state effective (r_o) and equilibrium (r_e) distances:

$$\mathbf{r}_{e} = 2\mathbf{r}_{s} - \mathbf{r}_{o} \tag{5.3}$$

The r_e values thus calculated are in Table 5.15.

Since r_e should in principle be independent of isotopomer, uncertainties in the r_e values will arise from the variations in r_s and r_o derived above. The outside error limit from this source is ~±0.005 Å for Ne-Kr, ~±0.003 Å for Ne-Xe, and ~±0.001 Å for Ar-Xe and Kr-Xe.

On the other hand, the accuracy of these r_e values depends on the validity of the approximation used in deriving Eq.(5.3). This is a particularly important consideration for these dimers because they are so weakly bound, and their internuclear potentials can be expected to be quite anharmonic. Eq.(5.3) was derived [26] using the equation:

$$\Delta I_{b}^{o} = \left(\frac{h}{8\pi^{2}}\right) \left[\left(\frac{1}{B_{o}'}\right) - \left(\frac{1}{B_{o}}\right)\right]$$
(5.4)

with the approximation

$$B_o = B_e - \frac{\alpha_e}{2}$$
 (5.5)

This gives the equation

$$\Delta I_{b}^{o} - \Delta I_{b}^{e} + \left(\frac{h}{8\pi^{2}}\right) \left[\frac{\alpha_{e}'}{2(B_{e}')^{2}} - \frac{\alpha_{e}}{2B_{e}^{2}}\right] + \dots$$
(5.6)

where the primed terms refer to the isotopically substituted species. In Eq.(5.6) terms of the form α_e^2/B_e^3 are ignored; this approximation is tantamount to saying that $(\alpha_e/\alpha_e') = (B_e/B_e')^{\gamma}$ with $\gamma = 1.5$.

To test whether Eqs.(5.4)-(5.6) are valid in the present case, it is assumed that α_e has the form

$$\alpha_{e} = -\left(6 \frac{B_{e}^{2}}{\omega_{e}}\right) (1 + a_{1})$$
(5.7)

where a_1 is a cubic potential constant. Eq.(5.7) gives the first approximation to α_e in Dunham's [27] expressions, given by Townes and Schawlow [28]; α_e also takes this form if the Morse potential is adequate to describe rare gas pairs around the potential minimum [29]. In this case $\gamma=1.5$, and the terms in α_e^2/B_e^3 become independent of isotopomer, so that their differences in Eq.(5.6) vanish. Any further approximation to B_o , by adding a term $\gamma_e/4$, would be ignored.

There are enough data in Ref.[6] to check whether Eq.(5.7) is a reasonable approximation for the case of ${}^{40}\text{Ar}_2$. The cubic coefficient a_1 was calculated using the values of B_e , α_e and ω_e given there: it came to a_1 =-6.23. This was then used to estimate r_o with the equation

$$\frac{r_{o} - r_{e}}{2r_{e}} = \frac{r_{o} - r_{s}}{2r_{s} - r_{o}} = -\frac{3B_{e}}{4\omega_{e}} (1 + a_{1})$$
(5.8)

which can be obtained [26] from the derivation of Eq.(5.3). Using the r_e value of Ref.[6], this gives $r_o=3.818$ Å, which is within 0.004 Å of the value 3.822 Å derived from B_o [6]. Evidently Eq.(5.7) is a good approximation for Ar_2 . Uncertainties in r_e from breakdown of Eq.(5.3) are probably roughly ± 0.005 Å. In the cases of the heavier pairs such as Ar-Xe and Kr-Xe, the uncertainties is probably less than stated. However, in the cases of the lighter pairs such as Ne-Kr and Ne-Xe, whose potentials support only three bound vibrational states [18], it is likely that there is bigger deviation than ~ ± 0.005 Å. The total uncertainties in r_e are thus conservatively estimated to be ~ ± 0.01 Å for Ne-Kr, ~ ± 0.008 Å for Ne-Xe, and ~ ± 0.005 Å for Ar-Xe and Kr-Xe. The above method has the advantage of using solely the microwave data with a simple assumption. The Morse potential approximation for the bottom of the well has been used in the construction of several other rare gas pair potentials [30]. However, the Morse potential has proven to be inadequate for a characterization of the *entire* potential [31], because it has only two adjustable parameters. For example, in the case of Ar_2 , the Morse potential failed to predict the rotational and vibrational spacings measured [31] by Colbourn and Douglas [5].

However, the relatively large error bounds attached to the r_e values do not reflect the accuracy of the microwave data presented here. Furthermore, several new types of potentials have been developed for these rare gas pairs in the last ten years [9,11,32], and it was highly desirable to test these new potentials with the high resolution microwave data presented and also to try to incorporate these data into the potential parameters.

5.5.2 Comments on the newest potentials available for Ne-Kr, Ne-Xe, Ar-Xe and Kr-Xe

One motivation of this work was to provide accurate spectroscopic data for these mixed rare gas dimers near the bottom of the potential well. Highly accurate spectroscopic data would help to refine the existing pair

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potentials of these dimers. It might also act as a discriminator between different potentials proposed for some pairs.

The HFD-B [32,9] and HFD-C [11] type potentials from Aziz and co-workers for these four dimers were used for this purpose. These potential functions have been widely used in the theoretical research work involving rare gas systems, such as dipole moment studies of rare gas systems [33] and three-body nonadditive studies [34]. The analytical form of HFD-B type potential V(r) is given by Aziz [32,9]:

$$V(r) - \epsilon V^{*}(x),$$

$$V^{*}(x) - A^{*} \exp(-\alpha^{*} x + \beta^{*} x^{2}) - F(x) \sum_{j=0}^{3} c_{2j+6} / x^{2j+6},$$
(5.9)

with the damping function

$$F(x) = \exp[-(D/x-1)^{2}], \quad x < D$$

= 1, $x \ge D$, (5.10)
and
 $x = r/r_{e}$

 c_6 , c_8 , and c_{10} are the dispersion coefficients, usually fixed at the values from *ab initio* calculations. This potential has five fully adjustable parameters: ϵ , r_e , D, B, and in some cases c_{12} [32,9] to add some more flexibility to the potential. D is a damping parameter; ϵ is the dissociation energy from the potential minimum; and r_e is the equilibrium distance. A^{*}, α^* and β^* are the reduced parameters, which can be calculated from the above input. Here α^* is positive and β^* is negative.

The analytical form of HFD-C type potential V(r) is [11]:

$$V(\mathbf{r}) = \mathbf{e} V^{*}(\mathbf{x}),$$

$$V^{*}(\mathbf{x}) = A^{*}\mathbf{x}^{\gamma} \exp(-\alpha^{*}\mathbf{x}) - F(\mathbf{x}) \sum_{j=0}^{2} C_{2j+6} / \mathbf{x}^{2j+6},$$
(5.11)

with F(x) the same as defined in Eq.(5.10). The potential has four adjustable parameters: ϵ , r_e , γ , and D [11]; ϵ , r_e , D have the same meaning as before, and γ is a repulsive parameter. The rest of parameters are the same as defined before.

All these potentials have been fitted to certain scattering and/or bulk experimental data for various rare gas pairs, and have then successfully predicted the majority of all other existing experimental data within experimental uncertainties [32,9,11]. However, the measurement accuracies of these experiments are in general not as high as those of the microwave measurements presented here. It was very interesting to see how well these potentials would predict the measured frequencies of the rotational transitions.

For this purpose, the program LEVEL, kindly provided by Dr.R.J.LeRoy, was used [35]. This program calculates vibration-rotation energy levels and $B_{v,J}$ rotational constants for diatomic molecules for a wide choice of potential functions, including HFD-B and HFD-C. For Ne-Kr and Ne-Xe, the absolute differences between the measured and predicted frequencies and the corresponding percentage differences are tabulated in Table 5.16, and in Table 5.17 for Ar-Xe and Kr-Xe. The deviations are in the order of 1.0% to 1.5%, with predicted values systematically larger than the measured ones. This indicates that the r_e values of all these potentials were underestimated. This observation is consistent with the new r_e values presented in Section 5.5.1.

5.5.3 Manual adjustment of r and ϵ

There is no doubt that the microwave measurements presented are by far more sensitive to the r_e values than the scattering and the "bulk" experimental data, which had been incorporated in the original fitting of the rare gas dimer potentials [32,9,11]. It was very interesting to see how much one needs to shift r_e in order to bring the predictions into agreement with the experimental frequencies.

This was done by manually adjusting the r_e values until agreement between the predicted B_o and experimental rotational constants was achieved. The best results are shown in Table 5.16 for Ne-Kr and Ne-Xe and in Table 5.17 for Ar-Xe and Kr-Xe. The new r_e values are given in Tables 5.16 and 5.17, as well as Table 5.18. The agreements are much better now as shown by the much smaller deviations in Tables 5.16 and 5.17.

However, the frequencies of higher J transitions were still not in good agreement. In each case, the absolute deviations increase systematically with increase of the rotational quantum number J. Such discrepancies possibly depend on the dissociation energy and/or the shape of the potentials, which are connected with the experimental centrifugal distortion constants.

In a second attempt, both r_e and ϵ were adjusted manually. It was possible to bring the predicted frequencies into excellent agreement with the experimental data. The deviations are in the ranges of 0.1 kHz to 20 kHz, close to the experimental uncertainty (1 kHz). The best results are listed in Table 5.16 for Ne-Kr and Ne-Xe, and in Table 5.17 for Ar-Xe and Kr-Xe.

The adjustments described above have been done for the most abundant isotopomer of each species. To estimate the uncertainty in the adjustment procedure, the final potentials with the adjusted ϵ and r_e were checked on other isotopomers. The result for ²²Ne-⁸⁴Kr, which has the biggest relative mass change in all these pairs, is given here. The potential adjusted for ²⁰Ne-⁸⁴Kr predicted the experimental frequency measurements of ²²Ne-⁸⁴Kr to better

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than 0.01%, as compared to 0.00004% in the case of 20 Ne-⁸⁴Kr. In order to predict the 22 Ne-⁸⁴Kr frequencies with the same quality as for 20 Ne-⁸⁴Kr, one would need to change r_e in the order of less than 0.0002 Å, with ϵ held constant. For other isotopomers, the relative mass changes are smaller, and the necessary changes in r_e are also smaller. From the above consideration, the uncertainty for r_e is estimated to be ± 0.0002 Å. The r_e values from the adjustments are listed in Table 5.18, along with the r_e values obtained in section 5.5.1 from the isotopic data and the literature values. The uncertainties in the ϵ values are more difficult to estimate.

From Table 5.18, it is clear that the r_e values obtained from the present work, despite different approaches used in the data analyses, are all larger than the literature values obtained from "bulk" experiments. For the heavier pairs Ar-Xe and Kr-Xe, the r_e values obtained using conventional microwave structural approaches are very similar to those obtained using newest available potentials, with deviations in the order of 0.001~0.002 Å. However, for the lighter pairs Ne-Xe and Ne-Kr, especially Ne-Kr, the deviations are much larger, in the order of 0.01 Å, indicating the possible break down of the conventional approaches.

It should also be pointed out that the rare gas

potentials are still an active research area, and the results presented here are by no means the final answers. The uncertainties quoted for the r values, obtained from the microwave data by manually adjusting r_{j} and ϵ , reflect rather the reproducibility of the measured frequencies by the adjusted potentials than the absolute uncertainties. For example, even though the adjusted potentials can predict the microwave measurements to a very high accuracy, it is still outside the experimental uncertainty (1 in 10⁷). Moreover, Aziz's HFD-B potentials have difficulty in being consistent with high energy beam scattering data without distorting the well [34]. An initial test run using the newly adjusted r_e and ϵ values shifted the predicted the total collision cross section experiments even further away from those from experiments [36]. Clearly, the rare gas potentials have to be reexamined. The microwave data have to be included in the fitting procedure of all adjustable parameters in the analytical forms [36]. Furthermore, there is also theoretical interest in developing more flexible rare gas pair potentials [36].

5.6 Comments on the dipole moments of the

mixed rare gas dimers

It has been possible in this work to estimate values

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for the dipole moments of the dimers, using the optimization of the MW pulse excitation condition. They represent the first experimental values available at the separation of the potential minimum. The induced dipole moments are somewhat surprisingly large, in the order of 0.01 D, comparable to that of $Ar-N_2$ [16]. It was not possible to obtain the direction of the dipole moment with the technique applied.

Certain difficulties were encountered in the experiments an R' + U + (he accuracy of the finalresults. The difficulties arose from the relatively smallavailable MW power, especially in the lower frequencyrange. The problem was severe for Kr-Xe, where pulselengths > 20µs were necessary. The molecules travel inthis time distances in the order of 1 cm and variation ofthe field strength in the MW cavity may well not benegligible. In addition, the spectrometer performancevaries with frequency range and the conditions mightchange in tuning from the transition frequency of thecomparison molecule (Ar-CO₂) to the correspondingfrequencies of the mixed rare gas dimers.

The only other available experimental source of information about the dipole moments are the CIA spectra [37]. Bar-Ziv et al. [38] derived a "reduced" dipole moment function from these spectra which is applicable to a number of mixed RG pairs. The 'meaningful' range of this function is, according to these authors, from $0.6*r_e$ to $0.85*r_e$, thus reflecting that the CIA spectra probe the repulsive wall of the interaction potentials. Nonetheless, an extrapolation to the separation at the potential minimum was done [38] and the magnitudes of the values in Table 5.14 are in relatively good agreement with those obtained in this work. The sign of their dipole moments is such that the lighter atom is the negative end.

However, theoretical calculations of some lighter mixed RG dimers suggest a different sign [39]. The dipole moment is usually decomposed into two contributions [40]: i) a short range part, resulting from electronic overlap and distortion of the electron cloud, making the more polarizable atom the negative end; ii) a long range part due to electron correlation effects with opposite sign. Future theoretical work might clarify which is the dominant contribution at potential minimum separation.

5.7 Discussion of the nuclear guadrupole coupling constants of ⁸³Kr and ¹³¹Xe

The observed nuclear quadrupole hyperfine structures due to 83 Kr and 131 Xe arise through the coupling of their nuclear spins (I=9/2 for 83 Kr, and I=3/2 for 131 Xe) with the overall rotation of the complexes. Figure 5.1 shows the hyperfine splitting of the J=2-1 rotational transition due to 83 Kr nucleus of 20 Ne- 83 Kr, while Figure 5.2 shows the hyperfine splitting of the J=2-1 rotational transition due to 131 Xe nucleus of 20 Ne- 131 Xe. The mechanism requires a non-zero electric field gradient at the site of the 83 Kr or 131 Xe nuclei. This field gradient is zero in a free atom in a 1 S state. Clearly the observed structures are due to a perturbing effect of the attached RG atom.

Several van der Waals complexes consisting of a molecule and a RG atom with a quadrupolar nucleus such as 83 Kr or 131 Xe have been investigated earlier, using cavity MWFT or molecular beam electric resonance techniques (see for example Refs.[41-44]). In these cases, the hyperfine effects are expressed in terms of the permanent electric multipole moments of the polar molecule. The field gradients q_o at the sites of RG nuclei due to these electric multipole moments can be calculated using [42]:

$$q_{o} = -6\mu < \frac{P_{1}(\cos\theta)}{r^{4}} > -12Q < \frac{P_{2}(\cos\theta)}{r^{5}} > -20\Omega < \frac{P_{3}(\cos\theta)}{r^{6}} > -\cdots$$
(5.12)

where μ , Q, and Ω are the electric dipole, quadrupole, and higher order multipoles of the polar molecule; $P_1(\cos\theta)$, $P_2(\cos\theta)$, and $P_3(\cos\theta)$ etc. are the Legendre polynomials; and the angular brackets indicate the expectation values in the vibrational ground state. However, the actual field gradient q, experienced by the quadrupolar nucleus is not directly the external field gradient q_o . The reason is that the electron cloud surrounding the nucleus is distorted and polarized by the external field, and that changes the field gradient sensed by the nucleus. Such effects have been analyzed by Sternheimer and co-workers [45-47], and the phenomenological outcome of their analyses was that q can be taken to be a "shield" external field gradient [45-47]:

$$q = q_o (1 - \gamma_{\infty})$$
 (5.13)

where γ_{∞} is the Sternheimer shielding factor, which is a constant for a certain nucleus. It should be pointed out that the value of $|\gamma_{\infty}|$ is not necessarily smaller than 1.0. For example, in case of ⁸³Kr, γ_{∞} =-77.5±15 [42]. The nuclear quadrupole coupling constants, χ , can then be obtained using the relation χ =eQq.

However, since RG atoms in a ¹S state have no permanent electric moments, such a consideration would result in a zero χ value. Yet the observed ⁸³Kr and ¹³¹Xe coupling constants (Table 5.13) are remarkably large: their absolute values are about 10% of those of the constants measured in Refs.[41-44]. For example, for ⁸³Kr-HF, χ =10.23(8) MHz [41]; ⁸³Kr-HCl, χ =5.2(1) MHz [42]; ⁸³Kr-HCN, χ =7.46(6) MHz [43]; 131Xe-HF, χ =-8.54(4) MHz [44]; for ¹³¹Xe-HCl, χ =-4.64(5) MHz [42]. Furthermore, the coupling constants in the mixed rare gas dimers have opposite sign of those of the RG-small molecule complexes. It is clear that formation of a van der Waals bond causes a measurable distortion of the electron clouds of the rare gas atoms, even though there are no permanent multipoles involved.

There is an earlier indication that these effects might not be negligible. Campbell *et al*. [43] have plotted the observed ⁸³Kr quadrupole coupling constants of ⁸³Kr-HX and ⁸³Kr-DX (X=F [41], Cl [42], CN [43]) as a function of the electric field gradients q_0 at the Kr nuclei, calculated from the electric multipole moments of the RG binding partner (see Fig. 5.3). A similar plot (Fig. 5.4) had also been done for the ¹³¹Xe-HX and ¹³¹Xe-DX (X=F [44], Cl[42]) complexes. The χ axis intercept (q_0 =0) is at -0.44±1.7 MHz in case of ⁸³Kr, and at +0.243 ±1.6 MHz in case of ¹³¹Xe. Both observations are consistent in sign and order of magnitude with the coupling constants obtained in this work, where by definition q_n =0. However, because of the attached error



Fig.5.3 Experimentally determined values of the 83 Kr nuclear quadrupole coupling constants plotted as a function of the electric field gradient q_o at the site of Kr nucleus calculated from Eq.(5.12). The solid line is obtained from a weighted least squares fit to the data. The horizontal bar indicates the uncertainty in the calculated q_o [43].



Fig.5.4 Experimentally determined values of the 131 Xe nuclear quadrupole coupling constants plotted as a function of the electric field gradient q_o at the site of Xe nucleus calculated from Eq.(5.12) [43].

limits of ± 1.7 MHz and ± 1.6 MHz, the agreement must be regarded as fortuitous.

It is interesting to note that no quadrupole coupling effects were observed in the investigation of the rotational spectra of the ²⁰¹Hg-Ar dimer [48]. From the lack of those effects, an upper limit for the ²⁰¹Hg coupling constant of 0.5 MHz was estimated in Ref.[48]. From a comparison of the ¹³¹Xe and ²⁰¹Hg coupling constants in the pairs ¹³¹Xe-HCl (χ =-4.64(5) MHz) [42], ²⁰¹Hg-HCl (χ =6.0(2) MHz) [49] and ¹³¹Xe-CO₂ (χ =-3.05(6) MHz) [50], ²⁰¹Hg-CO₂ (χ =4.80(6) MHz) [51], respectively, one would expect the magnitude of the ²⁰¹Hg quadrupole coupling constant to be slightly larger than that of Ar-¹³¹Xe.

5.8 Conclusions and some future prospects

The spectra observed were of quite high intensity and it has been possible to observe a multitude of different isotopomers in natural abundance. An overview of all the isotopomers observed is given in Fig.5.5. The rarest one is ${}^{21}Ne-{}^{84}Kr$ with a natural abundance of ~0.12%, which is about 500 times less abundant than the main isotopomer ${}^{20}Ne-{}^{84}Kr$.

It has been possible to incorporate the high resolution microwave data presented here into the newest rare gas pair potentials of Ne-Kr, Ne-Xe, Ar-Xe and Kr-Xe to obtain r_e values. It was found that the present literature r_e values for these dimers, had been underestimated in the order of 1~2%. Clearly, these pair potentials need to be reexamined. Furthermore, such differences, although small, have significant impact on studies concerned with nonpairwise additive contributions in many-body systems.

The values for the dipole moments and nuclear quadrupole coupling constants are surprisingly large. The magnitudes of these parameters suggest that electron correlation and/or overlap effects must be considered in attempts to account for these properties in RG-molecule complexes. It might be feasible to measure the FIR spectra of these dimers to obtain vibrational frequencies, which are important for characterizing the pair potentials.

| 20 Ne- 80 Kr | 20 Ne- 128 Xe | $Ar^{-128}Xe \ 1.9\%$ | $^{84}\mathrm{Kr}$ - $^{129}\mathrm{Xe}$ |
|--|---|-------------------------|--|
| $^{20}\mathrm{Ne}$ - $^{82}\mathrm{Kr}$ | 20 Ne- 129 Xe | $ m Ar-^{129}Xe$ | ⁸⁴ Kr- ¹³¹ Xe |
| 20 Ne- 83 Kr | ²⁰ Ne- ¹³⁰ Xe | $ m Ar-^{130}Xe$ | 84 Kr- 132 Xe 15% |
| 20 Ne- 84 Kr 51.6% | 20 Ne- 131 Xe | Ar- ¹³¹ Xe | 86 Kr- 129 Xe 4.6% |
| $^{20}\mathrm{Ne}\text{-}^{86}\mathrm{Kr}$ | 20 Ne- 132 Xe 24% | $\rm Ar-^{132}Xe~27\%$ | $^{86}\mathrm{Kr}$ - $^{132}\mathrm{Xe}$ |
| $^{22}\mathrm{Ne}\text{-}^{80}\mathrm{Kr}$ | 20 Ne- 134 Xe | Ar- ¹³⁴ Xe | |
| $^{22}\mathrm{Ne}$ - $^{82}\mathrm{Kr}$ | 20 Ne- 136 Xe | Ar- ¹³⁶ Xe | |
| $^{22}\mathrm{Ne}$ - $^{84}\mathrm{Kr}$ | $^{22}\mathrm{Ne}\text{-}^{129}\mathrm{Xe}$ | | |
| 22 Ne- 86 Kr | ²² Ne- ¹³¹ Xe | | |
| 21 Ne- 84 Kr 0.12% | 22 Ne- 132 Xe | | |
| | 22 Ne- 134 Xe 0.96% | | |

Fig.5.5 List of all isotopomers of the four mixed rare gas dimers observed in natural abundance.

The highest and the lowest natural abundance of each dimer are indicated.

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| molecule | J'- J" | v _{obs} (MHz) | ∆v (kHz) |
|------------------------------------|--------|---------------------------|-------------|
| | | | |
| ²⁰ Ne- ⁸⁶ Kr | 1 - 0 | 4411.0577 | 0.1 |
| | 2 - 1 | 8819.3663 | -0.1 |
| | 3 - 2 | 13222.1597 | 0.0 |
| | 4 - 3 | 17616.6345 | 0.0 |
| ²⁰ Ne- ⁸⁴ Kr | 1 - 0 | 4430.2661 | -0.2 |
| | 2 - 1 | 8857.7571 | 0.2 |
| | 3 - 2 | 13279.6785 | -0.1 |
| | 4 - 3 | 17693.2023 | 0.0 |
| ²⁰ Ne- ⁸³ Kr | 1 - 0 | 4440.1936 | -0.5 |
| | 2 - 1 | 8877.5987 | 0.3 |
| ²⁰ Ne- ⁸² Kr | 1 - 0 | 4450.3964 | 0.3 |
| | 2 - 1 | 8897.9882 | -0.3 |
| | 3 - 2 | 13339.9561 | 0.1 |
| | 4 - 3 | 17773.4422 | 0.0 |
| ²⁰ Ne- ⁸⁰ Kr | 1 - 0 | 4471.5179 | -0.2 |
| | 2 - 1 | 8940.2024 | 0.1 |

3 - 2 13403.2012

0.0

Table 5.1 Observed frequencies of Ne-Kr

Table 5.1 (continued)

| molecule | J'- J | V OBS | Δν |
|------------------------------------|-------|--------------|-------|
| | | (MHz) | (kHz) |
| | | | |
| ²² Ne- ⁸⁴ Kr | 1 - (| 0 4114.7964 | 0.8 |
| | 2 - 3 | 1 8227.2299 | -0.8 |
| | 3 - 2 | 2 12334.9322 | 0.3 |
| | 4 - 3 | 3 16435.5011 | -0.1 |
| | | | |
| ²² Ne- ⁸⁶ Kr | 1 - (| 4095.5134 | 0.0 |
| | 2 - 3 | 8188.6913 | -0.0 |
| | 3 - 2 | 2 12277.1850 | 0.0 |
| | 4 - 3 | 3 16358.6186 | -0.0 |
| | | | |
| ²² Ne- ⁸² Kr | 1 - (| 4135.0015 | 0.1 |
| | 2 - 1 | 8267.6170 | -0.1 |
| | 3 - 2 | 2 12395.4490 | 0.0 |

| Та | b | 1 | е | 5 | | 2 |
|------------|---|---|----------|---|---|---|
| T O | ~ | ᆂ | <u> </u> | ~ | • | ~ |

Observed frequencies of $^{20}\text{Ne-}^{83}\text{Kr}$

| J' – J" | v _{obs} | Δν |
|-----------|------------------|-------|
| F' - F" | (MHz) | (kHz) |
| 1 - 0 | | |
| 3.5 - 4.5 | 4440.2408 | -0.5 |
| 5.5 - 4.5 | 4440.2197 | 0.1 |
| 4.5 - 4.5 | 4440.1247 | 0.5 |
| 2 - 1 | | |
| 3.5 - 4.5 | 8877.6709 | -0.3 |
| 5.5 - 4.5 | 8877.6250 | 0.2 |
| 4.5 - 4.5 | 8877.6250 | 0.2 |
| 6.5 - 5.5 | 8877.6112 | 1.3 |
| 3.5 - 3.5 | 8877.5533 | -0.8 |
| 5.5 - 5.5 | 8877.5286 | -0.8 |
| 4.5 - 5.5 | 8877.5286 | -0.8 |
| 4.5 - 3.5 | 8877.5086 | 0.9 |
| | | |

| Table 5.3 Spectroscopic constants of Ne- |
|--|
|--|

| Parameter | B (MHz) | D _j (kHz) | H _j (Hz) |
|------------------------------------|----------------|-----------------------------|----------------------------|
| 20 0/ | | | |
| ²⁰ Ne- ⁸⁴ Kr | 2215.36414(12) | 115.453(13) | -24.68(42) |
| ²⁰ Ne- ⁸⁶ Kr | 2205.75756(73) | 114.3322(83) | -25.02(26) |
| ²⁰ Ne- ⁸³ Kr | 2220.32925(13) | 116.045(fixed) ^a | -24.68(fixed) ^b |
| ²⁰ Ne- ⁸² Kr | 2225.43140(20) | 116.636(23) | -24.35(73) |
| ²⁰ Ne- ⁸⁰ Kr | 2235.99489(8) | 117.88(51) | -24.35(fixed) ^b |
| | | | |
| ²² Ne- ⁸⁴ Kr | 2057.59433(51) | 98.221(58) | -17.4(18) |
| ²² Ne- ⁸⁶ Kr | 2047.95108(2) | 97.1598(20) | -18.675(63) |
| ²² Ne- ⁸² Kr | 2067.69929(6) | 99.2636(37) | -17.4(fixed) ^c |

- a fixed at the value interpolated from $^{20}\mathrm{Ne}-^{84}\mathrm{Kr}$ and $^{20}\mathrm{Ne}-^{82}\mathrm{Kr}$.
- ^b fixed at the value of 20 Ne- 84 Kr.
- ^c fixed at the value of 22 Ne- 84 kr.

| molecule | J | '_ | J" | ν _{obs} (MHz) | Δv (kHz) |
|-------------------------------------|---|----|--------|---------------------------|-------------|
| ²⁰ Ne- ¹²⁸ Xe | 2 | _ | 1 | 7326.1225 | -0.1 |
| | 3 | - | 2 | 10984.7648 | 0.1 |
| | 4 | - | 3 | 14638.0801 | 0.0 |
| ²⁰ Ne- ¹²⁹ Xe | 2 | _ | 1 | 7318,6471 | 0.0 |
| NC AC | 2 | _ | - 2 | 10973 5605 | 0.0 |
| | 4 | _ | 2 | 14623.1584 | 0.0 |
| | 5 | - | 4 | 18265.6300 | 0.0 |
| | | | | | |
| ²⁰ Ne- ¹³⁰ Xe | 2 | - | 1 | 7311.3041 | 0.3 |
| | 3 | - | 2 | 10962.5552 | -0.3 |
| | 4 | - | 3 | 14608.5033 | 0.1 |
| | | | | | |
| ²⁰ Ne- ¹³¹ Xe | 2 | | 1 | 7304.0521 | 0.1 |
| | 3 | - | 2 | 10951.6875 | -0.2 |
| | 4 | - | 3 | 14594.0307 | 0.1 |
| | 5 | - | 4 | 18229.2759 | 0.0 |
| 20 172 | | | | | |
| ²⁰ Ne ⁻¹³² Xe | 2 | - | 1 | 7296.9286 | 0.1 |
| | 3 | - | 2 | 10941.0109 | -0.2 |
| | 4 | - | 3 | 14579.8121 | 0.1 |
| | 5 | - | 4 | 18211.5310 | 0.0 |
| ²⁰ Ne- ¹³⁴ Xe | 2 | _ | 1 | 7282.9757 | -0.1 |
| | 3 | - | 2 | 10920.1015 | 0.1 |

Table 5.4 (continued)

| molecule | J | '' <u> </u> | J" | ν _{obs} (MHz) | Δv (kHz) |
|-------------------------------------|---|-------------|----|---------------------------|-------------|
| ²⁰ Ne- ¹³⁴ Xe | 4 | _ | 3 | 14551.9672 | -0.1 |
| | 5 | - | 4 | 18176.7790 | 0.0 |
| | | | | | |
| ²⁰ Ne- ¹³⁶ Xe | 2 | - | 1 | 7269.4304 | -0.1 |
| | 3 | - | 2 | 10899.8006 | 0.2 |
| | 4 | - | 3 | 14524.9324 | -0.1 |
| | 5 | - | 4 | 18143.0415 | 0.0 |
| | | | | | |
| ²² Ne- ¹²⁹ Xe | 2 | - | 1 | 6757.9258 | -0.1 |
| | 3 | - | 2 | 10133.1820 | 0.2 |
| | 4 | - | 3 | 13503.9703 | -0.1 |
| | 5 | - | 4 | 16868.7708 | 0.0 |
| | | | | | |
| ²² Ne- ¹³¹ Xe | 2 | - | 1 | 6743.2790 | -0.2 |
| | 3 | | 2 | 10111.2289 | 0.2 |
| | 4 | - | 3 | 13474.7320 | -0.1 |
| | | | | | |
| ²² Ne- ¹³² Xe | 2 | - | 1 | 6736.1296 | 0.2 |
| | 3 | - | 2 | 10100.5123 | -0.2 |
| | 4 | - | 3 | 13460.4597 | 0.1 |
| | 5 | - | 4 | 16814.4617 | 0.0 |
| | | | | | |
| ²² Ne- ¹³⁴ Xe | 2 | - | 1 | 6722.1277 | -0.2 |
| | 3 | - | 2 | 10079.5267 | 0.2 |
| | 4 | - | 3 | 13432.5084 | -0.1 |

| | ²⁰ Ne- | - ¹³¹ Xe | ²² Ne- ¹ | ³¹ Xe |
|------------------|-------------------|---------------------|--------------------------------|------------------|
| J" - J' | v_{obs} | Δν | v _{obs} | Δν |
| F" - F' | (MHz) | (kHz) | (MHz) | (kHz) |
| 2 - 1 | | | | |
| 05-15 | 7303 8778 | 0 1 | 6743 1050 | 0.4 |
| 1 5 1 5 | 7303.0747 | 0.1 | 6743.2018 | 0.2 |
| 1.5 - 1.5 | /303.9/4/ | 0.1 | 6/43.2018 | 0.3 |
| 3.5 - 2.5 | 7304.0435 | -0.3 | 6743.2701 | -0.6 |
| 2.5 - 1.5 | 7304.0435 | -0.3 | 6743.2701 | -0.6 |
| 2.5 - 2.5 | 7304.1408 | 0.0 | 6743.3678 | 0.2 |
| 1.5 - 0.5 | 7304.1492 | 0.1 | 6743.3763 | 0.4 |
| 3 - 2 | | | | |
| 2.5 - 1.5 | 10951.7070 | 0.1 | 10111.2488 | 0.6 |
| 1.5 - 0.5 | 10951.7070 | 0.1 | 10111.2488 | 0.6 |
| 3.5 - 2.5 | 10951.6828 | -0.1 | 10111.2237 | -0.6 |
| 4.5 - 3.5 | 10951.6828 | -0.1 | 10111.2237 | -0.6 |
| 4 - 3 | | | | |
| 3.5 - 2.5 | 14594.0389 | -0.1 | 13474.7400 | -0.3 |
| 2.5 - 1.5 | 14594.0389 | -0.1 | 13474.7400 | -0.3 |
| 4.5 - 3.5 | 14594.0278 | 0.1 | 13474.7294 | 0.3 |
| 5.5 - 4.5 | 14594.0278 | 0.1 | 13474.7294 | 0.3 |
| 5 - 4 | | | | |
| 4.5 - 3.5 | 18229.2814 | 0.9 | | |
| 3.5 - 2.5 | 18229.2814 | 0.9 | | |
| 5.5 - 4.5 | 18229.2729 | -0.9 | | |
| 6.5 - 5.5 | 18229.2729 | -0.9 | | |
| | | | | |

Table 5.5 Observed frequencies of Ne-¹³¹Xe

Table 5.6Spectroscopic constants of Ne-Xe

| Colorado de Calendar de | | | |
|---|----------------------|----------------------|----------------------------|
| Parameter | B _o (MHz) | D _j (kHz) | H _J (Hz) |
| | | | |
| ²⁰ Ne- ¹²⁸ Xe | 1832.11859(3) | 73.4167(12) | -11.79(fixed) ^a |
| ²⁰ Ne- ¹²⁹ Xe | 1830.24854(3) | 73.27059(22) | -11.5850(45) |
| ²⁰ Ne- ¹³⁰ Xe | 1828.41138(12) | 73.1011(45) | -11.79(fixed) ^a |
| ²⁰ Ne- ¹³¹ Xe | 1826.59707(9) | 72.9300(61) | -12.09(12) |
| ²⁰ Ne- ¹³² Xe | 1824.81506(10) | 72.7913(68) | -11.79(14) |
| ²⁰ Ne- ¹³⁴ Xe | 1821.32426(7) | 72.4594(52) | -12.31(10) |
| ²⁰ Ne- ¹³⁶ Xe | 1817.93574(8) | 72.1886(56) | -11.66(11) |
| | | | |
| ²² Ne- ¹²⁹ Xe | 1689.97473(8) | 61.5953(57) | -9.41(10) |
| ²² Ne- ¹³¹ Xe | 1686.31083(73) | 61.3215(28) | -8.97(fixed) ^b |
| ²² Ne- ¹³² Xe | 1684.52228(12) | 61.1811(84) | -8.97(17) |
| ²² Ne- ¹³⁴ Xe | 1681.01973(8) | 60.9104(32) | -8.97(fixed) ^b |
| | | | |

 $^{\rm a}$ fixed at the value of $^{\rm 20}{\rm Ne}{\rm -}^{\rm 132}{\rm Xe}{\rm .}$

^b fixed at the value of 22 Ne- 132 Xe.

Observed frequencies of Ar-Xe

| molecule | J | ۰ <u>-</u> | J" | ν _{obs} (MHz) | Δv (kHz) |
|-----------------------|---|------------|--------|---------------------------|-------------|
| - 128 | • | | | | |
| Ar-""Xe | 3 | - | 2 | 5808.5116 | -0.2 |
| | 4 | - | 3 | 7743.9259 | -0.1 |
| | 5 | - | 4 | 9678.6913 | 0.5 |
| | 6 | - | 5 | 11612.6445 | -0.2 |
| Ar- ¹²⁹ Xe | 3 | - | 2 | 5797.8927 | 0.3 |
| | 4 | - | 3 | 7729.7703 | 0.0 |
| | 5 | _ | 4 | 9661.0015 | -0.3 |
| | 6 | - | 5 | 11591.4235 | 0.0 |
| | 7 | - | 6 | 13520.8730 | -0.2 |
| | 8 | - | 7 | 15449.1858 | 0.4 |
| | 9 | | 8 | 17376.1968 | -0.1 |
| Ar- ¹³⁰ Xe | 3 | _ | 2 | 5787.4639 | 0.1 |
| | 4 | _ | 3 | 7715.8674 | -0.1 |
| | 5 | - | 4 | 9643.6265 | -0.1 |
| | 6 | _ | 5 | 11570 5796 | 0.2 |
| | 7 | _ | с с | 12496 5644 | 0.0 |
| | ' | | 0 | 13490.3044 | 0.0 |
| Ar- ¹³¹ Xe | 3 | _ | 2 | 5777.1636 | -0.1 |
| | 4 | - | 3 | 7702.1367 | 0.1 |
| | 5 | - | 4 | 9626.4681 | 0.1 |
| | 6 | _ | 5 | 11549.9965 | -0.2 |
| | 7 | - | 6 | 13472.5600 | 0.0 |

Table 5.7 (continued)

| molecule | 9 J | '_ | J" | ν _{obs} (MHz) | ∆v (kHz) |
|-----------------------|-----|----|----|---------------------------|-------------|
| Ar- ¹³² Xe | 3 | - | 2 | 5767.0446 | 0.0 |
| | 4 | - | 3 | 7688.6476 | 0.1 |
| | 5 | - | 4 | 9609.6112 | -0.1 |
| | 6 | - | 5 | 11529.7746 | 0.0 |
| | 7 | - | 6 | 13448.9764 | -0.3 |
| | 8 | - | 7 | 15367.0544 | 0.3 |
| | 9 | - | 8 | 17283.8456 | -0.1 |
| | | | | | |
| Ar- ¹³⁴ Xe | 3 | - | 2 | 5747.2292 | -0.3 |
| | 4 | - | 3 | 7662.2322 | 0.4 |
| | 5 | - | 4 | 9576.6003 | -0.2 |
| | 6 | - | 5 | 11490.1742 | 0.0 |
| | 7 | - | 6 | 13402.7943 | 0.0 |
| | | | | | |
| Ar- ¹³⁶ Xe | 3 | - | 2 | 5727.9905 | -0.2 |
| | 4 | - | 3 | 7636.5861 | 0.3 |
| | 5 | - | 4 | 9544.5513 | -0.2 |
| | 6 | - | 5 | 11451.7274 | 0.1 |
| | 7 | - | 6 | 13357.9551 | 0.0 |

Observed frequencies of $Ar^{-131}Xe$

| • | | |
|--------------------|---------------------------|-------------|
| J" - J' F" - F' | v _{obs} (MHz) | Δv (kHz) |
| 3 - 2 | | |
| 3.5 - 3.5 | 5777.3362 | 0.5 |
| 2.5 - 1.5 | 5777.1990 | -0.8 |
| 1.5 - 0.5 | 5777.1990 | -0.8 |
| 4.5 - 3.5 | 5777.1556 | 0.6 |
| 3.5 - 2.5 | 5777.1556 | 0.6 |
| 2.5 - 2.5 | 5777.0699 | -0.8 |
| 1.5 - 1.5 | 5777.0199 | 0.8 |
| | | |
| 4 - 3 | | |
| 3.5 - 2.5 | 7702.1522 | 0.0 |
| 2.5 - 1.5 | 7702.1522 | 0.0 |
| 4.5 - 3.5 | 7702.1312 | -0.0 |
| 5.5 - 4.5 | 7702.1312 | -0.0 |
| | | |
| 5 - 4 | | |
| 4.5 - 3.5 | 9626.4767 | 0.0 |
| 3.5 - 2.5 | 9626.4767 | 0.0 |
| 5.5 - 4.5 | 9626.4643 | 0.0 |
| 6.5 - 5.5 | 9626.4643 | 0.0 |
| | | |

Table 5.8 (continued)

| J" – J' F" – F' | v _{obs} (MHz) | Δv (kHz) |
|----------------------|---------------------------|-------------|
| 6 - 5 | | |
| 5.5 - 4.5 | 11550.0016 | -0.3 |
| 4.5 - 3.5 | 11550.0016 | -0.3 |
| 6.5 - 5.5 | 11549.9940 | 0.3 |
| 7.5 - 6.5 | 11549.9940 | 0.3 |
| 7 - 6 | | |
| 6.5 - 5.5 | 13472.5648 | 1.0 |
| 5.5 - 4.5 | 13472.5648 | 1.0 |
| 7.5 - 6.5 | 13472.5568 | -1.0 |
| 8.5 - 7.5 | 13472.5568 | -1.0 |
| 8 - 7 | | |
| 7.5 - 6.5 | 15394.0011 | 2.4 |
| 6.5 - 5.5 | 15394.0011 | 2.4 |
| 8.5 - 7.5 | 15393.9919 | -2.4 |
| 9.5 - 8.5 | 15393.9919 | -2.4 |

| Parameter | B _o (MHz) | D _j (kHz) | H _J (Hz) |
|-----------------------|----------------------|----------------------|---------------------|
| | | | |
| Ar- ¹²⁸ Xe | 968.20670(6) | 6.7444(11) | -0.1922(fixed) |
| Ar- ¹²⁹ Xe | 966.43643(5) | 6.7182(10) | -0.1922(66) |
| Ar- ¹³⁰ Xe | 964.69798(5) | 6.7018(18) | -0.122(18) |
| Ar- ¹³¹ Xe | 962.98073(1) | 6.6723(4) | -0.1558(30) |
| Ar- ¹³² Xe | 961.29377(4) | 6.64655(78) | -0.1714(51) |
| Ar- ¹³⁴ Xe | 957.99043(10) | 6.6037(36) | -0.113(37) |
| Ar- ¹³⁶ Xe | 954.78304(8) | 6.5507(26) | -0.196(27) |
| | | | |

Table 5.9Spectroscopic constants of Ar-Xe

Table 5.10

Observed frequencies of Kr-Xe

| molecule | J | ' _ | J" | ν _{obs} (MHz) | Δv (kHz) |
|-------------------------------------|---|-----|----|---------------------------|-------------|
| 8417-0 12937- | | | 2 | | 0.1 |
| Kr-~xe | 4 | - | 3 | 4436.5638 | -0.1 |
| | 5 | - | 4 | 5545.3947 | 0.7 |
| | 6 | - | 5 | 6654.0189 | -0.9 |
| | 7 | - | 6 | 7762.3951 | 0.3 |
| | | | | | |
| 84 Kr- 132 Xe | 4 | - | 3 | 4397.0832 | -0.1 |
| | 5 | - | 4 | 5496.0492 | -0.1 |
| | 6 | - | 5 | 6594.8119 | 0.4 |
| | 7 | - | 6 | 7693.3307 | -0.2 |
| | | | | | |
| ⁸⁴ Kr- ¹³¹ Xe | 4 | - | 3 | 4410.0332 | 0.6 |
| | 5 | - | 4 | 5512.2346 | -0.5 |
| | | | | | |
| ⁸⁶ Kr- ¹²⁹ Xe | 4 | - | 3 | 4374.4932 | 0.5 |
| | 5 | - | 4 | 5467.8167 | -0.8 |
| | 6 | - | 5 | 6560.9403 | 0.3 |
| | | | | | |
| ⁸⁶ Kr- ¹³² Xe | 4 | - | 3 | 4335.0076 | -0.1 |
| | 5 | - | 4 | 5418.4642 | 0.1 |
| | 6 | - | 5 | 6501.7240 | -0.0 |

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Table 5.11

Observed frequencies of ${}^{84}\mathrm{Kr}-{}^{131}\mathrm{Xe}$

| J" – J' F" – F' | v _{obs} (MHz) | Δv (kHz) |
|--------------------|---------------------------|-------------|
| 4 - 3 | | |
| 3.5 - 2.5 | 4410.0482 | -0.2 |
| 2.5 - 1.5 | 4410.0482 | -0.2 |
| 4.5 - 3.5 | 4410.0280 | 0.2 |
| 5.5 - 4.5 | 4410.0280 | 0.2 |
| | | |
| 5 - 4 | | |
| 4.5 - 3.5 | 5512.2433 | 0.3 |
| 3.5 - 2.5 | 5512.2433 | 0.3 |
| 5.5 - 4.5 | 5512.2306 | -0.3 |
| 6.5 - 5.5 | 5512.2306 | -0.3 |

Table 5.12

Spectroscopic constants of Kr-Xe

| Parameter | B _o (MHz) | D _j (kHz) |
|-------------------------------------|----------------------|----------------------|
| 9/ 120 | | |
| °4Kr-127Xe | 554.62559(12) | 1.7224(16) |
| ⁸⁴ Kr- ¹³² Xe | 549.68960(5) | 1.6936(6) |
| ⁸⁴ Kr- ¹³¹ Xe | 551.30842(6) | 1.6936ª |
| ⁸⁶ Kr- ¹²⁹ Xe | 546.86496(21) | 1.6658(36) |
| ⁸⁶ Kr- ¹³² Xe | 541.92845(3) | 1.6406(5) |
| | | |

 $^{\rm a}$ Fixed at the value of $^{\rm 84}{\rm Kr}{\rm -}^{\rm 132}{\rm Xe}{\rm .}$

Table 5.13

Nuclear Quadrupole coupling constants of 83 Kr and 131 Xe in RG- 83 Kr and RG- 131 Xe dimers.

| complex | x |
|-------------------------------------|-----------------------------|
| 2022 8325- | 0.5005(00) MIL- |
| $20_{\rm Me} = 131_{\rm Me}$ | -0.5205(23) MHZ |
| ²² Ne ⁻¹³¹ Xe | 0.3877(9) MHz 0.3875(9) MHz |
| $Ar - \frac{131}{Xe}$ | 0.7228(36) MHz |
| 84 Kr- 131 Xe | 0.7079(86) MHz |
| | (|

Table 5.14

Estimated electric dipole moments in Debye of the mixed rare gas dimers.

| molecule | this work | Bar-Ziv ^a |
|----------|--------------------|----------------------|
| | | |
| Ne-Kr | 0.011 ^b | |
| Ne-Xe | 0.012 ^b | 0.00696 |
| Ar-Xe | 0.014 ^b | 0.0124 |
| Kr-Xe | 0.007 ^b | - |
| | | |

^a The values of μ_o in Table I of Ref.38.

^b The number of digits given does not reflect the uncertainty. See text for evaluation procedure.

| complex RG-RG' | subst. o Z _{RG} | <u>coordinates</u> Z _{RG'} | r _s | r _s +c.m.ª | r _o | re ^b | r _e |
|-------------------------------------|-----------------------------|--|----------------|-----------------------|----------------|-----------------|--------------------|
| ²⁰ Ne- ⁸⁴ Kr | 2.9865 | -0.7117 | 3.6982 | 3.???? | 3.7589 | 3.6375 | |
| ²² Ne- ⁸⁴ Kr | 2.9301 | -0.7677 | 3.6978 | - | 3.7544 | 3.6412 | 3.639° |
| ²⁰ Ne- ¹³² Xe | 3.4191 | -0.5184 | 3.9375 | 3.9385 | 3.9940 | 3.8810 | |
| ²² Ne- ¹³² Xe | 3.3820 | -0.5553 | 3.9373 | - | 3.9896 | 3.8850 | 3.883 ^c |
| ⁴⁰ Ar- ¹³² Xe | - | -0.9573 | - | 4.1171 | 4.1402 | 4.0940 | |
| ⁴⁰ Ar- ¹³⁶ Xe | _ | -0.9355 | - | 4.1170 | 4.1400 | 4.0940 | 4.094 |
| ⁸⁴ Kr- ¹³² Xe | 2.5783 | -1.6401 | 4.2184 | 4.2184 | 4.2340 | 4.2028 | |
| ⁸⁶ Kr- ¹³² Xe | 2.5546 | -1.6637 | 4.2182 | 4.2183 | 4.2338 | 4.2026 | 4.203 |
| | | | | | | | |

Table 5.15. Coordinates and bond lengths (Å) of rare gas dimers.

^a The substitution procedure was used for the Xe or Kr coordinate. The remaining atom was located with the first moment condition.

^b The equilibrium distance $r_e = 2r_s - r_o$.

^c Estimated uncertainties are ± 0.01 Å for Ne-Kr and ± 0.008 Å for Ne-Xe, with those for Ar-Xe and Kr-Xe estimated as ± 0.005 Å.

Table 5.16 Direct comparison of the observed rotational frequencies with those predicted from HFD-B potentials for Ne-Kr and for Ne-Xe respectively. Not all figures displayed for r_e and ϵ are significant. Some are displayed only to avoid roundoff errors. "%" here denotes (obs-calc)/obs %.

| | observed | Ne- original r_e and ϵ $r_e=3.631$, $\epsilon=50.28 \text{ cm}^{-1}$ | -Kr adjust r_e $r_e=3.65058$ $\epsilon=50.28 \text{ cm}^{-1}$ | adjust r_e and ϵ $r_e=3.6480165$ $\epsilon=48.20 \text{ cm}^{-1}$ |
|-------|----------------|---|--|--|
| | MHz | obs-calc. % | obs-calc. % | obs-calc. % |
| 1-0 | 4430.2261 | -46.3869 -1.047 | -0.0171 $-3.9E-4$ | -0.0012 -0.3E-4 |
| 2-1 | 8857.7571 | -92.8501 -1.048 | -0.1729 -19.5E-4 | -0.0017 -0.2E-4 |
| 3-2 | 13279.6785 | -139.4696 -1.050 | -0.6072 -45.7E-4 | -0.0026 -0.2E-4 |
| 4-3 | 17693.2023 | -186.3213 -1.053 | -1.4614 -82.6E-4 | 0.0006 0.0E-4 |
| B/MHz | 2215.36414(12) | 2238.5510 | 2215.36113 | 2215.3646 |
| D/kHz | 115.453(13) | 112.229 | 109.682 | 115.434 |
| H/Hz | -24.68(42) | -24.455 | -23.408 | -26.111 |

| Table | 5.16 | (continued) |
|-------|------|-------------|
|-------|------|-------------|

| | Ne-Xe | | | | |
|-------|---|------------------|---|--|--|
| | observed original r_e and ϵ $r_e=3.8610$, $\epsilon=51.57$ cm ⁻¹ | | adjust r_{e} r_{e} =3.889818 ϵ =51.57 cm ⁻¹ | adjust r_e and ϵ $r_e=3.88691$ $\epsilon=49.00 \text{ cm}^{-1}$ | |
| | MHz | obs-calc. % | obs-calc. % | obs-calc. % | |
| 2-1 | 7296.9286 | -106.3415 -1.457 | -0.1373 -18.8E-4 | -0.0105 -1.4E-4 | |
| 3-2 | 10941.0109 | -159.6380 -1.459 | -0.4641 -42.4E-4 | -0.0165 -1.5E-4 | |
| 4-3 | 14579.8121 | -213.0846 -1.462 | -1.1010 -75.5E-4 | -0.0271 -1.9E-4 | |
| 5-4 | 18211.5310 | -266.7318 -1.465 | -2.1541 -118.3E-4 | 0.0451 2.5E-4 | |
| B/MHz | 1824.81506(10) | 1851.38376 | 1824.81506 | 1824.8125 | |
| D/kHz | 72.7913(68) | 70.7007 | 68.5024 | 72.7928 | |
| H/Hz | -11.79(14) | -11.81 | -11.28 | -12.79 | |

Table 5.17 Direct comparison of the observed rotational frequencies with those predicted from HFD-C potentials for Ar-Xe and for Kr-Xe respectively. Not all figures displayed for r_e and ϵ are significant. Some are displayed only to avoid roundoff errors. "%" here denotes (obs-calc)/obs %.

| | Ar-Xe | | | | | |
|-------|--------------|--|---|---|--|--|
| | observed | $r_e = 4.0668,$ $\epsilon = 131.10 \text{ cm}^{-1}$ | $r_e = 4.093187$ $\epsilon = 131.10 \text{ cm}^{-1}$ | $r_e = 4.092245$ $\epsilon = 126.19 \text{ cm}^{-1}$ | | |
| | MHz | obs-calc. % | obs-calc. % | obs-calc. % | | |
| 3-2 | 5767.0446 | -74.2055 -1.287 | -0.0300 -5.2E-4 | -0.0006 -0.1E-4 | | |
| 4-3 | 7688.6476 | -98.9514 -1.287 | -0.0701 -9.1E-4 | -0.0004 -0.1E-4 | | |
| 5-4 | 9609.6112 | -123.7065 -1.287 | -0.1358 -14.1E-4 | -0.0004 -0.0E-4 | | |
| 6-5 | 11529.7746 | -148.4730 -1.288 | -0.2335 -20.3E-4 | 0.0001 0.1E-4 | | |
| 7-6 | 13448.9764 | -173.2529 -1.288 | -0.3697 -27.5E-4 | 0.0010 0.1E-4 | | |
| 8-7 | 15367.0544 | -198.0485 -1.289 | -0.5506 -35.8E-4 | 0.0027 0.2E-4 | | |
| 9-8 | 17283.8456 | -222.8618 -1.289 | -0.7824 -45.3E-4 | 0.0058 0.3E-4 | | |
| B/MHz | 916.29377(4) | 973.65962 | 961.29395 | 961.29384 | | |
| D/kHz | 6.64655(78) | 6.54993 | 6.37820 | 6.64640 | | |
| H/Hz | -0.1714(51) | -0.1861 | -0.1806 | -0.1924 | | |

Table 5.17 (continued)

| | observed | original r_e and ϵ $r_e=4.174$ $\epsilon=162.275$ cm ⁻¹ | adjust r_{e} r_{e} =4.20160 ϵ =162.275 cm ⁻¹ | adjust r_e and ϵ r_e =4.200903 ϵ =155.062 cm ⁻¹ | |
|-------|--------------|---|--|--|--|
| | MHz | obs-calc. % | obs-calc. % | obs-calc. % | |
| 4-3 | 4397.0832 | -106.3415 -1.457 | -0.1373 -18.8E-4 | -0.0105 -1.4E-4 | |
| 5-4 | 5496.0492 | -159.6380 -1.459 | -0.4641 -42.4E-4 | -0.0165 -1.5E-4 | |
| 6-5 | 6594.8119 | -213.0846 -1.462 | -1.1010 -75.5E-4 | -0.0271 -1.9E-4 | |
| 7-6 | 7693.3307 | -266.7318 -1.465 | -2.1541 -118.3E-4 | 0.0451 2.5E-4 | |
| B/MHz | 549.68960(5) | 556.94261 | 549.68576 | 549.68953 | |
| D/kHz | 1.6939(6) | 1.6572 | 1.6133 | 1.6941 | |

| complex | r _e ª isotopic data | r ^b adjusted r _e only | r_e^b adjusted r_e^c and ϵ | r _e (Ref.) literature value |
|---------|--------------------------------------|---|---|--|
| | | | | |
| Ne-Kr | 3.639 | 3.6506 | 3.6480 | 3.631 (32) |
| Ne-Xe | 3.883 | 3.8898 | 3.8869 | 3.861 (9) |
| Ar-Xe | 4.094 | 4.0932 | 4.0922 | 4.067 (11) |
| Kr-Xe | 4.203 | 4.2016 | 4.2009 | 4.174 (11) |

Table 5.18 Equlibrium distances (Å) of rare gas dimers.

^a The values are those in Table 5.15.

.

- ^b Obtained from the potentials by adjusting only r_e . See text for the procedure.
- $^{\rm c}$ Obtained from the potentials by adjusting both $\rm r_{e}$ and $\epsilon.$ See text.

CHAPTER 6.

<u>Microwave Spectroscopic Investigation of the Mixed Rare</u> <u>van der Waals Trimers Ne,-Kr and Ne,-Xe</u>

6.1 Introduction

Many-body nonpairwise additive effects have attracted much attention for several decades [1]. An understanding of these effects is essential for a description of bulk phase properties in terms of microscopic scale properties. The most common correction term to the pairwise additive calculation of three-body systems is the triple-dipole term given by Axilrod and Teller (AT term) [2], which was derived directly from the study of liquid and solid phase matter. Although this correction term has proven to work fairly well in practice, recent theoretical investigation has shown that its success implies fortuitous cancellation involving a negative contribution from short-range nonpairwise additive repulsive forces and a positive contribution from higher order dispersion corrections [3]. Meath and Aziz have shown that inclusion of first order nonpairwise additive three-body exchange energies and the AT term at the same time would result in a significant cancellation, and thus be in disagreement with experiments [4]. On the other hand, the accuracy of "bulk" experiments is usually

not high enough to separate the AT term and higher order correction terms. Furthermore, sophisticated computer simulations are usually needed in order to extract information from those experiments. In some complicated systems, even pairwise additive calculations are difficult to perform [3].

Recent success in high resolution microwave (MW), infrared (IR) and far infrared (FIR) spectroscopic investigations of van der Waals trimers Ar₂-HX (X=F,Cl) [5-10] has shown great promise in providing direct information on the nonpairwise additivity of intermolecular forces. Several papers concerned with the theoretical description of such systems have been published [11,12]. Furthermore, recent FIR investigation [10] has indicated that a fully dynamical theoretical treatment of such systems is necessary in order to obtain quantitative information about three-body nonpairwise additive contributions. Additional challenge was faced in theoretically modelling such complicated dynamic problems. Meanwhile, hope has also been given to measure spectra of simpler rare gas (RG) van der Waals trimers, without the aid of polar monomers to provide a large transition moment [13].

Rare gas trimers are among the simplest types possible for the investigation of three-body nonpairwise additive effects, since the respective pair potentials are isotropic, exhibiting no orientational dependence on the individual constituents (atoms). Furthermore, the rare gas dimers have been extensively studied, and their pair interaction potentials are known with very high precision [14]. This makes them excellent prototypes for the investigation of nonpairwise additive effects.

Two potential difficulties are expected in the spectroscopic (MW, FIR) investigation of rare gas trimers: production of enough trimers in the molecular beam expansion, and a small magnitude of the induced dipole moments for providing observable intensity for the experimental technique being used. A recent theoretical calculation on the Ar_3 trimer has evaluated the transition dipole moment for the lowest infrared-allowed transitions to be ~7x10⁻⁵ D, making it unlikely to be observable using current FIR techniques [13].

The search for the mixed rare gas van der Waals trimers in this work was inspired by the success of the MW investigations of the rare gas dimers [Chapter 5] and of two trimers Ar_2 -OCS and Ar_2 -CO₂ [Chapter 7]. The induced dipole moments in the rare gas dimers were estimated to be about 0.01 D and were found to be sufficiently large for their rotational spectra to be observed. Furthermore, a fairly high intensity has been observed for the rotational spectra of the van der Waals trimer Ar_2 -CO₂ [Chapter 7], despite its low dipole moment; this observation suggested that there is an abundance of trimers in the molecular beam expansion.

In this chapter, the pure rotational spectra of various isotopomers of the rare gas trimers Ne,-Kr and Ne₂-Xe are described. Rotational constants and centrifugal distortion constants have been determined and have been used to obtain structural parameters. The narrow nuclear hyperfine splitting of rotational transitions of ⁸³Kr- and ¹³¹Xe-containing isotopomers have been resolved and have yielded accurate nuclear quadrupole coupling constants. Estimates of the induced electric dipole moments in these two trimers have been obtained from values of excitation pulse lengths, optimized for maximum signal strength (" $\pi/2$ condition") [15, see also Chapter 2]. Observation of the spectra of these fundamental trimers makes it possible to compare their properties to those of their constituent rare gas dimers.

6.2 Search and assignments

In the present work gas mixtures of 1% Kr or Xe in Ne were used for Ne_2 -Kr and Ne_2 -Xe, respectively, with backing pressures of up to 5 atm.

A. Ne₂-Kr

The search for the spectrum of Ne₂-Kr was carried out assuming that the structure of the trimer is dominated by the influence of pairwise additive interatomic forces. Using the bond lengths of the Ne-Ne [16] and Ne-Kr [Chapter 5] dimers, the complex was predicted to be a highly asymmetric prolate top (κ ~-0.748) with C_{2V} symmetry, with Kr lying on the *a*-principal axis of inertia. Because of the large uncertainty in the bond lengths, especially for the Ne₂ dimer, the uncertainty in the estimated rotational constants was very large.

The predicted frequency for the $3_{0,3}-2_{0,2}$ transition was near 8.5 GHz. A systematic search was carried out in this region, varying the excitation frequency in 0.2 MHz steps, using 10 averaging cycles at each step. The first line found was at 8379.928 MHz. It clearly arose from a species with a very low dipole moment because it required very long excitation pulses to optimize the signal strength (i.e. to reach the " $\pi/2$ condition") [15, see also Chapter 2]. It was later identified as being due to $Ne_2^{-84}Kr$ by finding the corresponding lines of $Ne_2^{-86}Kr$ and $Ne_2^{-82}Kr$. Because the trimer is highly asymmetric, it was very difficult to predict further transitions. In practice, searches were carried out for some of the lowest J transitions of each isotopomer, and the assignments were supported utilizing the lengths of the excitation pulse, isotopic data, the relative intensities observed, and the analysis described below. The measured frequencies and assignments are in Table 6.1.

The assignment difficulties were compounded by the

effects of nuclear spin statistics. A complex with C_{2V} symmetry would have two equivalent ²⁰Ne atoms, with I=0, and Bose-Einstein statistics would apply. The total wave function would thus be symmetric with respect to exchange of these two nuclei (i.e. to the C₂ operation). The result would be that only K_a=even levels are allowed, and transitions involving levels with K_a=1 are missing. On the other hand, failure to observe these transitions was strong evidence that the observed lines were due to the desired complex Ne₂-Kr.

This evidence was strengthened further by the discovery of lines due to the mixed isotopomers $^{20}\text{Ne}^{22}\text{Ne}^{-84}\text{Kr}$ and $^{20}\text{Ne}^{22}\text{Ne}^{-86}\text{Kr}$. In this case there are no longer two equivalent nuclei, and it has been possible to measure both $K_a=0$ and $K_a=1$ *a*-type R branch transitions. Their frequencies and assignments are in Table 6.2.

Final confirmation of the assignments was made with transitions due to ${}^{20}\text{Ne}_2-{}^{83}\text{Kr}$. In this case nuclear quadrupole hyperfine structure due to ${}^{83}\text{Kr}$ was observed. Because of its high nuclear spin (I=9/2), and because of the relatively small field gradient at the ${}^{83}\text{Kr}$ nucleus in the complex, the hyperfine structure is very congested. Computer simulation of the hyperfine splitting patterns with different assumed coupling constants were necessary to match the experimental spectrum and to assign quantum numbers. An example, showing the transition $3_{0,3}-2_{0,2}$, is given in Figure 6.1. The spectrum



Fig.6.1 Hyperfine splitting due to 83 Kr in the rotational transition $3_{0,3}$ - $2_{0,2}$ of 20 Ne₂- 83 Kr

The spectrum is composed from three experiments, with 200 up to 1000 experimental cycles.

is composed from three experiments. The frequencies and assignments of the individual hyperfine components of the transitions of $^{20}Ne_2-^{83}Kr$ are in Table 6.3.

B. Ne₂-Xe

The search for the spectrum of Ne₂-Xe followed essentially the same procedure as for Ne₂-Kr. However, because Ne₂-Xe is heavier, transitions with the same J values as in Ne₂-Kr occur at lower frequencies (\leq 7 GHz). Unfortunately the sensitivity of the spectrometer is much lower here than in the higher frequency range (~8-18 GHz). The search was therefore carried out for the transition 4_{0,4}-3_{0,3} at 8.8 GHz. Furthermore, Xe has several major isotopes with similar abundances. The observed signal-to-noise ratios were much lower for this complex. As a result, only a few transitions could be measured for ²⁰Ne₂-Xe, and lines due to the mixed isotopomers ²⁰Ne²²Ne-Xe were too weak to be observed.

The measured frequencies for the isotopomers ${}^{20}\text{Ne}_2 - {}^{129}\text{Xe}$, ${}^{20}\text{Ne}_2 - {}^{132}\text{Xe}$, ${}^{20}\text{Ne}_2 - {}^{134}\text{Xe}$ and ${}^{20}\text{Ne}_2 - {}^{136}\text{Xe}$ are listed in Table 6.4. Once again only lines having K_a=0 could be observed, consistent with C_{2V} symmetry for the complex.

Three transitions were measured for ${}^{20}\text{Ne}_2 - {}^{131}\text{Xe}$; all showed nuclear quadrupole hyperfine structure due to ${}^{131}\text{Xe}$ (I=3/2). Their frequencies and assignments are in Table 6.5 with the corresponding hypothetical unsplit line frequencies in Table 6.4. No hyperfine splitting due



4450.7MHz

4451.3 MHz

Fig.6.2 Nuclear quadrupole hyperfine components of transition $2_{0,2}-1_{0,1}$ of ${}^{20}\text{Ne}_2-{}^{131}\text{Xe}$

The spectrum is composed from three experiments, with 200 experimental cycles each.

to 129 Xe (I=1/2) was observed for Ne₂- 129 Xe. An example transition of 20 Ne₂- 131 Xe showing hyperfine splitting is depicted in Fig.6.2.

6.3 Spectral analyses

For Ne₂-Kr, all the measured rotational transition frequencies were fit to Watson's semirigid rotor Hamiltonian, using the A-reduction in its I^r representation [17]. Because the observed lines are comprised of only a limited number of *a*-type R branch transitions, there is not enough information to determine experimentally all the rotational and quartic centrifugal distortion constants.

In the cases of the mixed isotopomers ${}^{20}\text{Ne}{}^{22}\text{Ne}{}^{84}\text{Kr}$ and ${}^{20}\text{Ne}{}^{22}\text{Ne}{}^{86}\text{Kr}$, three quartic centrifugal distortion constants, namely Δ_J , Δ_{JK} , and δ_J could be determined, with Δ_K and δ_K fixed at the values predicted by the force field analysis, as discussed in Section 6.5.2. In the cases of ${}^{20}\text{Ne}_2$ -Kr, all quartic distortion constants were necessarily constrained at the values predicted by the harmonic force field analysis. Nevertheless, this has produced reasonable fits for the ${}^{20}\text{Ne}_2$ -Kr isotopomers. More significantly, this has allowed values of A_o to be determined for ${}^{20}\text{Ne}_2$ - ${}^{84}\text{Kr}$ and ${}^{20}\text{Ne}_2$ - ${}^{86}\text{Kr}$, with 5 and 4 measured lines, respectively. The asymmetry of these complexes is evidently high enough that this could be done, even though only rotational transitions having $K_a=0$ were measured. There is even a small, but real, measurable isotopic variation in A_o . Furthermore, B_o and C_o both show a roughly linear variation with Kr mass number in these two isotopomers and in ${}^{20}\text{Ne}_2-{}^{83}\text{Kr}$ and ${}^{20}\text{Ne}_2-{}^{82}\text{Kr}$. Consequently, an isotopic scale factor was used to determine the fixed values of A_o in the fits for ${}^{20}\text{Ne}_2-{}^{83}\text{Kr}$ and ${}^{20}\text{Ne}_2-{}^{83}\text{Kr}$ and

The derived spectroscopic constants for all the isotopomers of Ne₂-Kr are in Table 6.6. The residuals, designated $\Delta v_{obs-calc}$ in Table 6.1, are all less than 6 kHz for the fitted lines. These residuals could probably be reduced if there were enough data to include sextic distortion constants in the analysis; this was found for Ar₂-HF [5] and Ar₂-HCl [6], where inclusion of these parameters reduced the standard deviations of the fits from 10-20 kHz down to ~2 kHz.

For Ne₂-Xe, the rotational analysis followed the same procedure as for Ne₂-Kr. However, there were not enough experimental data to evaluate both the rotational and the quartic centrifugal distortion constants. All quartic centrifugal distortion constants were fixed at 0.0 in the fitting procedures. Furthermore, in the analyses, the rotational constant A_0 were necessarily fixed at the A_0 value of ${}^{20}Ne_2 - {}^{84}Kr$ for all the isotopomers because of high correlations (≥ 0.999) between the A_0 , B_0 , and C_0 rotational constants; the lines were fit to the rotational constants B_0 and C_0 only for all the isotopomers. The resulting spectroscopic constants are in Table 6.7.

Because the nuclear quadrupole hyperfine splittings due to 83 Kr in the 20 Ne₂- 83 Kr complex were closely spaced, the displayed line shapes were often distorted. Accurate frequencies were obtained using the DECAYFIT program [18] which directly analyses the time-domain signals. The 83 Kr nuclear quadrupole coupling constants and hypothetical unsplit line frequencies were fit to the observed hyperfine components. The standard deviation of the fit is reasonable (~1.4 kHz), considering the congested patterns observed. The coupling constants are in Table 6.8, and the unsplit line frequencies with their assignments are in Table 6.1.

For ${}^{20}\text{Ne}_2 - {}^{131}\text{Xe}$, the analysis followed the same procedure as for ${}^{20}\text{Ne}_2 - {}^{83}\text{Kr}$, and the resulting ${}^{131}\text{Xe}$ nuclear quadrupole coupling constants are in Table 6.8.

6.4 Estimation of the dipole moments of Ne,-Kr and Ne,-Xe

Again, the " $\pi/2$ condition" [15, see also Chapter 2] method was used for the estimation of the induced dipole moments of the trimers, as already described in Chapter 5 for the mixed rare gas dimers. Again, the spectrometer was calibrated using Ar-CO₂ and the method was checked for consistency against Ne-CO₂. For Ne₂-Kr, the pulse length optimization for the transition $3_{0,3}-2_{0,2}$ of ${}^{20}\text{Ne}_2-{}^{84}\text{Kr}$ at 8379.928 MHz produced a value of 0.015 Debye. For Ne₂-Xe, the dipole moment has been estimated using the transition $3_{0,3}-2_{0,2}$ of ${}^{20}\text{Ne}_2-{}^{132}\text{Xe}$ at 6626.259 MHz and a value of 0.011 Debye has been obtained. These two values are listed in Table 6.9, along with the corresponding dimer values of Ne-Kr and Ne-Xe. However, the uncertainty of this method is large, as has been discussed already in Section 5.4. The measured dipole moments are believed to be of the right order of magnitude.

6.5 Possible evidence of three-body effects

A primary interest of this work was to detect any deviations from pairwise additive behaviour. Possible information about three-body nonpairwise additive contributions will be discussed in the following sections in terms of three different types of measurable properties: the rotational constants i.e. the structures, the induced dipole moments, and the nuclear quadrupole coupling constants of these two trimers.

6.5.1 Structures of Ne,-Kr and Ne,-Xe

The observed spectra of several isotopomers of Ne_2 -Kr and Ne_2 -Xe indicate that the assumed geometries are essentially correct. The strongest evidence comes from the effect of spin statistics in $^{20}Ne_2$ -Kr and $^{20}Ne_2$ -Xe
described earlier: these complexes have C_{2V} symmetry, with the symmetry axis being the *a*-inertial axis.

However, because the trimers observed here are extremely flexible, as indicated by the relatively large quartic distortion constants as well as by their large inertial defects, it is expected that the usual structural concepts do not apply in a straightforward fashion.

There have been some different approaches to evaluate the structural information for this type of floppy complex in the literature. The microwave data for the Ar_2 -HX (X=F [5], Cl [6]) trimers have been interpreted in terms of semirigid models, an approach which has often been taken in microwave spectroscopic investigations. However, Hutson and co-workers have recently taken a slightly different approach for the floppy systems in their theoretical treatments of Ar_2 -HCl [11,12] and Ar_3 [13]. The reason for such an approach is that the separation of rotation and vibration may not be entirely complete because of the very low vibrational modes with large vibrational amplitudes in these complexes.

By analogy with the theoretical treatment of Ar_2 -HCl [11], the instantaneous elements of the inertial tensors of Ne_2 -RG (RG=Kr or Xe) can be written as [11]:

$$I_{aa} = I_{Ne_{2}} \sin^{2} \chi$$

$$I_{bb} = \mu R_{c.m.}^{2} + I_{Ne_{2}} \cos^{2} \chi$$

$$I_{cc} = \mu R_{c.m.}^{2} + I_{Ne_{2}}$$

$$I_{ab} = I_{Ne_{2}} \cos \chi \sin \chi$$

$$I_{bc} = I_{ac} = 0$$
(6.1)

where $I_{Ne2}(=2M_{Ne}r_{Ne-Ne}^{2})$ is the moment of inertia of the diatomic subunit Ne₂; $R_{c.m.}$ is the line connecting the centres of mass of Ne₂ and the third RG atom; χ is the instantaneous angle between $R_{c.m.}$ and the Ne-Ne bond; μ is the pseudodiatomic reduced mass:

$$\mu = \frac{M_{Ne_2} M_{RG}}{M_{Ne_2} + M_{RG}}$$
(6.2)

with RG=Kr or Xe. In the semirigid model treatment of Ar_2 -HX (X=F [5], Cl [6]), the observed rotational constants A, B, and C were related to the expectation values of the inverse of the inertial tensor elements I_{aa} , I_{bb} , and I_{cc} directly. However, in Hutson's treatment, the A, B, and C rotational constants are related to the expectation values of the diagonal elements of the inverse ternsor of I (i.e. I^{-1}) [11]:

$$A \sim \langle \frac{\hbar^2}{2 I_{Ne_2} \sin^2 \chi} + \frac{\hbar^2}{2 \mu R_{c.m.}^2 \tan^2 \chi} \rangle$$

$$B \sim \langle \frac{\hbar^2}{2 \mu R_{c.m.}^2} \rangle$$

$$C \sim \langle \frac{\hbar^2}{2 \mu R_{c.m.}^2 + 2 I_{Ne_2}} \rangle$$

(6.3)

where I is the inertial tensor with its elements defined as in Eq.(6.1). The angular brackets indicate average over the ground state vibrational wavefunction. Evidently the equations for the A and B rotational constants are not the same as would be obtained by simply inverting I_{aa} and I_{bb} . This model is used here since it approximates the large amplitude motions more properly than the semirigid model.

The above equations can be rewritten to calculate the structures from the experimental rotational constants:

$$\mu R_{c.m.}^{2} = \frac{505379}{B}$$

$$\mu R_{c.m.}^{2} + I_{Ne_{2}} = \frac{505379}{C}$$
(6.4)
$$\sin^{2} \chi = \frac{B^{2}}{(B-C)(A+B)}$$

It should be noted that the bracket expressions are no longer used in Eq.(6.4); and the structural parameters calculated from Eq.(6.4) have slightly different physical meanings when different types of rotational constants (e.g. effective, ground state average) are used. When the effective rotational constants (in MHz) are used, $R_{c.m.}$ and r_{Ne-Ne} calculated from Eq.(6.4) denote the effective distances. In order to understand the physical meaning of χ calculated from Eq.(6.4) and to compare the result here with other trimer studies, an angle ß defined as $(90^{\circ}-\chi)$ is introduced, which is referred to as the average vibrational bending amplitude. When the average rotational constants are used, the $R_{c.m.}$ and r_{Ne-Ne} denote the average bond distances; and χ denotes approximately the average structural angle between Ne-Ne bond and $R_{c.m.}$.

For Ne₂-Kr, there are enough data to carry out a reasonably complete structural determination. With C_{2V} symmetry it is possible to obtain complete geometries independently for each isotopomer utilizing Eq. (6.4). The effective structures calculated by using the effective rotational constants in Table 6.6 are listed in Table 6.10 for the two most abundant isotopomers ${}^{20}Ne_2 - {}^{84}Kr$ and ${}^{20}Ne_2 - {}^{86}Kr$. The structural parameters calculated for the other two isotopomers ${}^{20}Ne_2 - {}^{83}Kr$ and ${}^{20}Ne_2 - {}^{82}Kr$ showed less than 0.001 Å differences in the bond lengths of Ne-Ne and Ne-Kr, and less than 0.1° difference in the angles, compared to ${}^{20}Ne_2 - {}^{84}Kr$. The angle ß here indicates the average vibrational amplitude of the Ne-Ne bend, as defined in the previous paragraph.

Another approach has been to evaluate a ground state average (r_z) structure. A harmonic force field is required for this purpose. An approximation was obtained using the measured quartic centrifugal distortion constants of ²⁰Ne²²Ne-Kr. The detailed analysis is in section 6.5.2. To evaluate the r_z parameters the harmonic contributions to the α -constants were first subtracted from the ground state rotational constants for each isotopomer. The resulting values are listed as A_z , B_z and C_z in Table 6.6, as are the corresponding inertial defects Δ_z . The r_z parameters were evaluated separately for each symmetric isotopic species. The resulting structural parameters for the two most abundant isotopomers ${}^{20}\text{Ne}_2 - {}^{84}\text{Kr}$ and ${}^{20}\text{Ne}_2 - {}^{86}\text{Kr}$ are listed in Table 6.10. It should be emphasized that the angle χ calculated here is defined as approximately the average angle between $R_{c.m.}$ and Ne-Ne bond, different from the ones calculated from effective rotational constants.

Since rotational constants for the mixed isotopomers $^{20}Ne^{22}Ne-Kr$ have also been obtained it has been possible to obtain a full substitution (r_s) structure [19]. Kraitchman's equations for a planar molecule [19] have been applied in two separate calculations using B_o and C_o rotational constants taking $^{20}Ne_2-^{84}Kr$ and $^{20}Ne_2-^{86}Kr$ as parent molecules. The a, b and c coordinates of a substituted atom can be evaluated by:

$$|\mathbf{a}| = \left[\frac{\Delta I_{b}}{\mu} \left(1 + \frac{\Delta I_{c} - \Delta I_{b}}{I_{c} - 2I_{b}}\right)\right]^{\frac{1}{2}}$$

$$|\mathbf{b}| = \left[\frac{\Delta I_{c} - \Delta I_{b}}{\mu} \left(1 + \frac{\Delta I_{b}}{2I_{b} - I_{c}}\right)\right]^{\frac{1}{2}}$$

$$|\mathbf{c}| = 0$$

(6.5)

with $\Delta I_b = I_b - I_b$ and $\Delta I_c = I_c - I_c$ the differences between the moments of inertia of the different isotopomers. The results are also given in Table 6.10.

Similar structural analysis procedures as above have been applied for Ne₂-Xe, using Eq.(6.4). However, since it has not been possible to perform a harmonic force field analysis, because of the lack of centrifugal distortion data, an r_2 structure could not be evaluated for Ne₂-Xe. The calculated r_0 structures for two most abundant isotopomers Ne₂-¹²⁹Xe and Ne₂-¹³²Xe using the effective rotational constants in Table 6.7 are listed in Table 6.10.

The structural parameters of the corresponding dimers, Ne-Kr, Ne-Xe and Ne-Ne are also summarized in Table 6.10 to allow comparison with the trimers. For the Ne-Ne distance, since there is no accurate experimental value available [16], an r_o value predicted from the most recent Ne-Ne potential [20] is given in Table 6.10. The program LEVEL [21] was used to calculate r from the original potential [20]. The Ne-Ne potential has an uncertainty in the bond length of better than 1%. Apparently there is a lengthening of the Ne-Ne distance of ~0.07 Å in the trimers compared to that of the dimer. Such lengthening has also been observed in the bond lengths of Ar-Ar in trimers, such as Ar_2-HX (X=F [5], Cl [6]), Ar_2 -OCS and Ar_2 -CO₂ [Chapter 7]. This can possibly be attributed to the existence of an overall three-body repulsive force in the trimers [5,6,11]. There seems to be also a lengthening in the order of 0.005 Å, although less obvious, in the Ne-RG (RG=Kr and Xe) distances.

The Ne-Ne vibrational bending amplitude (B) is about 11.8° in Ne₂-Kr and 13.6° in Ne₂-Xe, although the latter value is probably not very accurate since the A_o rotational constants could not be determined for the Ne₂-Xe complexes. These two values can be compared with the bending amplitude of 4.2° for Ar-Ar in Ar₂-HCl [6], calculated using Eq.(6.4) and the effective rotational constants in Ref.[6]. The larger amplitudes observed for the Ne₂ motion reflect the higher floppiness due to smaller mass and weaker bonding of Ne.

Although the above structural analyses allow qualitative comparison of the effective structures of different complexes, the large uncertainties in the structural parameters do not reflect the accuracy of the microwave measurements. In order to extract three-body nonpairwise additive contributions, it is highly desirable to compare these experimental rotational constants directly with those predicted by rigorous pairwise additive potentials for Ne,-Kr and Ne,-Xe, respectively. Such a pairwise additive potential has recently been constructed for Ar, [13]. The inclusion of three-body nonpairwise additive contributions showed that there is a significant cancellation between the leading three-body dispersion term described by the triple-dipole model and the short-range nonpairwise additive term, leaving the final rotational constants almost unchanged [13]. Similar cancellation phenomena have also

been observed in the theoretical investigation of three-body nonpairwise additive effects in Ar_2 -HCl [11,12], where inclusion of these three-body nonpairwise additive contributions still cannot account for the discrepancy between theoretical and experimental rotational constants. From the rough comparison discussed above, it seems that there would be detectable deviation from pairwise behaviour for Ne₂-Kr and Ne₂-Xe. These triatomic trimers should be easier to deal with theoretically, as opposed to those containing molecular subunits, especially since the theory for nonpairwise additive effects in atomic systems is much more advanced [4,12].

6.5.2 Harmonic force field approximation of Ne,-Kr

For the triatomic Ne₂-Kr complex, there are three normal modes of vibration. The basis set was defined with the following symmetry coordinates: $S_1=(1/\sqrt{2}) (\Delta d_1 + \Delta d_2)$, $S_2=\Delta r$, and $S_3=(1/\sqrt{2}) (\Delta d_1 - \Delta d_2)$ with Δd_i and Δr the NeKr and NeNe bond stretches, respectively. In the C_{2V} point group, S_1 and S_2 have A_1 symmetry and S_3 has B_2 symmetry; there are four force constants in this case, designated f_{11} , f_{22} and f_{33} with off-diagonal constant f_{12} .

Because only three quartic centrifugal distortion constants were obtained for ²⁰Ne²²Ne-⁸⁴Kr and ²⁰Ne²²Ne-⁸⁶Kr, respectively, there is not enough information to fit all four force constants. Instead, four trial fits were

carried out, each with one of the force constants held fixed. The structure used was the r_o structure. When a diagonal force constant was fixed at its value for the corresponding dimer (a reasonable approximation if the potential were all pairwise additive), the off diagonal force constant f_{12} was found to be at least an order of magnitude smaller than the diagonal elements. Furthermore, f₁₂ could not be well determined, even though the Jacobian in the least squares fit indicated that the measured distortion constants were sensitive to it. When f_{12} was set to zero the diagonal constants were little changed from those from the fits when f_{12} was included. Consequently, the final fit assumed $f_{12}=0$; the resulting force field, as well as the corresponding vibrational frequencies, is given in Table 6.11. The estimated values of the strength force constants of the two corresponding dimers Ne-Kr and Ne-Ne are also listed in Table 6.11 for comparison purpose.

It should be pointed out that the force field determination was part of an iterative process which included the fitting of the observed spectra to the spectroscopic constants. Preliminary distortion constants Δ_J , Δ_{JK} and δ_J were obtained for ${}^{20}\text{Ne}{}^{22}\text{Ne}{}^{-84}\text{Kr}$ and ${}^{20}\text{Ne}{}^{22}\text{Ne}{}^{-86}\text{Kr}$ from the spectra and were used in the first force field calculation. Distortion constants Δ_K and δ_K were then predicted from this force field and fixed in the next fit of the spectra, which produced new values for the other three constants. The procedure was repeated until it converged. The final values of the distortion constants obtained from semirigid rotor fits are compared with those predicted from the force field analysis for $^{20}Ne^{22}Ne$ -Kr in Table 6.11. Distortion constants predicted from the final force field were used in the fits to the rotational constants of the $^{20}Ne_2$ -Kr complexes.

Because of the constraint $(f_{12}=0)$ in the harmonic force field analysis, the very large vibrational amplitudes involved, and the expected high anharmonicity of the vibrations, the derived force field must be viewed with caution. Inclusion of the quartic distortion constants predicted from the force field reduced the standard deviations in the fits from ~10 kHz to 1~3 kHz for $^{20}Ne^{22}Ne$ -Kr and from ~50 kHz to less than 6 kHz for $^{20}Ne_2$ -Kr. More importantly, the force field can account for over 97% of the inertial defects.

6.5.3 Induced dipole moments of the trimers

Much attention has been given to the study of collision induced absorption spectra which are due to colliding rare gas pairs [22,23]. In recent years, such attention has been extended to rare gas triatomic systems in connection with the observed features in FIR absorption spectra [24], in particular to explore possible three-body effects on their dipole moments [25,26]. At present the theoretical treatment for such triatomic systems is still aiming at a qualitative understanding. However, it is established that the sign and the magnitude of the three-body contribution to the induced dipole moment depend on the actual properties of the constituents and the geometry of trimers [25,26]. Moreover, theoretical treatments near potential minima have been extremely difficult, since both long and short range interactions contribute significantly in this region. The estimated induced dipole moments presented here are important additional experimental information for theoreticians in order to describe such systems.

The dipole moments of the trimers can be described in terms of pairwise and nonpairwise additive contributions [25,26]. The pairwise contribution is simply the vector sum of the dipole moments of all the pairs in the trimers [25,26]. However, there are possible nonpairwise additive contributions. For example, when two Ne atoms approach each other, an electric quadrupole moment is induced. This quadrupole moment can in turn induce a dipole moment in Kr or Xe, which would not exist in the corresponding dimers [26]. In a similar fashion, the Ne-Kr or Ne-Xe dipole in these two trimers can induce a dipole moment in the other Ne atom [26].

The estimates of the dipole moments of the two trimers studied here are listed in Table 6.9. The order of magnitude of the induced dipole moments of the trimers is about the same as that of the corresponding

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dimers [Chapter 5], in the order of 0.01 D. Considering only the pairwise additive contribution from the vector sum of the dimer constituents and taking into account the structures of the trimers, the magnitudes of the dipole moments for Ne_2 -Kr and Ne_2 -Xe are expected to be about 1.8 times the values of Ne-Kr and Ne-Xe, respectively. The experimental estimated values in Table 6.9 are slightly smaller than the expected pairwise additive values, and the discrepancies might be attributable to three-body effects. Unfortunately, since the uncertainties involved in the experimental determinations are large, as discussed before [Chapter 5], no explicit conclusion can be drawn.

6.5.4 Nuclear quadrupole hyperfine structures

In both Ne₂-Kr and Ne₂-Xe trimers, the nuclear quadrupole coupling constants have been determined for ⁸³Kr and ¹³¹Xe containing complexes. Such information is very important as it provides detailed information about the electronic charge distribution at the sites of the quadrupolar rare gas nuclei.

However, because only a-type transitions were observed, $\chi_{bb}-\chi_{cc}$ is in general not as well determined as χ_{aa} . Nonetheless, the highly asymmetric structures of these two trimers made it possible to obtain also values for $\chi_{bb}-\chi_{cc}$, and thus values for χ_{cc} by using Laplace's equation [see Chapter 2]. This provides a unique

opportunity to compare them with the magnitudes in the corresponding dimers in the light of three-body interactions. χ_{cc} in the trimers, which is not influenced by the large van der Waals vibrational motions, is compared with the $\chi_{_{\perp}}$ values in the corresponding dimers in Table 6.8. If one assumes pairwise additivity for this property, one would expect χ_{\downarrow} values of the dimers to be doubled in the trimers (χ_{cc}) upon approaching of the second Ne atom, as illustrated in Fig.6.3 for Ne₂- 131 Xe. In both cases, $Ne_2 - {}^{83}Kr$ and $Ne_2 - {}^{131}Xe$, the simple combination sum rule does not apply here, i.e. $\chi_{cc} \neq 2\chi_{\perp}$, although the considerable large uncertainty attached, in case of Ne2-Kr, makes it not possible to draw definite conclusion for this trimer. The directions and the percentages of the deviations from pairwise additivity are of opposite sign and different magnitudes, i.e. 4.7% $(\pm 7.4\%)$ for ⁸³Kr and -20.8% $(\pm 4.8\%)$ for ¹³¹Xe. The values in brackets indicate the error limits arising from the uncertainties in $\chi_{cc}.$ The different signs and sizes of the deviations

seem to suggest that three-body effects on the field gradient at the site of the quadrupolar nuclei depend on the actual properties of the constituents and the structures of the trimers, paralleling the theoretical observations of the many-body effects on dipole moments [25,26].



Fig.6.3 Nonpairwise additivity of χ_{cc} (¹³¹Xe) in the Ne₂-¹³¹Xe trimer.

 $2\chi_{\perp}$ indicates twice the χ_{\perp} value of the Ne-¹³¹Xe dimer, which is the value expected for χ_{cc} (¹³¹Xe) in Ne₂-¹³¹Xe assuming pairwise additivity. χ_{cc} (¹³¹Xe) is the experimental determined value for Ne₂-¹³¹Xe.

6.6 Conclusion and future prospect

In this chapter, the first high resolution spectra of the mixed rare gas van der Waals trimers Ne_2 -Kr and Ne_2 -Xe have been described. The observed rotational constants, the dipole moments and the quadrupole coupling constants indicate possible three-body nonpairwise additive contributions to these quantities.

The magnitude of the measured induced dipole moment suggests that it might be feasible to observe these mixed trimers in the FIR region where complementary information on nonpairwise additivity of interatomic (molecular) forces could be obtained.

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Table 6.1 Observed frequencies of ²⁰Ne₂-Kr

| Transi | tion | ²⁰ Ne ₂ | - ⁸⁴ Kr | ²⁰ Ne ₂ - ⁸⁶ | Kr | ²⁰ Ne ₂ - ⁸³ K | r | ²⁰ Ne ₂ - ⁸ | ² Kr |
|---|--------------------------|-------------------------------|------------------------|---|----------------------|---|-----------------------|--|-----------------------|
| J " K _a K _c | - J' K _a K | v _{obs} | Δν _{obs-calc} | v _{obs} | $\Delta v_{obs-cal}$ | c ^V obs | $\Delta v_{obs-calc}$ | v _{obs} | $\Delta v_{obs-calc}$ |
| | | | | | - <u></u> | | | | |
| 2 _{0,2} - | 1 _{0,1} | 5660.3974 | 4.4 5 | 5624.3018 | 1.1 | 5679.0228° | 1.8 | 5698.1425 | 3.4 |
| 3 _{0,3} - | 20,2 | 8379.9282 | -2.8 8 | 3328.7513 | -1.6 | 8406.3113 ^b | -2.3 | 8433.3762 | -4.2 |
| 4 _{0,4} - | 3 _{0,3} | 10982.7663 | -3.7 10 | 919.2181 | 0.8 | 11015.5066° | 19.3 | 11049.0451 | 1.4 |
| 5 _{0,5} - | 4 _{0,4} | 13469.0183 | 4.4 13 | 3394.9018 | -0.2 | | | | |
| 6 _{0,6} - | 5 _{0,5} | 15870.7364 | -1.3 | | | | | | |

 a ν_{obs} in MHz and $\Delta\nu_{obs\text{-calc}}$ in kHz.

^b Hypothetical unsplit line frequencies, free of the ⁸³Kr hyperfine structure.

^c Estimated frequency with hyperfine structure due to ⁸³Kr unresolved.

| $\frac{J''}{K_a''K_c''} \frac{J'_k''}{K_a''K_c''}$ | ²⁰ Ne ²² Ne- ζ'ν _{obs} ^a Δ | ⁸⁴ Kr v _{obs-calc} | ²⁰ Ne ²² Ne v _{obs} | - ⁸⁶ Kr Δν _{obs-calc} |
|--|---|---|---|--|
| 2 _{0,2} - 1 _{0,1} | 5469.9686 | 0.6 | 5433.971 | 9 -0.2 |
| $2_{1,2} - 1_{1,1}$ | 5082.1565 | -0.9 | 5050.549 | 3 -1.4 |
| $2_{1,1} - 1_{1,0}$ | 5946.0218 | 2.8 | 5903.099 | 7 0.3 |
| $3_{0,3} - 2_{0,2}$ | 8095.4319 | -0.4 | 8044.468 | 5 0.3 |
| 3 _{1,3} - 2 _{1,2} | 7595.5323 | 1.0 | 7548.878 | 5 1.5 |
| $3_{1,2} - 2_{1,1}$ | 8887.1467 | -3.4 | 8823.6693 | 3 -0.2 |
| $4_{0,4} - 3_{0,3}$ | 10605.9192 | 0.1 | 10542.730 | 5 -0.1 |
| $4_{1,4} - 3_{1,3}$ | 10079.6175 | -0.3 | 10018.6534 | 4 -0.4 |
| 4 _{1,3} - 3 _{1,2} | 11786.1746 | 1.1 | 11703.3900 | 9 4.6 |

Table 6.2 Observed frequencies of $^{20}\mathrm{Ne}^{22}\mathrm{Ne}-\mathrm{Kr}$

 a ν_{obs} in MHz and $\Delta\nu_{obs\text{-calc}}$ in kHz.

| $J''_{K''_{a}K''_{c}} - J'_{K'_{a}K'_{c}}$ | v_{obs} | $\Delta v_{obs-calc}$ |
|--|-----------|-----------------------|
| F" - F' | (MHz) | (kHz) |
| | | |
| $2_{0,2} - 1_{0,1}$ | | |
| 3.5 - 4.5 | 5679.1194 | -2.5 |
| 5.5 - 4.5 | 5679.0578 | 1.0 |
| 4.5 - 4.5 | 5679.0578 | 1.0 |
| 6.5 - 5.5 | 5679.0401 | 0.3 |
| 3.5 - 3.5 | 5678.9618 | -0.8 |
| 4.5 - 3.5 | 5678.8984 | 0.9 |
| | | |
| $3_{0,3} - 2_{0,2}$ | | |
| 2.5 - 3.5 | 8406.3744 | 2.2 |
| 6.5 - 5.5 | 8406.3322 | 0.3 |
| 7.5 - 6.5 | 8406.3222 | -2.3 |
| 5.5 - 4.5 | 8406.3049 | 0.5 |
| 5.5 - 5.5 | 8406.3049 | 0.5 |
| 4.5 - 3.5 | 8406.2634 | 0.8 |
| 6.5 - 6.5 | 8406.2171 | -1.9 |
| | | |

Table 6.3 Observed frequencies of $^{20}\text{Ne}_2^{-83}\text{Kr}$

| $\frac{\text{Transitio}}{J''_{K_a'K_c'} - J_K'}$ | on ²⁰ Ne ₂ - 'K' v _{obs} a | ¹²⁹ Χe Δν ^a _{obs-calc} | ²⁰ Ne ₂ -1 v _{obs} | ³¹ Xe Δν _{obs-calc} | ²⁰ Ne ₂ - ¹³ v _{obs} | ⁵² Xe Δν _{obs-calc} | ²⁰ Ne ₂ - ¹³⁴ Xe v _{obs} | ²⁰ Ne ₂ - ¹³⁶ Xe v _{obs} | |
|--|--|--|--|--|---|--|---|---|---|
| $2_{0,2} - 1_{0,1}$ | 4465.2255 | 48.7 | 4450.9000 | -20.2 | 4444.0399 | 48.1 | 4430.4199 | | |
| $3_{0,3} - 2_{0,2}$ | 6657.2379 | -5.6 | 6636.4217 | 23.7 | 6626.2586 | -4.6 | 6606.3324 | 6586.9693 | l |
| $4_{0,4} - 3_{0,3}$ | 8802.6900 | -39.9 | 8775.8800 | -7.6 | 8762.7902 | -39.4 | | | |
| $5_{0,5} - 4_{0,4}$ | 10892.1250 | 4.2 | | | 10844.2422 | 2.6 | | | |
| 6 _{0,6} - 5 _{0,5} | 12924.2453 | 9.6 | | | 12869.1157 | 10.3 | | | |

Table 6.4 Observed frequencies of $^{20}\text{Ne}_2$ -Xe

 a ν_{obs} in MHz and $\Delta\nu_{obs\text{-calc}}$ in kHz.

| J" _{K"a} K" - J' _{ka} K' | v_{obs} | $\Delta v_{obs-calc}$ |
|--|-----------|-----------------------|
| F" - F' | (MHz) | (kHz) |
| 2 _{0,2} - 1 _{0,1} | | |
| 3.5 - 2.5 | 4450.9796 | -0.7 |
| 2.5 - 1.5 | 4450.9796 | -0.8 |
| 1.5 - 1.5 | 4450.8804 | 0.8 |
| 2.5 - 2.5 | 4451.1217 | 0.2 |
| 1.5 - 0.5 | 4451.1339 | 0.5 |
| | | |
| $3_{0,3} - 2_{0,2}$ | | |
| 4.5 - 3.5 | 6636.4194 | 0.9 |
| 3.5 - 2.5 | 6636.4194 | 0.6 |
| 2.5 - 2.5 | 6636.3522 | -0.6 |
| 2.5 - 1.5 | 6636.4531 | -0.6 |
| 1.5 - 0.5 | 6636.4531 | -0.3 |
| | | |
| $4_{0,4} - 3_{0,3}$ | | |
| 5.5 - 4.5 | 8776.8833 | 1.1 |
| 4.5 - 3.5 | 8776.8833 | 0.8 |
| 3.5 - 2.5 | 8776.8977 | -1.1 |
| 2.5 - 1.5 | 8776.8977 | -0.8 |
| | | |

Table 6.5 Observed frequencies of ${}^{20}\mathrm{Ne_2}-{}^{131}\mathrm{Xe}$

| Paramet | ter ²⁰ Ne ₂ - ⁸⁴ Kr | ²⁰ Ne ₂ - ⁸⁶ Kr | ²⁰ Ne ₂ - ⁸³ Kr | 20 Ne ₂ - 82 Kr | ²⁰ Ne ²² Ne- ⁸⁴ Kr | ²⁰ Ne ²² Ne- ⁸⁶ Kr | |
|------------------|--|--|--|--------------------------------------|---|---|----|
| Ground | <u>state effective</u> | <u>e rotational cor</u> | stants /MHz | | | | |
| A | 4728.39(32) | 4727.00(38) | 4729.09 ^a | 4729.78ª | 4529.258(79) | 4529.249(37) | |
| B | 1648.9885(66) | 1636.793(10) | 1655.3001(91) | 1661.7762(54) | 1595.2281(13) | 1583.07491(71 |) |
| c | 1204.1318(82) | 1197.653(11) | 1207.4657(58) | 1210.8914(126 | 1162.4545(14) | 1155.96567(51 |) |
| Ground | <u>state average</u> | <u>rotational const</u> | ants /MHz | | | | |
| A _z | 4578.2220 | 4576.975 | 4578.849 | 4579.464 | 4388.584 | 4388.713 | |
| B _z | 1623.4785 | 1611.575 | 1629.638 | 1635.958 | 1571.0071 | 1559.1409 | Ч |
| Cz | 1197.9508 | 1191.521 | 1201.260 | 1204.660 | 1156.6255 | 1150.1837 | 68 |
| <u>Centri</u> | <u>fugal distortio</u> | <u>n constants /kHz</u> | 2 | | | | |
| Δ., | 38.58 ^b | 38.05 ^b | 38.86 ^b | 39.15 ^b | 35.713(32) | 35.290(21) | |
| Δ _{.IK} | 30.91 ^b | 29.93 ^b | 31.41 ^b | 31.93 ^b | 33.54(93) | 31.71(38) | |
| Δκ | 1473.0 ^b | 1474.0 ^b | 1472.0 ^b | 1471.0 ^b | 1339.16 ^b | 1340.63 ^b | |
| δ | 11.92 ^b | 11.72 ^b | 12.02 ^b | 12.13 ^b | 11.046(20) | 10.910(16) | |
| δ _κ | 131.5 ^b | 130.5 ^b | 132.0 ^b | 132.5 ^b | 122.35 ^b | 121.43 ^b | |
| Inertia | al defect /amu / | <u>Ų</u> | | | | | |
| ۵. | 6.3440 | 6.2995 | 6.3696 | 6.3909 | 6.3639 | 6.3720 | |
| Δ _z | 0.1880 | 0.1352 | 0.2174 | 0.2431 | 0.0939 | 0.0962 | |
| <u>Standa</u> | <u>rd deviation /k</u> | Hz | | | | | |
| σ | 5.6 | 2.1 | 5.9 | 5.6 | 2.8 | 1.2 | |

Spectroscopic Constants of Ne₂-Kr Table 6.6

^a Fixed at the values extrapolated from $^{20}Ne_2-^{84}Kr$ and $^{20}Ne_2-^{86}Kr$. ^b Fixed at the values from the force field analysis.

| Table | 6.7 | Spectroscopic | Constants | of | ²⁰ Ne ₂ -Xe |
|-------|-----|---------------|-----------|----|-----------------------------------|
| | | I I | | | 2 |

| Paramete | er ²⁰ Ne ₂ - ¹²⁹ Xe | ²⁰ Ne ₂ - ¹³¹ Xe | ²⁰ Ne ₂ - ¹³² Xe | | | | | |
|---------------------------|--|---|---|--|--|--|--|--|
| Rotational constants /MHz | | | | | | | | |
| A _o | 4728.39ª | 4728.39ª | 4728.39ª | | | | | |
| B _o | 1260.844(30) | 1256.236(52) | 1254.163(29) | | | | | |
| Co | 979.967(13) | 977.296(34) | 975.891(12) | | | | | |
| <u>Inertial</u> | <u>Inertial defect /amu Å²</u> | | | | | | | |
| <u>Standard</u> | deviation /kHz | /.94 | 0.02 | | | | | |
| σ | 63.6 | 38.0 | 60.0 | | | | | |

^a Fixed at the value of $^{20}\text{Ne}_2^{-84}\text{Kr}$.

Table 6.8

Quadrupole coupling constants (MHz) of $^{83}\mathrm{Kr}$ and $^{131}\mathrm{Xe}$ in Ne_2-RG trimers and in the corresponding dimers

| complex | ²⁰ Ne ₂ - ⁸³ Kr | ²⁰ Ne- ⁸³ Kr | ²⁰ Ne ₂ - ¹³¹ Xe | ²⁰ Ne- ¹³¹ Xe |
|-----------------------------------|--|------------------------------------|---|-------------------------------------|
| X _{aa} | -0.7080(63) | -0.5205(23) | 0.5641(23) | 0.3877(9) |
| X _{bb} | 0.163(35) | - | -0.257(18) | - |
| X _{cc} or X ₁ | 0.545(36) | 0.2602(12) | -0.307(18) | -0.1939(5) |
| Ref. | this work | Chapter 5 | this work | Chapter 5 |

Table 6.9

Estimated electric dipole moments of Ne_2-RG trimers and the corresponding dimers

| molecule | dipole moment ^a (Debye) | Ref. |
|---------------------|---------------------------------------|-----------|
| | | |
| Ne ₂ -Kr | 0.015 | this work |
| Ne-Kr | 0.011 | Chapter 5 |
| Ne ₂ -Xe | 0.011 | this work |
| Ne-Xe | 0.012 | Chapter 5 |
| | | |

^a The number of digits given does not reflect the uncertainty. See text for evaluation procedure.

Table 6.10 Structural parameters^a of Ne_2 -Kr, Ne_2 -Xe and the corresponding dimers^b

| parameter | R _{c.m.} | r _{Ne-Kr} | r _{Ne-Ne} | x | ß | r _{Ne-Kr} | r _{Ne-Ne} |
|----------------|---|---------------------------------|--------------------|------|------|-------------------------------------|------------------------------------|
| | | ²⁰ Ne ₂ - | - ⁸⁴ Kr | | | ²⁰ Ne- ⁸⁴ Kr | ²⁰ Ne- ²⁰ Ne |
| r _o | 3.364 | 3.762 | 3.366 | 78.2 | 11.8 | 3.759 | 3.290 |
| rz | 3.390 | 3.776 | 3.326 | 88.0 | - | - | - |
| r _s | - | 3.700 | 3.179 | - | - | 3.698 | - |
| | | | | | | | |
| | | ²⁰ Ne ₂ - | . ⁸⁶ Kr | | | ²⁰ Ne- ⁸⁶ Kr | ²⁰ Ne- ²⁰ Ne |
| r _o | 3.364 | 3.761 | 3.365 | 78.3 | 11.7 | 3.759 | 3.290 |
| rz | 3.390 | 3.776 | 3.326 | 88.3 | - | - | - |
| r _s | - | 3.700 | 3.186 | - | - | 3.698 | - |
| | | | | | | | |
| parameter | R _{c.m.} | r _{Ne-Xe} | r _{Ne-Ne} | χ | ß | r _{Ne-Xe} | r _{Ne-Ne} |
| | ²⁰ Ne ₂ - ¹³² Xe | | | | | ²⁰ Ne- ¹³² Xe | ²⁰ Ne- ²⁰ Ne |
| r _o | 3.624 | 4.001 | 3.390 | 76.4 | 13.6 | 3.994 | 3.290 |
| | | | | | | | |
| | | ²⁰ Ne ₂ - | ¹²⁹ Xe | | | ²⁰ Ne- ¹²⁹ Xe | ²⁰ Ne- ²⁰ Ne |
| r _o | 3.624 | 4.001 | 3.390 | 76.4 | 13.6 | 3.994 | 3.290 |

^a Bond length in (Å), angle in (°).

^b The values for Ne-Kr and Ne-Xe were those in Table 5.15; the value for Ne-Ne distance was calculated using the potential in Ref.20 (see text).

Table 6.11

The harmonic force field analysis of Ne₂-Kr

Structural parameters:

$$r(Ne(1)-Ne(2))=r=3.366 \text{ Å}$$

 $r(Ne(1)-Kr)=r_1=r(Ne(2)-Kr)=r_2=3.762 \text{ Å}$

Symmetry coordinates:

A₁:
$$S_1 = (1/2)^{\frac{1}{2}} (\Delta r_1 + \Delta r_2)$$

 $S_2 = \Delta r$
B₂: $S_3 = (1/2)^{\frac{1}{2}} (\Delta r_1 - \Delta r_2)$

Harmonic force constants of Ne₂-Kr and those of the corresponding dimers:

| | Ne ₂ -Kr | Dimer |
|---|--------------------------|----------------------|
| f ₁₁ (mdyn Å ⁻¹) | 0.00408(3) | 0.00397 ^b |
| f ₁₂ (mdyn rad ⁻¹) | 0.0 (fixed) ^a | |
| f ₂₂ (mdyn Å rad ⁻²) | 0.00146(4) | 0.00221 ^c |
| f ₃₃ (mdyn Å ⁻¹) | 0.00362(5) | 0.00397 ^b |

| <u>Predicted</u> | <u>van der</u> | Waals | <u>vibrational</u> | | | |
|-------------------------------|----------------|-------|--------------------|--|--|--|
| frequencies /cm ⁻¹ | | | | | | |
| ν ₁ | 23.1 | | | | | |
| ν ₂ | 13.3 | | | | | |
| v ₃ | 18.4 | | | | | |

Table 6.11 (continued)

<u>Comparison of observed and calculated</u> <u>centrifugal distortion constants (kHz):</u>

| | ²⁰ Ne ²² Ne- ⁸⁴ Kr | | ²⁰ Ne ²² Ne ⁻⁸⁶ K | r | |
|-----------------|---|------------|--|------------|--|
| | Observed | Calculated | Observed | Calculated | |
| Δ _J | 35.713(32) | 35.77 | 35.290(21) | 35.26 | |
| Δ _{JK} | 33.54(93) | 32.82 | 31.71(38) | 31.86 | |
| Δ _κ | 1339.16(fixed) | 1339.16 | 1340.63(fixed) | 1340.63 | |
| δ _J | 11.046(20) | 11.08 | 10.910(16) | 10.89 | |
| δ _κ | 122.35(fixed) | 122.35 | 121.43(fixed) | 121.43 | |

^a See discussion in the text.

^b Ne-Kr stretch force constant calculated from the spectroscopic constants of ²⁰Ne-⁸⁴Kr in Chapter 5 Table 5.3, using formulae $f_s=16\pi^2\mu_{Ne-Kr}B_o^3/D_J$

^c Caluclated from Ne-Ne stretch frequency in Ref.16.

CHAPTER 7

The Microwave Spectra of the van der Waals trimers

Ar2-OCS and Ar2-CO2

7.1 Introduction

In the previous chapter, the microwave investigation of two of the simplest possible van der Waals trimers was described. In this chapter, another important, but more complicated, type of van der Waals trimer, namely Ar_2 -OCS and Ar_2 -CO₂, is discussed.

The first observed pure rotational spectrum of a neutral trimer was that of Ar,-HF, studied and analyzed by Gutowsky et al. [1] in 1987. Subsequently, this group has succeeded in obtaining the microwave spectra of other Ar₂-small molecule complexes, such as: Ar₂-HF, DF [1], HCl [2], DCl [3], and HCN [4], as well as some larger clusters. Their work provided the first accurate ground state structural information of larger clusters, and raised the possibility of determining accurate potentials for three- and four-body interactions and of obtaining in particular direct information on the nonpairwise additivity of intermolecular forces [5]. Following these observations on Ar2-HCl, Hutson et al. [5] have been able to develop and test a theory for treating the dynamics of polymeric van der Waals clusters. They calculated pairwise additive and "adjusted" potential energy

surfaces (adjusted empirically to account for nonpairwise additive effects in the ground state) for Ar_2 -HCl, to determine whether high resolution spectroscopy could, in principle, characterize the nature of three-body forces. It is very encouraging that, guided by this theoretical prediction, Elrod *et al.* [6] have been successful in observing the first far infrared intermolecular vibration-rotation spectrum of Ar_2 -HCl.

Although these trimers, especially Ar₂-HCN, have their own peculiarities, they share some general properties: (1) Ar₂-HX (X=F [1], Cl [2,3], CN [4]) trimers have C_{2V} symmetry, and are T-shaped; (2) The Ar-Ar distances are very similar in these different trimers (see Table 7.11 for details), and is also very similar to the reported value of Ar-Ar distance, 3.821(10) Å, in the free Ar, dimer [7]; (3) The distance from Ar to the center of mass (c.m.) of HX is almost the same as that in the corresponding linear dimers Ar-HF [8,9] and Ar-HCl [10], although this distance is, surprisingly, rather shorter in Ar2-HCN [4,11,12] (see also Table 7.11); (4) All these trimers have large inertial defects, ranging from 3.379 amu $Å^2$ for Ar_2 -HF to 13.9 amu $Å^2$ for Ar_2 -HCN, which is enormous for a nominally planar species.

The distinctive behaviour of Ar₂-HCN, as Gutowsky et al. pointed out [4], is caused by the

cylindrical shape of HCN. Because of this shape the HCN can get closer to a spherical species with a side-on approach, rather than by an end-on one. To maintain this condition, it undergoes an in-plane internal rotation with respect to Ar₂. In contrast, both HF and HCl are virtually spherical, and can easily maintain a T-shaped structure at close contact without undergoing complex internal rotation. On the other hand, some other cylindrically shaped small molecules, such as OCS and CO2, with the most positive atom in the middle, prefer side-on approaches while bonding weakly to rare gas atoms. It was thus of considerable interest to study other types of Ar2-small molecule trimers such as Ar2-OCS and Ar_2-CO_2 , for a better understanding of the nature of the intermolecular forces. How do the structures and the strength of the forces change upon replacing the small molecules? How do the properties of the Ar-small molecule dimers change as the second rare gas atom approaches? If one classifies the dimers according to the essential shapes of the small molecules, spherical or cylindrical, a trend is easily seen: Ar-HF, Ar-HCl (semirigid, linear) \rightarrow Ar-HCN (highly nonrigid, linear) \rightarrow Ar-OCS, Ar-CO₂(semirigid, planar T-shaped). Here Ar-HCN can be viewed as intermediate between the two different structure types. This may be the reason for its high nonrigidity and its peculiarities, such as its unusually

large centrifugal distortion constants and its abnormal sensitivity to isotopic substitution, as well as its unexpectedly large bending amplitude [11,12]. The aim was then to learn whether the trend of the trimers would be similar.

The only previous study on Ar₂-OCS appears to be that of Leopold [13]. Six very weak radio frequency and microwave transitions were found by molecular beam electric resonance (MBER), and were tentatively ascribed to the trimer, but were insufficient to determine its structure or to lead to other detectable transitions. As a result of the present work, five of the lines have been assigned and are listed in Table 7.1.

In the work reported here, the search for Ar_2 -OCS was triggered by the observation of two "mystery" lines at the frequencies 7516.1554 MHz and 9930.3470 MHz during the search for lines of the Ar-¹⁸OCS [14] complex. Following the elimination of transitions due to Ar-OCS isotopomers [14], complexes due to clusters of argon with OCS, other than the dimer Ar-OCS, appeared most likely. In fact, these two lines turned out to be very helpful for the entire search procedure, and were eventually identified as two transitions of the Ar₂-OCS trimer.

For Ar_2-CO_2 , there is no previous study reported, to the best of my knowledge. The search for Ar_2-CO_2 was more or less straightforward though tedious, following the study of Ar₂-OCS. These two trimers were the first two trimers studied in this work.

7.2 Experimental Conditions

The Ar_2 -OCS trimer was formed by the expansion of Ar with 0.2% OCS at a backing pressure of 1.5 atm. It was found later that use of mixtures of 15% Ar and 85% Ne as the carrier gas with 0.2% OCS would increase the sigal-to-noise (S/N) ratio by a factor of four to five, especially for the low J(<4) transitions. This significant improvement made it possible to search for lines of the Ar_2 -OC³⁴S isotopomer in natural abundance. The line strength of Ar_2 -OCS was about six or seven times smaller than that of Ar-OCS under the same conditions.

For Ar_2-CO_2 , the trimer was formed by the expansion of a gas mixture consisting of 0.5% CO_2 and 1% Ar in Ne at a backing pressure of 3.5 atm. Because of the anticipated low dipole moment of the trimer Ar_2-CO_2 (μ ~0.068 Debye for Ar-CO₂ [15]), the microwave excitation pulses were amplified using the microwave power amplifier.

When this project was almost complete and a draft for a publication had been written, I learned of a parallel study by Connelly and Howard at the University of Oxford, who had measured transitions of the normal and

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³⁴S-containing isotopomers of Ar_2 -OCS. The data were combined in the final analyses in the following way. Only measurements made with a parallel nozzle at the University of British Columbia were included, along with those made with a perpendicular nozzle at Oxford. The latter, indicated by "*" in Table 7.1, had measurement accuracies of ±4 kHz. In the final fit, made by this author, the data were weighted according to the (measurement accuracy)⁻².

The ¹⁸OCS-enriched sample was synthesized by the method of Ref. 16, using isotopically enriched water. The percentage of ¹⁸OCS was estimated to be about 4% by comparing the line strength of $Ar-OC^{34}S$ in natural abundance with that of $Ar-^{18}OCS$ using the enriched sample.

Finally, examples of transitions in Ar_2 -OCS and Ar_2 -CO₂, are shown in Fig.7.1 to give an indication of the signal-to-noise ratio and the resolution achieved.

7.3 Search and rotational assignment

A. Ar_2 -OCS

The possible sources of the aforementioned two "mystery" transitions were first carefully checked. These lines had very similar properties: (1) They could be seen easily with 0.2% OCS in Ar. The optimized microwave



Fig.7.1 (a) The rotational transition $3_{1,2}-2_{0,2}$ of Ar_2 -OCS recorded with 1 experimental cycle. The transition is split into a Doppler doublet.



Fig.7.1 (b) The rotational transition $3_{3,1}-2_{2,0}$ of Ar_2-CO_2 recorded with 5 experimental cycles.

excitation pulse length indicated that the dipole moment of the unknown substance was similar to that of OCS. These lines were weaker than those of Ar-OCS but stronger than those of $Ar-OC^{34}S$ in natural abundance under the same conditions. (2) They could not be seen with pure Ar. (3) They could not be seen with 0.2% OCS in Ne. The second and the third observations suggested that the source was Ar+OCS. The first, from a comparison with the line strengths observed for the Ar_2 -HX [1,2] and Ar-HX (X=F [8,9] and Cl [10,11]) systems, suggested that it was most likely to be Ar_2 -OCS.

Following Ar₂-HX (X=F [1], Cl [2,3], CN [4]) as examples, a C_{2V} T-shaped structure for Ar₂-OCS was first assumed. However, to keep a planar structure and a R_{c.m.} similar to Ar-OCS would result in an Ar-O distance of 2.5 Å, which is far too short compared with the sum of the van der Waals radii of argon (1.91 Å) and oxygen (1.4 Å). A reasonable structure to meet the general properties observed for Ar₂-small molecule complexes, as described in the introduction, was a C_s, distorted tetrahedral shape with both Ar-OCS [14] and Ar-Ar [7] moieties remaining similar to their corresponding free dimers. With these dimensions the trimer would be an oblate, highly asymmetric top (Fig.7.2). Since the *a* and *c* axes would be in the C_s symmetry plane, making the projection of the OCS dipole moment on the *c* axis about
twice as large as that on the a axis, strong c and weak a type transitions were expected.

The initial calculation based on this assumed structure predicted a series of c-type transitions of J=3-2 and J=4-3 with frequencies around 7.5 GHz and 10.0 GHz respectively. If the assumed structure were more or less correct, the two "mystery" lines should probably belong to these two series respectively. The assignment of the quantum numbers was made by comparing the frequency ratio of each pair of predicted frequencies in J=3-2 and J=4-3 to that of the two lines observed. Two pairs of possible candidates were found, namely: $3_{1,2}-2_{0,2}$, $4_{2,2}-3_{1,2}$ and $3_{2,2}-2_{1,2}$, $4_{2,3}-3_{1,3}$. For the second case, search for other lines belonging to the same $\Delta K_c = 0$ stack was unsuccessful. However for the first possibility, two other lines, namely $3_{2,2}-2_{1,2}$ and $4_{3,2}-3_{2,2}$ were observed. With these four lines, an approximate set of rotational constants was obtained. Ultimately 65 lines were observed for the main isotopomer; their frequencies are given in Table 7.1. The a-type transitions were observed with about three times less intensity than the c-type, as predicted.

The spectra of $Ar_2-OC^{34}S$ and $Ar_2-^{18}OCS$ isotopomers were also measured to confirm the assignments and to provide more information on the structure and the force field of the trimer. Transitions for these two

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isotopomers were easily located using rotational constants calculated from the preliminary structure and distortion constants derived for the main isotopomer. The transitions measured for these two isotopomers are listed in Table 7.2.

The line intensities of these two isotopomers were about four or five times smaller than those of their corresponding Ar-OCS dimers under the same experimental conditions. This observation was consistent with what had been observed in the case of the main isotopomer.

B. Ar_2-CO_2

The search for Ar_2-CO_2 followed essentially the procedure used in Ar_2-OCS . An initial structure was proposed for Ar_2-CO_2 . It is a C_{2V} , distorted tetrahedral shape, with both $Ar-CO_2$ [15] and Ar-Ar [7] moieties remaining similar to their corresponding free dimers. With these dimensions, the trimer is an oblate, highly asymmetric top (κ =~0.360, see Fig.7.3). Because of the C_{2V} symmetry of the complex, the only non-zero induced dipole moment is along the axis connecting the centres of mass of the Ar_2 and CO_2 subunits, coinciding with the *b*-inertial axis; only *b*-type transitions are allowed. The initial rotational constants were predicted from the assumed structure, and were used to predict *b*-type transition frequencies. Searches were carried out for low J transitions because of the expected low rotational temperature in the jet expansion. Most low J (\leq 4) lines were located within \pm 50 MHz of the predicted frequencies. Further lines were easily found by bootstrapping. Eventually twenty-one lines, all *b*-type, with K_a+K_c=even, were found (See Table 7.3). The intensities of these lines were about five to six times less than those of the Ar-CO₂ dimer under the same conditions. A rough estimate from the optimized microwave excitation pulse lengths for both Ar-CO₂ and Ar₂-CO₂ suggested that the induced dipole moment of Ar₂-CO₂ is very similar to that of Ar-CO₂.

7.4 Analyses of the Ar,-OCS and Ar,-CO, spectra

The observed frequencies of Ar_2 -OCS were fit to a III^r representation, Watson A-reduction, semirigid rotor model [18] consisting of 3 rotational constants and 5 quartic centrifugal distortion constants. The spectroscopic constants for all three isotopomers of Ar_2 -OCS are listed in Table 7.4. The differences between them and those calculated using the constants tabulated in Table 7.4, are listed in Tables 7.1 and 7.2. Table 7.1 also contains the MBER measurements [13], and their assignments. Although they were not included in the fit, they are very well predicted by our constants.

Similarly, all observed frequencies of Ar_2-CO_2 were

fit to the same semirigid rotor model used above, consisting of three rotational constants, five quartic distortion constants, as well as three sextic distortion constants. The spectroscopic constants for Ar_2-CO_2 are listed in Table 7.5. The observed frequencies, along with the differences between the observed and calculated frequencies using the constants tabulated in Table 7.5, are listed in Table 7.3.

The standard deviations for all these fits are comparable to or less than the estimated measurement accuracies, demonstrating that the data are fitted adequately by the models employed. For Ar_2-CO_2 , a fit without the sextic distortion constants gave essentially the same quartic distortion constants with slightly larger standard deviations and a 2.4 kHz standard deviation for the fit.

7.5 Geometry and structure of Ar_2 -OCS and Ar_2 -CO₂ A. Ar_2 -OCS

All the observed transitions listed in Tables 7.1 and 7.2 are either a- or c-type. A search for b type transitions was unsuccessful, thus suggesting strongly that the b axis is perpendicular to the OCS axis, and that OCS lies in the ac plane [Fig.7.2]. This is also supported by the very small change in the planar moment



Fig.7.2 Ar₂-OCS in its principal inertial axis system.

 $R_{c.m.}$ connects the centres of mass of the Ar_2 and the OCS subunits. $R_{c.m.}$, r and θ are coordinates used in determining the structure of Ar_2 -OCS.

 P_b upon isotopic substitution, as shown in the next paragraph.

The inertial defect, defined as

$$\Delta_{o} = I_{c}^{o} - I_{a}^{o} - I_{b}^{o}$$
(7.1)

is expected to be zero for a rigid planar molecule. In Ar_2 -OCS, Δ_o is about -140 amu Å² for all three isotopomers, clearly indicating that the complex is nonplanar. The planar moment P_b is given by

$$P_{b} = \sum_{i} m_{i} b_{i}^{2} = \frac{1}{2} (I_{a}^{o} + I_{c}^{o} - I_{b}^{o})$$
(7.2)

where m_i is the mass of atom i, and b_i is its coordinate along the *b*-inertial axis. This quantity describes the mass located out of the *ac* plane. The P_b values for all three Ar₂-OCS isotopomers are tabulated in Table 7.4. If the OCS moiety were not lying in the *ac* plane, one would expect significant increases in the P_b values upon substitutions of ¹⁸O and ³⁴S for ¹⁶O and ³²S, respectively. However, the changes are very small, with different signs, for the two different substitutions: -0.0101 amu Å² for ¹⁶O to ¹⁸O and +0.0073 amu Å² for ³²S to ³⁴S. The OCS molecule is clearly in the symmetry plane of the complex, and the sole contributions to P_b are from the two Ar atoms, giving

$$P_{b} = 2 m_{Ar} b_{Ar}^{2}$$
 (7.3)

the b_{Ar} values obtained in this manner from the normal isotopomer are ± 1.921 Å, corresponding to an Ar-Ar distance of 3.842 Å, which is very close to its value in the Ar₂ dimer, and in the Ar₂-HX (X=F [1], Cl [2,3], CN [4]) trimers.

From the ¹⁸O and ³⁴S substitutions one can get the substitution coordinates of these two atoms using the usual formulae for nonplanar asymmetric top molecules [18],

$$|a| = \left[\frac{\Delta P_{a}}{\mu}\left(1 + \frac{\Delta P_{b}}{I_{a}^{\circ} - I_{b}^{\circ}}\right)\left(1 + \frac{\Delta P_{c}}{I_{a}^{\circ} - I_{c}^{\circ}}\right)\right]^{\frac{1}{2}}$$

$$|b| = \left[\frac{\Delta P_{b}}{\mu}\left(1 + \frac{\Delta P_{c}}{I_{b}^{\circ} - I_{c}^{\circ}}\right)\left(1 + \frac{\Delta P_{a}}{I_{b}^{\circ} - I_{a}^{\circ}}\right)\right]^{\frac{1}{2}}$$

$$|c| = \left[\frac{\Delta P_{c}}{\mu}\left(1 + \frac{\Delta P_{a}}{I_{c}^{\circ} - I_{a}^{\circ}}\right)\left(1 + \frac{\Delta P_{b}}{I_{c}^{\circ} - I_{b}^{\circ}}\right)\right]^{\frac{1}{2}}$$

$$(7.4)$$

where

$$\Delta P_{a} = \frac{1}{2} \left(-\Delta I_{a}^{\circ} + \Delta I_{b}^{\circ} + \Delta I_{c}^{\circ} \right)$$

$$\Delta P_{b} = \frac{1}{2} \left(-\Delta I_{b}^{\circ} + \Delta I_{c}^{\circ} + \Delta I_{a}^{\circ} \right) \qquad (7.5)$$

$$\Delta P_{c} = \frac{1}{2} \left(-\Delta I_{c}^{\circ} + \Delta I_{a}^{\circ} + \Delta I_{b}^{\circ} \right)$$

and where $\Delta I_a^o(=I_a^{o_1}-I_a^o)$, and so on, are the changes in the principal moments of inertia due to isotopic substitution. The *a* and *c* coordinates for S are calculated to be, respectively: 2.187 Å and -0.803 Å, and for 0: 1.101 Å and 1.694 Å. This gives an OCS length of 2.723 Å assuming it to be linear, which agrees very well with the r_s value in the free OCS molecule, 2.721(2) Å [19]. It seems that there is no significant change in the OCS structure upon weakly bonding to the Ar atoms, as is the case for most small molecules in their van der Waals complexes with rare gases [14].

Assuming that the two Ar atoms are equivalent, and using the known structure of OCS [19], there are three structural parameters to be determined for Ar_2 -OCS: the Ar-Ar distance (r), the Ar-Ar c.m. to OCS c.m. distance ($R_{c.m.}$), and the angle between $R_{c.m.}$ and OCS (θ). By fitting all these three parameters to the rotational constants A_0 , B_0 and C_0 of all three isotopomers, the r_0 structure for Ar_2 -OCS was obtained, which is listed in Table 7.6. The values are effective ground state values, and the quoted uncertainties are those from the least squares fit. For comparison, the structural parameters of Ar-OCS, as well as of the Ar dimer are also in Table 7.6.

B. Ar_2-CO_2

In the case of Ar_2-CO_2 , all of the observed

transitions listed in Table 7.4 are *b*-type, $K_a+K_b=even$. Efforts to measure *b*-type, $K_a+K_b=odd$ transitions turned out to be unsuccessful. This is consistent with the nuclear spin statistics associated with the C_{2V} equilibrium structure for Ar_2-CO_2 . The rotational wave functions are symmetric or antisymmetric with respect to a 180° rotation about the *b*-axis if $K_a+K_c=even$ or odd respectively, while the nuclear spin functions are always symmetric for the spinless nuclei. Since the two sets of equivalent spinless Bosons, namely the two oxygen nuclei and the two argon nuclei, require a totally symmetric wave function, only $K_a+K_c=even$ rotational levels are possible.

With the C_{2V} symmetric structure for Ar_2-CO_2 , and using the known structure of CO_2 [20], there are only two structural parameters to determine for Ar_2-CO_2 : the Ar-Ar distance (r), and the Ar-Ar c.m. to CO_2 c.m. distance $(R_{c.m.})$. The Ar-Ar distance can be calculated in a similar fashion as in case of Ar_2-OCS from the planar moment P_a , given by $P_a=2m_{Ar}a^2=(1/2)(I_b^0+I_c^0-I_a^0)$. The a_{Ar} values obtained in this manner are ± 1.922 Å, which corresponds to an effective Ar-Ar distance of 3.844 Å. This value is, of course, subject to the vibrational effects in the trimer. Nonetheless, it is consistent with the value of the Ar-Ar distance given earlier for Ar_2-OCS .

Because of the higher symmetry of Ar_2-CO_2 (C_{2v})





 $R_{c.m.}$ connects the centres of mass of the Ar_2 and the CO_2 subunits, respectively. $R_{c.m.}$ and r are coordinates used in determining the structure of Ar_2-CO_2 .

compared to Ar_2 -OCS (C_s), the R_{c.m.} can be simply calculated with either $I_{aa} = \mu R_{c.m.}^2 + I(CO_2)$, using the known value of $I(CO_2)$ from free CO_2 , or $I_{cc} = \mu R_{c.m.}^2 + I(Ar_2)$, using the $I(Ar_2)$ from the value of a_{Ar} derived earlier. The result from these two procedures yields values for $R_{c.m.}$ of 2.923 Å and 2.936 Å respectively, which in turn give the Ar-C distance as 3.498 Å and 3.509 Å. It is important to note that all three rotational constants are affected by the large amplitudes of the van der Waals vibrational motions, and that the structures calculated using different procedures will therefore differ. The r structure obtained for Ar_2 -CO₂ using the second procedure is listed in Table 7.7. The structural parameters of Ar-CO₂, as well as those of the Ar, dimer are also given in Table 7.7. Fig.7.3 shows the structure of Ar₂-CO₂ in its principal inertial axis system.

7.6 Harmonic Force Field Approximation

A. Ar₂-OCS

There is a significant fluctuation in the corresponding centrifugal distortion constants for the three isotopomers, as is shown in Table 7.4. A similar phenomenon observed in the earlier study of various isotopomers of Ar-OCS [14] turned out to be mainly mass and geometry dependent. A harmonic force field analysis would certainly help to rationalize these fluctuations and to confirm the assignments. At the same time, it would also provide force constants for the van der Waals modes in the trimer, giving some insight into the nature of the van der Waals interactions.

In principle, information about the force constants of Ar_2 -OCS can be obtained from an analysis of the centrifugal distortion constants of the complex. Such an analysis has been done for the Ar-OCS dimer [14]. Force constants are related to the asymmetric-top τ 's by the Eq.(2.22) in Chapter 2 [see also Ref.21]:

$$\tau_{\alpha\beta\gamma\delta} = -\frac{A\Delta}{I_{\beta\beta}I_{\gamma\gamma}} 2h \times 10^{17} \sum_{i,j} (J_{\alpha\beta}^{(i)})_o (f^{-1})_{ij} (J_{\gamma\delta}^{(j)})_o \qquad (2.22)$$

The variables are the same as defined before. The τ 's are related to the asymmetric-top distortion constants in Table 7.4 by the well-known equations in Ref. 22.

The nine vibrational modes of the Ar_2 -OCS complex transform as $6A_1+3A_2$. Those of A_1 symmetry are approximately: the C-O stretch (v_1) , the C-S stretch (v_2) , the in-plane OCS linear bend (v_3) , the symmetric Ar-C-Ar stretch (v_4) , the Ar-Ar stretch (v_5) , and the Ar-Ar "wag" (v_6) where two argon atoms bend towards OCS in the same direction; those of A_2 symmetry are: the out-of-plane OCS linear bend (v_7) , the Ar-C-Ar asymmetric stretch (v_8) , and the Ar-Ar "torsion" (v_9) , where two argon atoms bend towards OCS in opposite directions. These modes can be approximately characterized by the symmetry coordinates shown in Table 7.8. Shea *et al.* [23] showed that, in the case of Ar-OCS, the values of the force constants for the van der Waals modes were not significantly altered by neglect of the internal modes of OCS. This insensitivity of van der Waals force constants to the internal modes of the monomers has been confirmed by our previous study of various isotopomers of Ar-OCS [14], where the force constants for OCS were left the same as in the free monomer [24]. The same assumption will be made here.

There is only enough information to fit the five diagonal force constants. Some of the off-diagonal coupling terms, namely those between A1 and A2 modes, are identically zero because of symmetry. In addition, in the absence of three-body contributions to the intermolecular potential, the coupling terms f_{45} and f_{56} should be zero. However, rather than neglecting the remaining intermolecular coupling terms, f_{46} and f_{89} , their values have been estimated from the related Ar-OCS bend-stretch coupling term $f_{r\theta}$ [14]. From the definition of the symmetry coordinates in Table 7.8, and assuming negligible three-body contributions, one would expect both f_{46} and f_{89} to take the value $f_{r\theta}/\sqrt{2}\,,$ with $f_{r\theta} = -0.0015(2) \text{ mdyn rad}^{-1}$ [14]. Inclusion of these cross terms improves the fit to the centrifugal distortion constants. The five diagonal force constants, obtained by

fitting simultaneously to the centrifugal distortion constants of all three isotopomers, are shown in Table 7.8, along with the corresponding vibrational frequencies predicted for the five van der Waals modes. The distortion constants were weighted according to the squares of their standard deviations from the semirigid rotor fits.

The centrifugal distortion constants calculated from the force constants in Table 7.8 are compared with the experimental data in Table 7.9. As one can see from Table 7.9, the set of the force constants reproduces the observed distortion constants rather well, and particularly the observed variations with isotopomer. It has also been noticed that although small changes in the force constants give quite different values for the centrifugal distortion constants, the relative values between different isotopomers are basically the same and are rather insensitive to variations in the force constants. This confirms that the observed variations are mainly mass and geometry dependent as in the case of Ar-OCS [14], and that the assignment is consistent with the assumption of a distorted tetrahedral structure for the trimer.

B. Ar_2-CO_2

Similarly, a harmonic force field estimate was

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performed for Ar_2-CO_2 . There are nine vibrational modes of the Ar_2-CO_2 complex, which transform as $4A_1+A_2+2B_1+2B_2$. Those of A_1 symmetry are: the symmetric O-C-O stretch (v_1) , the CO_2 in-plane linear bend (v_2) , the symmetric Ar-C-Ar stretch (v_3) , and the Ar-Ar stretch (v_4) ; that of A_2 symmetry is the Ar-Ar "torsion" (v_5) , where two argon atoms bend towards CO_2 in opposite directions; those of B_1 symmetry are the O-C-O asymmetric stretch (v_6) , and the Ar-Ar "wag" (v_7) , where two argon atoms bend towards CO_2 in the same direction; those of B_2 symmetry are: the CO_2 out-of-plane linear bend (v_8) and the Ar-C-Arasymmetric stretch (v_9) . These modes can be approximately characterized by the symmetry coordinates shown in Table 7.10.

The force constants of the internal modes of CO_2 are constrained to the values obtained for the free CO_2 monomer [20]. Because of the symmetry, the only possible interaction between the van der Waals modes is f_{34} , the interaction between Ar-C-Ar symmetric stretch and Ar-Ar symmetric stretch. Unfortunately, since there are only five centrifugal distortion constants available, it is impossible to fit all five diagonal force constants and one off-diagonal force constant. Several fits with different combinations of four out of six force constants have been performed to see how the value of each constant and the quality of the fit vary. It was found that the

interaction force constant f_{34} is more than an order of magnitude smaller than other constants and is basically indeterminate. Thus f_{34} was fixed at 0.0 in the further fits, as might be expected if pairwise interactions were predominant. f_{55} and f_{77} are highly correlated and insensitive to the distortion constants. Since these two modes originate from the van der Waals bending motion of $Ar-CO_2$ (f_b=0.009428 mdyn Å⁻¹ [24]), a value of 0.01 mdyn $Å^{-1}$ has been used as an initial guess for these two constants. The Ar-C-Ar symmetric stretching constant f_{33} and Ar-C-Ar asymmetric stretching constant f_{99} , vary equally about 5~10% in opposite senses upon different choices, but the mean of f_{33} and f_{99} , which corresponds to the single Ar-C stretch constant, is largely unaffected. The Ar-Ar symmetric stretch force constant, f_{44} , is insensitive to the choices of fitting parameters. As long as the fit converges, the value of f_{44} varies less than 1% around 0.00816 mdyn Å⁻¹. One of the force field fits is shown in table 7.10, along with the comparison of the observed and calculated centrifugal distortion constants from the fit.

7.7 Comments on the Effects of Three-body Interaction and the General Geometric Trends for Ar₂-Molecule Trimers

The geometries of both trimers Ar2-OCS and Ar2-CO2

are found to be dominated by the pairwise additivity. The trimer Ar_2 -OCS has been found to have a distorted tetrahedral geometry, evidently determined mainly by pairwise van der Waals interactions between the two Ar atoms and between each individual Ar atom and OCS, taking these interactions to be comparable to those in the Ar_2 and Ar-OCS dimers. The trimer Ar_2 -CO₂ has a C_{2V} distorted tetrahedral geometry, with its properties also mainly determined by pair interactions between the two argon atoms and between each argon and the CO_2 , which are comparable with those in the Ar_2 and $Ar-CO_2$ dimers.

However, a structural prediction based on the parameters for Ar-OCS and Ar₂ overestimates the rotational constants by 1 to 2 %. A similar phenomenon has also observed for Ar₂-CO₂. This correlates with the increase in Ar-Ar distance in both trimers when compared with Ar₂ (3.821 Å), and might be expected if there were a small induced dipole repulsion [5]. In addition, the Ar-C distance is also greater in Ar₂-OCS than in Ar-OCS, a trend also observed with the Ar-X distance in Ar₂-HX and Ar-HX. A similar lengthening in Ar₂-CO₂ is not obvious, 3.509 Å vs 3.505 Å, comparable to the uncertainty (0.01 Å) in the structural determination.

A comparison of the structures of Ar_2 -OCS and Ar_2 -CO₂ with those of some other Ar_2 -small molecule trimers is given in Table 7.11. It is clear that the general trends for the trimers parallel those of the dimers, namely: Ar_2 -HF, Ar_2 -HCl(semirigid, planar) $\rightarrow Ar_2$ -HCN (highly nonrigid planar) $\rightarrow Ar_2$ -OCS, Ar_2 -CO₂(semirigid, distorted tetrahedral).

The force field analyses allow for some interesting deductions, which must, however, be made cautiously. In particular, some care must be exercised in attributing significance to small changes in the force constants. In carrying out the force field analyses, the r_o geometries used were only approximations to the equilibrium geometries. The harmonic force field for the van der Waals modes is similarly very approximate.

Nevertheless, the derived diagonal force constants for Ar_2 -OCS are reasonable. This is in spite of the neglect in the analysis of two off-diagonal constants, f_{45} and f_{56} , which may be significant, especially the former. It is interesting that $f_{44} \approx f_{88}$, suggesting that the interaction between the two Ar-C stretches is negligible. Similarly, $f_{66} \approx f_{99}$, suggesting that the interaction between the two Ar-OCS bends is likewise negligible. Both observations are consistent with the pairwise additive interaction model.

The constants f_{44} and f_{88} of Ar_2 -OCS, which correspond to the symmetric and asymmetric Ar-C-Ar stretches, respectively, are directly comparable to f_R , the Ar-Cstretch in Ar-OCS, which has the value 0.0222(10) mdyn Å⁻¹ [14]. Both f_{44} and f_{88} are smaller than f_R , suggesting a weakening of the van der Waals interaction on trimer formation, which is the reverse of that observed for Ar_n -HX. Similarly, the bend force constants f_{66} and f_{99} are comparable to $f_{\theta}/2\sim0.0127$ mdyn Å rad⁻², where f_{θ} is the van der Waals bend force constant in Ar-OCS [14]. This time the values are quite similar, suggesting that there is little change in the angular dependence between dimer and trimer.

The Ar-Ar stretch constant, f_{55} , has been found to be 0.008422(20) mdyn Å⁻¹. This value is very comparable to 0.0078 mdyn Å⁻¹, estimated for free Ar₂ from the v=1-0 energy difference from vibronic spectra [7]. It contrasts with the decrease of about 10% found in going from Ar₂ to Ar₂-HF/DF [1] and Ar₂-HCl [2]. In Ar₂-OCS the wavenumbers of the nominal Ar-Ar stretch cover the small range 23.3 to 24.6 cm⁻¹ for the three isotopomers, which is very close to the corresponding values for Ar₂, 25.7 cm⁻¹ [7]. There is, however, a significant contribution of the OCS moiety to the normal mode of the trimer, so this comparison is perhaps not entirely valid.

In the case of Ar_2-CO_2 , there is not enough information to obtain a complete force field. The force field analysis was performed with the goal of checking its consistency with the assumption of pairwise additivity rather than to detect effects of nonpairwise additive contributions. The individual Ar-C stretch constants, calculated using the mean of the symmetric and asymmetric Ar-C-Ar stretch force constants, is 0.01673 mdyn Å⁻¹, similar to that of the Ar-CO₂ dimer 0.01738 mdyn Å⁻¹ [24]. The value of f_{44} is quite reasonable compared with the value 0.0078 mdyn Å⁻¹ for the free Ar₂ dimer. The estimated vibrational frequency of the Ar-Ar stretch is about 23.5 cm⁻¹ in Ar₂-CO₂, which compares favourably with 25.69 cm⁻¹, the experimental value reported for the fundamental vibrational frequency in the free Ar₂ dimer [7].

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| Transition | Observed | Distortion ^a | ObsCalc. |
|---|--------------------|-------------------------|----------|
| ^J K' _{a,} K' _c ^{-J} "K'' _{a,} K'' _c | frequency (MHz) | contribution (MHz) | (kHz) |
| | | | |
| $3_{1,2} - 2_{0,2}$ | 7516.1554 | -0.7324 | -1.0 |
| $3_{2,2} - 2_{1,2}$ | 7708.9044 | -0.6231 | -1.7 |
| $3_{2,1} - 2_{1,1}$ | 7458.8154 | -0.7540 | -1.5 |
| $3_{3,1} - 2_{2,1}$ | 8028.4369 | -0.9705 | -0.6 |
| $3_{3,0} - 2_{2,0}$ | 7901.2192 | -0.9503 | 0.0 |
| $4_{1,3} - 3_{0,3}$ | 10137.6417 | -1.4875 | -0.8 |
| $4_{1,3} - 3_{1,2}$ | 7813.1040 | -0.9793 | 0.2 |
| $4_{2,3} - 3_{1,3}$ | 10193.4432 | -1.3757 | 0.1 |
| $4_{2,2} - 3_{1,2}$ | 9930.3470 | -1.7363 | 0.3 |
| $4_{2,2} - 3_{2,1}$ | 8704.8027 | -1.5570 | -0.6 |
| $4_{2,3} - 3_{2,2}$ | 7632.0945 | -1.0022 | -1.0 |
| $4_{3,1} - 3_{3,0}$ | 8738.9823 | -1.5440 | 1.8 |
| $4_{3,2} - 3_{3,1}$ | 8192.1509 | -1.2107 | -0.8 |
| $4_{3,1} - 3_{2,1}$ | 10031.4064 | -1.7592 | 0.0 |
| $4_{3,2} - 3_{2,2}$ | 10320.3771 | -1.7079 | -0.3 |
| $4_{4,0} - 3_{3,0}$ | 10668.3791 | -2.4749 | 0.5 |
| $4_{4,1} - 3_{3,1}$ | 10747.8599 | -2.5141 | -0.6 |
| $5_{0,5} - 4_{0,4}$ | 8282.9612 | -0.9736 | 0.2 |
| $5_{1,5} - 4_{1,4}$ | 8281.6753 | -0.9799 | -1.0 |
| 5 _{1,4} - 4 _{1,3} | 9308.8645 | -1.6199 | 0.0 |
| $5_{1,4} - 4_{0,4}$ | 12716.3144 | -2.5931 | 1.2 |
| 5 _{2,4} - 4 _{1,4} | 12727.7795 | -2.5382 | -0.8 |
| 5 _{2,3} - 4 _{1,3} | 12568.4400 | -3.2540 | 1.3 |
| 5 _{2,3} - 4 _{2,2} | 10451.1967 | -2.4970 | 0.9 |
| 5 _{2,4} - 4 _{2,3} | 9256.1581 | -1.6940 | 1.3 |
| 5 _{3,2} - 4 _{2,2} | 12373.0635 | -3.3122 | 0.7 |

Table 7.1 Observed transitions of Ar₂-OCS

Table 7.1 (continued)

| Transition ^J K' K' ^{-J} "K" K" | Observed frequency | Distortion ^a contribution | ObsCalc. |
|---|--------------------------|---|----------|
| | (MHZ) | (MHZ) | (KHZ) |
| 5 _{3,3} - 4 _{2,3} | 12739.9605 | -3.0386 | -0.5 |
| $5_{3,2} - 4_{3,1}$ | 11046.4592 | -3.1100 | -0.5 |
| 5 _{3,3} - 4 _{3,2} | 10051.6779 | -2.3329 | -1.2 |
| $5_{4,1} - 4_{3,1}$ | 12692.5764 | -3.5517 | 0.6 |
| 5 _{4,2} - 4 _{3,2} | 12964.4787 | -3.6352 | 1.8 |
| $5_{5,0} - 4_{4,0}$ | 13447.1916 | -5.1738 | 0.7 |
| 5 _{5,1} - 4 _{4,1} | 13485.5450 | -5.1975 | 0.3 |
| 6 _{0,6} - 5 _{0,5} | 9838.7579 | -1.6323 | 0.5 |
| 6 _{1,6} - 5 _{1,5} | 9838.5809 | -1.6340 | 0.3 |
| 6 _{1,5} - 5 _{1,4} | 10840.7131 | -2.5616 | 0.3 |
| 6 _{1,5} - 5 _{0,5} | 15274.0665 | -4.1811 | 1.4 |
| 6 _{2,4} - 5 _{1,4} | 15197.0802 | -5.1928 | 0.8 |
| 6 _{2,5} - 5 _{1,5} | 15276.0347 | -4.1626 | -0.8 |
| 6 _{2,5} - 5 _{2,4} | 10829.9318 | -2.6043 | 0.3 |
| $6_{3,3} - 5_{2,3}$ | 14945.4885 ^{*b} | -5.7369 | -0.6 |
| $6_{3,4} - 5_{2,4}$ | 15245.1664 | -5.0117 | -1.2 |
| 6 _{3,4} - 5 _{3,3} | 11761.3632 | -3.6671 | -0.2 |
| $6_{4,2} - 5_{3,2}$ | 14883.3312 | -5.6715 | 0.4 |
| $6_{4,3} - 5_{3,3}$ | 15307.8218 | -5.5926 | 0.6 |
| 6 _{5,1} - 5 _{4,1} | 15441.4746* | -6.5583 | 3.4 |
| 6 _{5,2} - 5 _{4,2} | 15642.6191* | -6.7208 | 2.2 |
| 6 _{6,0} - 5 _{5,0} | 16217.9809 | -9.3448 | -0.7 |
| 6 _{6,1} - 5 _{5,1} | 16233.8828* | -9.3510 | -2.8 |
| $7_{0,7} - 6_{0,6}$ | 11394.8760 | -2.5282 | 0.3 |
| 7 _{1,6} - 6 _{1,5} | 12390.6382* | -3.7855 | -0.7 |
| 7 _{1,6} - 6 _{0,6} | 17825.9445* | -6.3343 | -2.1 |

| Transition | Observed | Distortion ^a | ObsCalc. |
|-------------------------------------|---------------------|-------------------------|----------|
| J' - J" | frequency | contribution | |
| | (MHz) | (MHz) | (kHz) |
| | | | |
| 7 _{1,7} - 6 _{1,6} | 11394.8526 | -2.5286 | -0.4 |
| 7 _{2,6} - 6 _{2,5} | 12388.7951* | -3.8008 | -0.9 |
| 7 _{2,5} - 6 _{1,5} | 17776.4260* | -7.7083 | -1.3 |
| 7 _{2,6} - 6 _{1,6} | 17826.2502* | -6.3293 | -0.7 |
| $7_{3,4} - 6_{2,4}$ | 17622.6738* | -8.8419 | 0.4 |
| 7 _{3,5} - 6 _{2,5} | 17786.7559* | -7.6255 | -4.1 |
| $7_{4,3} - 6_{3,3}$ | 17323.8361* | -8.9994 | 0.5 |
| $7_{4,4} - 6_{3,4}$ | 17763.7970* | -8.4792 | -3.5 |
| 7 _{5,2} - 6 _{4,2} | 17486.7628 | -9.1096 | -0.9 |
| 7 _{5,3} - 6 _{4,3} | 17907.8822* | -9.3030 | 2.2 |
| 7 _{6,2} - 6 _{5,2} | 18350.5324* | -11.3140 | -1.3 |
| $8_{0,8} - 7_{0,7}$ | 12950.8181* | -3.6985 | -3.2 |
| $8_{1,8} - 7_{1,7}$ | 12950.8181* | -3.6985 | -0.4 |
| $4_{1,4} - 4_{0,4}$ | 1.485 ^{†°} | 0.008 | -2.0 |
| 6 _{2,5} - 6 _{1,5} | 2.173 | 0.021 | 0.0 |
| 8 _{3,6} - 8 _{2,6} | 2.233+ | 0.033 | -3.0 |
| $5_{5,0} - 5_{5,1}$ | 25.237 | 0.005 | 1.0 |
| $6_{5,1} - 6_{5,2}$ | 216.855 | -0.145 | -4.0 |
| | | | |

- ^a This is the fourth-degree centrifugal distortion contribution calculated from the constants of Table 7.4.
- ^b All frequencies indicated with * were measured with a perpendicular nozzle arrangement at Oxford by Connelly and Howard, with an accuracy of ~±4 kHz as compared to ~±1 kHz for the remainder.
- ^c All frequencies indicated with † were MBER measurements in ref.13 and were not included in the fit.

Measured Line Frequencies of Substituted Isotopomers of Ar_2 -OCS

| Transition | Observed Frequency Ar ₂ -OC ³⁴ S | obs calc. | Observed Frequency Ar ₂ - ¹⁸ OCS | obs calc. |
|---|--|--------------|--|--------------|
| $J_{K_a,K_c}^{\dagger} - J_{K_a,K_c}^{"}$ | (MHz) | (kHz) | (MHz) | (kHz) |
| | | | | |
| $3_{1,2} - 2_{0,2}$ | 7368.4543 | -0.5 | 7379.4749 | -0.4 |
| $3_{2,1} - 2_{1,1}$ | 7333.1594 | -0.4 | 7330.3773 | 0.3 |
| $3_{2,2} - 2_{1,2}$ | 7607.6196 | -0.9 | 7580.0018 | 0.9 |
| $3_{3,0} - 2_{2,0}$ | 7846.3588 | -1.1 | 7780.1205 | 0.0 |
| $3_{3,1} - 2_{2,1}$ | 7971.6663 | -1.1 | 7902.7897 | -0.9 |
| $4_{1,3} - 3_{0,3}$ | 9958.3463 | -0.4 | 9957.3371 | -0.4 |
| $4_{1,3} - 3_{1,2}$ | 7711.1272 | 0.2 | 7733.7695 | 0.0 |
| $4_{2,2} - 3_{1,2}$ | 9729.8940 | 0.1 | 9749.5700 | -0.0 |
| $4_{2,2} - 3_{2,1}$ | 8521.3158 | 0.3 | 8570.7407 | -0.0 |
| $4_{2,3} - 3_{1,3}$ | 10038.2629 | -0.4 | 10018.2534 | 0.0 |
| $4_{3,1} - 3_{2,1}$ | 9891.7127 | -0.6 | 9865.5555 | -0.4 |
| $4_{3,2} - 3_{2,2}$ | 10197.3571 | -0.6 | 10150.7406 | 0.2 |
| $4_{4,0} - 3_{3,0}$ | 10611.7984 | 0.7 | 10507.9703 | 0.5 |
| $4_{4,1} - 3_{3,1}$ | 10681.9300 | 0.1 | 10581.9255 | 0.1 |
| $5_{0,5} - 4_{0,4}$ | 8163.2458 | 0.3 | | |
| $5_{1,4} - 4_{0,4}$ | 12507.8003 | 0.7 | | |
| $5_{1,4} - 4_{1,3}$ | 9183.7733 | -0.7 | | |
| $5_{1,5} - 4_{1,4}$ | 8161.1506 | 0.1 | | |
| $5_{2,3} - 4_{1,3}$ | 12315.8059 | 1.8 | 12337.7260 | 0.4 |
| $5_{2,4} - 4_{1,4}$ | 12526.7095 | -0.7 | | |

| Table 7.2 (continued) |
|-----------------------|
|-----------------------|

| Transition | Observed Frequency Ar ₂ -OC ³⁴ S | obs calc. | Observed Frequency Ar ₂ - ¹⁸ OCS | obs calc. |
|--------------------------------------|--|--------------|--|--------------|
| $J'_{K'_a,K'_c} - J''_{K''_a,K''_c}$ | (MHz) | (kHz) | (MHz) | (kHz) |
| | | | | |
| 5 _{2,4} - 4 _{2,3} | 9110.8585 | -0.1 | | |
| 5 _{3,3} - 4 _{2,3} | 12551.8326 | 0.5 | 12522.6727 | -0.4 |
| 5 _{3,2} - 4 _{2,2} | 12140.4679 | 0.2 | | |
| 5 _{4,1} - 4 _{3,1} | 12561.6967 | 1.4 | 12493.5511 | -0.4 |
| 5 _{4,2} - 4 _{3,2} | 12828.0263 | 0.9 | 12755.5817 | 0.5 |
| $5_{5,0} - 4_{4,0}$ | 13382.0607 | -1.0 | | |
| $5_{5,1} - 4_{4,1}$ | 13412.3111 | -0.7 | 13279.3742 | -0.2 |
| 6 _{4,3} - 5 _{3,3} | 15096.3750 | 1.2 | | |
| 6 _{4,2} - 5 _{3,2} | 14643.1138 | 2.0 | | |
| 6 _{5,1} - 5 _{4,1} | 15323.9251 | -1.9 | | |
| 6 _{3,3} - 5 _{2,3} | 14625.9306 | -0.3 | | |
| 6 _{2,5} - 5 _{1,5} | 15034.1204 | 0.7 | | |
| 6 _{1,5} - 5 _{0,5} | 15030.4000 | -0.7 | | |
| $6_{2,4} - 5_{1,4}$ | 14923.6413 | -1.1 | | |
| 6 _{6,0} - 5 _{5,0} | 16141.9729 | 0.5 | | |
| 6 _{6,1} - 5 _{5,1} | 16153.2541 | 1.3 | | |
| 6 _{3,4} - 5 _{2,4} | 15001.0768 | 1.3 | | |
| | | | | |

| Transition J¦,K; ⁻ J"K",K; | Observed frequency (MHz) | Obs Calc. (kHz) |
|--|--------------------------------|-----------------------|
| $2_{2,0} - 1_{1,1}$ | 7182.2833 | -0.3 |
| $3_{3,1} - 2_{2,0}$ | 9879.5340 | 0.1 |
| $3_{1,3} - 2_{0,2}$ | 6351.0264 | 0.5 |
| $3_{2,2} - 2_{1,1}$ | 8115.4690 | -0.5 |
| $4_{4,0} - 3_{3,1}$ | 13818.4074 | 0.3 |
| $4_{2,2} - 3_{3,1}$ | 9327.4863 | 0.0 |
| $4_{2,2} - 3_{1,3}$ | 15800.2512 | -0.0 |
| $4_{0,4} - 3_{1,3}$ | 8171.3919 | 0.2 |
| $4_{3,1} - 3_{2,2}$ | 14094.8706 | 0.4 |
| $4_{1,3} - 3_{2,2}$ | 9340.0529 | -1.1 |
| $5_{5,1} - 4_{4,0}$ | 17144.5090 | 0.4 |
| $5_{3,3} - 4_{2,2}$ | 13371.3746 | 1.8 |
| 5 _{1,5} - 4 _{0,4} | 10052.2285 | -0.1 |
| 5 _{4,2} - 4 _{3,1} | 15560.6216 | -2.0 |
| $5_{2,4} - 4_{1,3}$ | 11485.8343 | 0.4 |
| 6 _{2,4} - 5 _{3,3} | 14492.2462 | 0.0 |
| 6 _{0,6} - 5 _{1,5} | 11922.7823 | -0.2 |
| 6 _{3,3} - 5 _{4,2} | 14624.3221 | -0.0 |
| 6 _{1,5} - 5 _{2,4} | 13288.1001 | -0.2 |
| 7 _{1,7} - 6 _{0,6} | 13794.5770 | 0.1 |
| 7 _{2,6} - 6 _{1,5} | 15169.2508 | -0.0 |

Table 7.3 Observed transitions of Ar_2-CO_2

| Pareme | ter Ar ₂ - ¹⁶ 0 ¹² C ³² S | $Ar_2 - {}^{16}O^{12}C^{34}S$ | $Ar_2 - {}^{18}O^{12}C^{32}S$ |
|-----------------------------|---|--------------------------------------|-------------------------------|
| <u>Rotat</u> | <u>ional constants /</u> | <u>MHz</u> ª | |
| A _o | 1381.53375(09) | 1376.89177(14) | 1360.66909(13) |
| B _o | 1188.30931(08) | 1159.18449(14) | 1166.19528(15) |
| C _o | 778.58576(06) | 767.39568(20) | 775.67736(42) |
| <u>Centr</u> | ifugal distortion | <u>constants /kHzª</u> | |
| Δ _J | 9.8113(14) | 9.5797(16) | 9.2427(21) |
| Δ_{JK} | -18.1894(66) | -17.7630(75) | -16.917(11) |
| Δ_{κ} | 9.8837(56) | 9.6613(82) | 9.252(42) |
| δ _၂ | 1.7345(08) | 1.7715(11) | 1.6470(16) |
| δ _κ | -15.310(10) | -13.219(11) | -14.588(13) |
| Inerti | al defect and p | <u>lanar moment P_b /a</u> | umu Å ² |
| ۵ _° ⊳ | -142.00388 | -144.45765 | -153.24408 |
| P _b ^b | 294.80816 | 294.81455 | 294.79743 |
| <u>Standa</u> | ard deviation of 1 | the fit /kHz | |
| | 1.0 | 1.0 | 0.5 |

^a III^r representation, A-reduction.

^b $\Delta_{o} = I_{c}^{o} - I_{a}^{o} - I_{b}^{o}; P_{b} = (I_{a}^{o} + I_{c}^{o} - I_{b}^{o})/2; I_{b}^{o}(amuÅ) = 505379/B_{o}$ (MHz),etc.

Spectroscopic Constants of $Ar_2-CO_2^{a}$

Rotational Constants

| A | (MHz)° | 1768.75772(18) |
|---|--------------------|----------------|
| в | (MHz) _o | 1502.63155(17) |
| С | (MHz) _o | 936.57347(20) |

Quartic Distortion Constants

| Δ _J | (kHz) | 18.9904(43) |
|-----------------|-------|-------------|
| Δ _{JK} | (kHz) | -40.019(20) |
| Δ _κ | (kHz) | 23.378(23) |
| δ _j | (kHz) | 0.2672(20) |
| δ _κ | (kHz) | -34.538(21) |

Sextic Distortion Constants

| Н _{ЈК} | (Hz) | -5.71(86) |
|-----------------|------|-----------|
| | | |

- H_{KJ} (Hz) 15.1(18)
- H_K (Hz) -9.47(99)

Standard Deviation of the Fit

 σ (kHz) 1.0

^a III^r representation, A-reduction.

| Ar ₂ -OCS | Ar-OCS | Ar ₂ |
|-------------------------|-------------------------|-----------------|
| | | |
| 1.1561(12) ^b | 1.1561(12) ^b | - |
| 1.5651(9) ^b | 1.5651(9) ^b | - |

Table 7.6 Structural parameters of Ar,-OCS, Ar-OCS and Ar,

| r | 3.8412(6) | - | 3.821(10) |
|--------------------|--------------------|--------------------|-----------|
| R ^c .m. | 3.1597(3) | - | - |
| θ° | 109.81(8) | - | - |
| | | | |
| r(Ar-c.m.of OCS) | 3.698 ^e | 3.651 ^f | - |
| r(Ar-C) | 3.581 ^e | 3.579 ^f | - |
| r(Ar-0) | 3.591 ^e | 3.652 ^f | - |
| ∆(Ar-c.m.of OCS-C) | 73.2 ^e | 73.6 ^f | - |
| | | | |

^a Bond lengths in Å; bond angles in degrees (°).

- ^b Fit to B_o values of various isotopomers of OCS reported in ref.19.
- ^c Fit parameters for Ar₂-OCS as described in the text; uncertainties are one standard deviation in units of the last quoted digits.

parameter^a

r(CO)

r(CS)

- e Structural parameters calculated from R $_{c.m}$ and $\boldsymbol{\theta}.$
- $^{\rm f}$ Fitted to $\rm A_{_{0}},~B_{_{0}}$ and C_ values of various isotopomers of Ar-OCS (except $^{17}\rm O)$ in ref.14.

^d Ref. 7.

| Та | b | 1 | е | 7 | • | 7 |
|----|---|---|---|---|---|---|
| | | | | | | |

Structural parameters of Ar_2-CO_2 , $Ar-CO_2$ and Ar_2

| Parameter ^a | Ar ₂ -CO ₂ | Ar-CO ₂ | Ar ₂ |
|------------------------|----------------------------------|------------------------|------------------------|
| r(CO) | 1.1632 ^b | 1.1632 ^b | - |
| r ^c | 3.843 | - | 3.821(10) ^d |
| | | | |
| R ^c .m. | 2.935 | - | - |
| r(Ar-C) | 3.509 | 3.5048(1) ^e | - |

- ^a Bond lengths in Å.
- ^b Ref.20.
- $^{\rm c}$ R_{c.m.} connects the center of mass of the Ar₂ subunit and the C atom of CO₂; r is Ar-Ar distance.
- ^d Ref.7.
- ^e Ref.15.

Structural parameters:

$$r (Ar (1) - Ar (2)) = r = 3.841 \text{ Å}$$

$$r (Ar (1) - C) = r_1 = r (Ar (2) - C) = r_2 = 3.581 \text{ Å}$$

$$r (CO) = r_3 = 1.1561 \text{ Å}$$

$$r (CS) = r_4 = 1.5651 \text{ Å}$$

$$\land (Ar (1) - C - O) = \alpha_1 = \land (Ar (2) - C - O) = \beta_1 = 81.2^{\circ}$$

$$\land (Ar (1) - C - S) = \alpha_2 = \land (Ar (2) - C - S) = \beta_2 = 98.8^{\circ}$$

Symmetry coordinates:

A₁:
$$S_1 = \Delta r_3$$

 $S_2 = \Delta r_4$
 $S_3 = in-plane \ OCS \ linear \ bend$
 $S_4 = (1/2)^{\frac{1}{2}} \ (\Delta r_1 + \Delta r_2)$
 $S_5 = \Delta r$
 $S_6 = (1/2) \ (\Delta \alpha_1 - \Delta \alpha_2 + \Delta \beta_1 - \Delta \beta_2)$
A₂: $S_7 = out-of-plane \ OCS \ linear \ bend$
 $S_8 = (1/2)^{\frac{1}{2}} \ (\Delta r_1 - \Delta r_2)$
 $S_9 = (1/2) \ (\Delta \alpha_1 - \Delta \alpha_2 - \Delta \beta_1 + \Delta \beta_2)$

Harmonic force constants:

| f ₁₁ /mdyn | Å ⁻¹ | 16.14ª |
|-----------------------|---------------------|--------------|
| f ₁₂ /mdyn | Å ⁻¹ | 1.040ª |
| f ₂₂ /mdyn | Å ⁻¹ | 7.443ª |
| f ₃₃ /mdyn | Å rad ⁻² | 0.6513ª |
| f ₄₄ /mdyn | Å-1 | 0.01901(15) |
| f ₅₅ /mdyn | Å-1 | 0.008422(20) |

 f_{46} /mdyn rad⁻¹-0.00110^b f_{66} /mdyn Å rad⁻²0.01127(57) f_{77} /mdyn Å rad⁻²0.6513^a f_{88} /mdyn Å⁻¹0.01933(17) f_{89} /mdyn rad⁻¹-0.00110^b f_{99} /mdyn Å rad⁻²0.01238(15)

<u>Predicted van der Waals vibrational</u> <u>frequencies /cm⁻¹:</u>

| DCS Ar ₂ -0 | C ³⁴ S Ar ₂ | - ¹⁸ 0CS |
|------------------------|--|---|
| .2 43 | 3.1 | 42.4 |
| .5 28 | 3.1 | 27.9 |
| .5 23 | 3.3 | 23.4 |
| .5 34 | .5 | 34.1 |
| .3 19 | .1 | 18.9 |
| | DCS $Ar_2 - 0$.2 43 .5 28 .5 23 .5 34 .3 19 | $\begin{array}{ccccccccccc} & \operatorname{Ar}_2 - \operatorname{OC}^{34} \mathrm{S} & \operatorname{Ar}_2 \\ & & & & & \\ & & & &$ |

^a Constrained at the values of ref. 24.

^b Constrained. See discussion in text.

| Ar ₂ -OCS | | | Ar ₂ -00 | 2 ³⁴ S | Ar ₂ - ¹⁸ 0CS | | |
|----------------------|------------------------|--------------|---------------------|-------------------|-------------------------------------|--------------|--|
| parame | ter Value ^a | Obs Calc. | Value ^a | Obs Calc. | Value ^a | Obs Calc. | |
| <u></u> | | <u></u> | | | <u></u> | | |
| Δ _J | 9.8113(14) | 0.003 | 9.5797(16) | -0.007 | 9.2427(21) | 0.001 | |
| Δ_{JK} | -18.1894(66) | -0.015 | -17.7630(75) | -0.031 | -16.917(11) | -0.036 | |
| Δ _κ | 9.8837(56) | -0.040 | 9.6613(82) | -0.015 | 9.252(42) | 0.092 | |
| δ _j | 1.7345(08) | -0.001 | 1.7715(11) | 0.001 | 1.6470(16) | -0.003 | |
| δ _κ | -15.310(10) | 0.049 | -13.219(11) | -0.118 | -14.588(13) | 0.034 | |

| Table | 7.9 | Compa | arison | of | observ | ved c | entri | ifugal | dis | stortic | on co | onsta | nts | (in | kHz) |
|-------|-----|-------|--------|-----|--------|-------|-------|--------|-----|---------|-------|-------|-----------------|------|------|
| | | with | those | obt | ained | from | the | harmor | nic | force | fiel | ld of | Ar ₂ | -ocs | 1 |

^a The values are those of Table 7.4.

Table 7.10 The harmonic force field of $Ar_2-CO_2^a$

<u>Structural parameters</u>: r(Ar(1) - Ar(2)) = r = 3.843 Å $r(Ar(1) - C) = r_1 = r(Ar(2) - C) = r_2 = 3.509 \text{ Å}$ $r(C - O(1)) = r_3 = r(C - O(2)) = r_4 = 1.1632 \text{ Å}$ $\Delta(Ar(1) - C - O(1)) = \alpha_1 = \Delta(Ar(2) - C - O(1)) = \beta_1 = 90.0^{\circ}$ $\Delta(Ar(1) - C - O(2)) = \alpha_2 = \Delta(Ar(2) - C - O(2)) = \beta_2 = 90.0^{\circ}$

Symmetry coordinates:

Harmonic force constants:

| f ₁₁ | (mdyn Å ⁻¹) | 16.87 ^b |
|-----------------|-----------------------------|--------------------|
| f ₂₂ | (mdyn Å rad ⁻²) | 0.77 ^b |
| f ₃₃ | (mdyn Å ⁻¹) | 0.01726(7) |
| f ₄₄ | (mdyn Å ⁻¹) | 0.00816(2) |
| f ₅₅ | (mdyn Å rad ⁻²) | 0.00985(11) |
| f ₆₆ | (mdyn Å ⁻¹) | 14.2 ^b |
| f ₇₇ | (mdyn Å rad ⁻²) | 0.01 ^c |
| f ₈₈ | (mdyn Å rad ⁻²) | 0.77 ^b |
| f ₉₉ | (mdyn Å ⁻¹) | 0.01619(3) |
Table 7.10 (continued)

| <u>Predicted van der</u> | Waals | <u>vibrational</u> |
|-------------------------------------|-------|--------------------|
| <u>frequencies /cm⁻¹</u> | | |
| Ar ₂ -CO ₂ | | |
| v ₃ 42.3 | | |
| v ₄ 23.5 | | |
| v ₅ 22.6 | | |
| v ₇ 35.9 | | |
| v ₉ 32.7 | | |

<u>Comparison of Observed and Calculated</u> <u>centrifugal distortion constants (kHz):</u>

| | Observed | Calculated | | | | |
|----------------------------|-------------|------------|--|--|--|--|
| Δ _J | 18.9904(43) | 19.001 | | | | |
| $\boldsymbol{\Delta}_{JK}$ | -40.019(20) | -40.002 | | | | |
| Δ _κ | 23.378(23) | 23.388 | | | | |
| δ _J | 0.2672(20) | 0.266 | | | | |
| δ _κ | -34.538(21) | -34.531 | | | | |

- ^a The number of digits quoted in this table do not reflect the uncertainties of the values, see text.
- ^b Constrained at the values of ref. 20.
- ^c See discussion in the text.

| Table 7.11 | Comparison of | f structures | and f | orce | constants | derived | for | the | Ar |
|------------|---------------|---------------------------|---------|-------|------------|---------|-----|-----|----|
| | aı | nd Ar ₂ comple | exes of | f HX(| X=F,Cl,CN) | and OCS | • | | |

| Complex | Structure | bond le Ar-c.m. HX/OCS | ngth(Å) Ar-Ar | force c (×10 ⁻⁵ f(R _{c.m.}) : | constant ^a dyn Å ⁻¹) f(Ar-Ar) | Vibrati Frequen ω(R _{c.m.}) φ | onal ^c cy(cm ⁻¹) o(Ar-Ar) | Reference |
|-----------------------|-----------------|------------------------------|------------------|--|--|---|--|-----------|
| Ar-HF | linear | 3.510 | _ | 1.47 | _ | 43.3 | _ | 9 |
| Ar-DF | linear | 3.461 | - | 1.79 | - | 47.0 | - | 9 |
| Ar-H ³⁵ Cl | linear | 3.980 | - | 1.17 | - | 32.4 | - | 10 |
| Ar-D ³⁵ Cl | linear | 3.967 | - | 1.34 | - | 34.4 | - | 10 |
| Ar-HCN | linear | 4.343 | - | 0.099 | - | 10.2 | - | 11,12 |
| Ar-OCS p | lanar,T-shaped | 3.651 | - | 2.22 ^b | - | 41.4 | - | 14 |
| Ar-OCO p | planar,T-shaped | 3.306 | - | 1.74 | - | 37.5 | - | 15 |
| | | | | | | | | |
| Ar ₂ | linear | - | 3.821 | - | 0.78 | - | 25.69 | 7 |

| Complex | Structure | bond le Ar-c.m HX/OCS | ength(Å) Ar-Ar | force ((×10 ⁻⁵ f(R _{c.m.}) | constant ^a dyn Å ⁻¹) f(Ar-Ar) | Vibrat. Frequer ω(R _{c.m.}) | ional ^c ncy(cm ⁻¹) ω(Ar-Ar) | Reference |
|-------------------------------------|----------------------------|-----------------------------|-------------------|--|--|---|--|-----------|
| | | | | | | | | |
| Ar ₂ -HF | C _{2V} ,T-shaped | 3.541 | 3.825 | 1.86 | 0.66 | 55.3 | 22.3 | 1 |
| Ar ₂ -DF | C _{2v} ,T-shaped | 3.510 | 3.819 | 1.97 | 0.68 | 55.3 | 23.0 | 1 |
| Ar ₂ -H ³⁵ Cl | C _{2v} ,T-shaped | 3.988 | 3.832 | 1.66 | 0.68 | 44.6 | 21.8 | 2,3 |
| Ar ₂ -D ³⁵ Cl | C _{2v} ,T-shaped | 3.970 | 3.828 | - | - | 45.1 | 22.1 | 3 |
| Ar ₂ -HCN | C _{2v} ,T-shaped | 4.16 | 3.850 | - | - | - | - | 4 |
| Ar ₂ -OCS C | _s ,Tetrahedral | 3.698 | 3.841 | 1.90 ^b | 0.84 | 43.2 | 23.5 | This work |
| Ar ₂ -oco c | _{2v} ,Tetrahedral | 3.509 | 3.843 | 1.73 ^b | 0.82 | 42.3 | 23.5 | This work |

Table 7.11 (continued)

- ^a $f(R_{c.m.})$ is the stretch force constant between Ar and HX c.m. in the case of Ar-HX, and it is the symmetric stretch constant of $r_1(Ar(1)-HX c.m.)$ and $r_2(Ar(2)-HX c.m.)$ in the case of Ar₂-HX. f(Ar-Ar) is the stretch force constant between the two Ar atoms.
- ^b $f(R_{c.m.})$ is the stretch force constant between the Ar and C atoms in the case of Ar-OCS; and it is the symmetric stretch constant of Ar-C-Ar in the case of Ar₂-OCS.
- ^c The predicted van der Waals vibrational frequencies corresponding to the van der Waals modes in footnotes a and b.

<u>Appendix</u>

In addition to the work on this thesis, the author has also been involved in other investigations which have resulted in the following publications:

- Yunjie Xu, Wolfgang Jäger, and M.C.L.Gerry, "The rotational spectrum of the isotopically substituted van der Waals complex Ar-OCS, obtained using a pulsed beam microwave Fourier transform spectrometer", J.Mol.Spectrosc. <u>151</u>, 206-216 (1992).
- 2. Yunjie Xu, M.C.L.Gerry, D.L.Joo and D.J.Clouthier, "The microwave spectrum, spin-rotation coupling constants, and structure of thiocarbonyl fluoride, SCF₂, observed with a cavity microwave Fourier transform spectrometer", J.Chem.Phys. <u>97</u>, 3931-3939 (1992).
- 3. Wolfgang Jäger, Yunjie Xu and M.C.L.Gerry, "A microwave spectroscopic investigation of the weakly bound dimer OC-Cl₂", J.Phys.Chem. <u>97</u>, 3685 (1993).
- 4. Yunjie Xu, Wolfgang Jäger, M.C.L.Gerry and Ilona Merke, "The rotational spectrum of bromoacetonitrile, measured with Stark modulated and microwave Fourier transform spectrometers", J.Mol.Spectrosc. <u>160</u>, 258 (1993).
- 5. Wolfgang Jäger, Yunjie Xu, Nils Heineking, and M.C.L.Gerry, "The microwave rotational spectrum of the van der Waals complex Kr-N₂", J.Chem.Phys., 1993 (in press).