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Fourier Transform Microwave Spectroscopy Investigation of the Structure of Neon Cyanocyclobutane

by

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Abstract

Rotational spectrum of the van der Waals complex of Neon Cyanocyclobutane has been observed using pulsed-jet Fourier transform microwave spectroscopy between 5-26 GHz.806 transitions were observed that were associated with the Neon Cyanocyclobutane complex. *Ab Initio* calculations of the complex yielded two structures with rotational constants A=2.881 GHz, B=1.612 GHz, C=1.14GHz for the (a) complex and rotational constants A=2.607GHz, B=1.526 GHz, and C=1.135 GHz for the (b) complex. Though full assignment of the molecule is still work in progress, the current best fit has the rotational constants, A=2.837 GHz, B=1.419 GHz and C=1.1138 GHZ

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Introduction

This thesis investigates the structure of the Neon Cyanocyclobutane van der Waals complex. The Neon Cyanocyclobutane complex is a weakly- bound complex and therefore has an insignificant lifetime at room temperature and pressure, but at very low temperatures (≈5 K) the complex has a longer lifetime. This reduces both the number of collisions per time travelled and the intrinsic thermal energy of the molecule, allowing it to be scanned in a spectrometer. Noble gas- ring molecule complexes have been extensively studied using spectroscopic methods because of the unique nature of the weak van der Waals forces that hold them together.

While it has become clearer that van der Waals and hydrogen bonding forces must be involved in many types of bonds, science has yet to fully explain these forces. In Biology, these forces are critical in biomolecular interactions, from holding DNA strands together, to being an integral part of protein tertiary and quaternary structure.

Away from the physiological functions, the human venture into outer reaches of space has encountered molecules which due to the lack of thermal energy, and the emptiness of space, are able to exist. A replication of those conditions, as is the case in a microwave spectrometer, enables research to be conducted on in an extraterrestrial environment.

The first use of the microwave spectrometer is documented as the microwave investigation of ammonia by Cleeton and Williams in 1934[1]. Since then, various discoveries like that of the pulsed nozzle Fourier Transform Microwave spectrometer

[1] Cleeton, C., Williams, N. H., *Phys.Rev.*, **45,** 234-237 (1934)

by Balle and Flygare[2] and more recently the development of a portable spectrometer by Grabow et al[3] at the National Institute for Standards and Technology, has led much research into weakly-bound molecules. Additionally, the enhancement of quantum calculations by the use of aggregated computer clusters has resulted in more accurate calculations and enabled microwave spectroscopists to take on more complex problems. For this reason, though current spectrometers offer a wide frequency range of approximately 3 to 30 GHz for scanning, this limit and accuracy in instrumentation is continually being enhanced by ongoing innovations.

van der Waals interactions

The weakly bound complex investigated in this experiment is held together by van der Waals forces. The van der Waals force is termed as the net attractive force between two neutral bodies and is expressed as a function of the distance between the two neutral bodies. The weakness of the van der Waals bond causes it to be relatively longer compared to stronger intramolecular bonds; the average van der Waals bond distance is ≈3 Å.

Types of van der Waals

Van der Waals forces are classified according to how they arise in a neutral molecule:

- **London dispersion forces** arise as a result of temporary induced dipoles. Temporary dipoles are possible because electrons are in constant flux. As electrons

[2] Balle T. J., Flygare W H, *Rev. Sci. Instrum,* **52,** 33-45,**(**1981)
[3] Grabow, J., Suenram, R., Zuban, A., Leonov, I. , *Rev. Sci. Instrum.,* **70**, 2127-2135, (1999)

move randomly in a molecule or atom, they can induce an opposite charge in a non polar molecule which is close enough. A significant aggregation of ordered but fluctuating induced dipoles, leads to the formation of a weak van der Waals bond. The involved potential energy is called the London dispersion energy. This energy is a function of *r*, the separation between the radii of the particles, and tends as $1/r^6$,

$$V = -\frac{3}{2}\frac{\alpha_1\alpha_2}{(4\pi\varepsilon_0)^2}\frac{1}{r^6}\frac{I_1 I_2}{I_1 + I_2}$$ [4]

where *I* is the ionization energy, I = hν, and *v* is the electronic absorption frequency for ionization.

- **Dipole-dipole interactions**, or **Keesom forces**, result from the interaction of permanent dipoles in molecules. A molecule like HCl has a permanent dipole because chlorine is more electronegative than hydrogen. This means in HCl, the negative chloride end will have a significant attraction for the hydrogen end of another molecule. The mathematical description of this force is includes the term for both dipole moments, $\boldsymbol{\mu_1}$ and $\boldsymbol{\mu_2}$, as well as the radius, *r*, separating the two molecules,

$$V = -\frac{2}{3kT}\left(\frac{\mu_1\mu_2}{4\pi\varepsilon_0}\right)^2\frac{1}{r^6}$$ [5]

The function also includes a temperature term, as the interaction of free rotating molecules is dependent upon the thermal energy of the system. Consequently, this weak interaction is significant enough to alter some macroscopic properties of the compound like boiling and melting points.

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[4] Israelachvili J. Intermolecular & Surface Forces, 2nd edition (Academic Press, New York, 1992)

[5] Ibid.

- **Debye forces** result from the interaction of a permanent dipole and a temporary induced dipole in a non polar molecule. The molecular dipole of one molecule perturbs the electronic wave functions of the second molecule, thus interacting with the dipole moment of this molecule. As with the other intermolecular forces other, the Debye force varies with respect to $1/r^6$,

$$V = -\frac{\mu^2 \alpha}{(4\pi\varepsilon_0)^2} \frac{1}{r^6}$$ [6]

Overall, the strength of a van der Waals force is directly proportional to the dipole moment strength in a Debye or Keesom interaction. A stronger permanent dipole moment in either particle results in stronger interactions between the molecules. Polarizability of the molecule also influences the strength of a van der Waals interaction. These property of the atom is intrinsic, and measure the ability of the electrons to move within the molecule in response to an electric field due to , in term, to net external influence.

The Lennard –Jonnes description of the intermolecular forces empirically describes the attractive van der Waals forces. This potential describes the intermolecular potential energy as a collection of the short range repulsions, V_{rep}, and the long range attractive forces that have been discussed above. The equation

$$V = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$ [7]

[6] Ibid.
[7] Ibid.

represents this energy, where ε, is the depth of the potential minimum, and σ, is the intermolecular distance at which v=0.

The graph below describes this relationship,

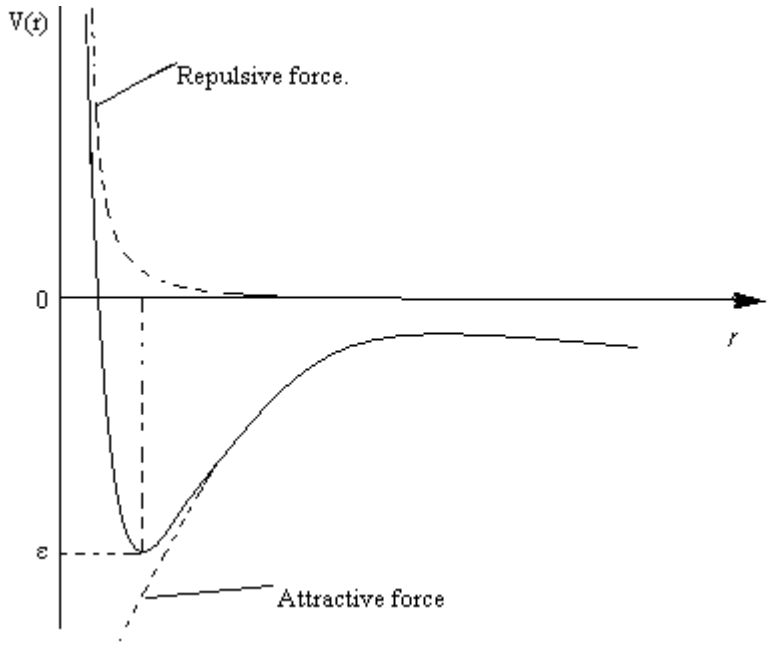


Figure 1: The Lennard Jones potential of intermolecular forces

Cyanocyclobutane

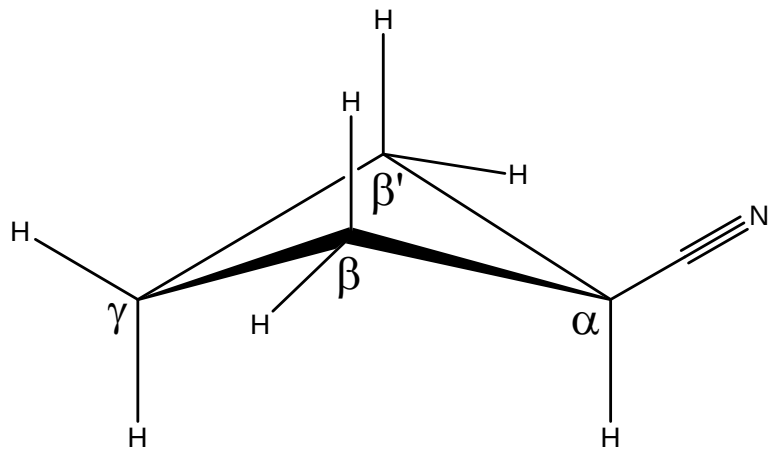


Figure 2: Cyanocyclobutane Monomer

Cyanocyclobutane is a four-membered carbon ring molecule with an attached cyanide group. The molecule has a strong dipole moment ≈4.11 Debye[8] due to the interaction of the more electronegative nitrogen with carbon in the cyano group. This dipole moment is distributed according to the symmetry of the molecule; the main dipole is the μ_a-dipole that runs from the nitrogen to the carbon in the cyano group and experimentally measured to be 4.00D, the other dipole in the molecule is μ_c, which is empirically determined to be 0.95 D. By symmetry, μ_b has to be 0D. This dipole is comparable to other cyano compounds like methyl cyanide (3.94 D)[9] and ethyl cyanide (4.02 D)[10].

The highly electronegative nitrogen in the cyano group means the electron density around the carbon is strongly drawn to the nitrogen center resulting in a strong dipole moment pointing away from the ring. The distribution of the dipole moments in the molecule is quite uneven, and it is evident that μ_b, and μ_c are close

[8] Harmony, M.D., Fong, M.Y., *J.Chem.Phys.* **58,** (1973)
[9] Ghosh, S.N., Trambarulo, R., Gordy, W., *J. Chem. Phys.* **21** (1953),
[10] Laurie, V.W., *J. Chem. Phys,* **31** (1959)

(0.95D and 0D respectively) but, both quite different from μ_a(4.02D).

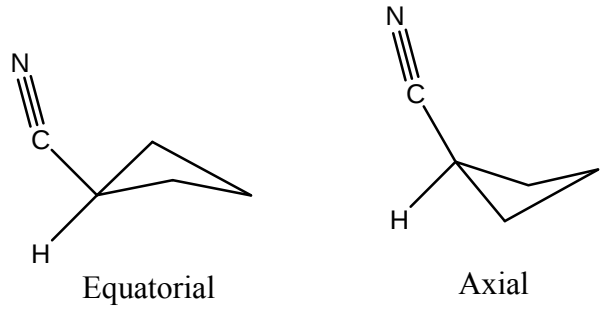


Figure 3: Equatorial and Axial forms of Cyanocyclobutane

Carreira et al[11] conducted far infrared studies that showed that a single substituent in the cyclobutane ring leads to conformational isomers and introduces asymmetry into the potential function of ring inversion. As the ring inverts, the substituent goes from the axial to the equatorial conformation and vice versa. Far-infrared spectroscopy studies of the cyanocyclobutane molecule by Blackwell et al[12] showed the evidence of ring puckering motion in the molecule, and microwave studies by Caminati et al[13] showed that the molecule had a single minimum in the potential energy surface of ring puckering equivalent to the equatorial configuration. Caminati et al[14] showed that this conformation was ≈300 cm^{-1} more stable than the axial form of the molecule and additionally, observed two smaller motions in the molecule, the in-plane and out-of plane bending of the cyano group.

[11] Durig R.J, Carreira L.A, *J. Mol. Chem.,* **46,** (1973)
[12] C.S. Blackwell, L.A. Carrejra, J.R. Durig, J.M. Karriker and R.C. Lord. *J. Chem. Phys.* **56** (1972), p. 1706
[13] Caminati W., Biagio V., Della Valle, D. R., J mol Spec. 129 (1988)
[14] Ibid.

Harmony et al[15] observed a near–prolate assymetric rotor rotational spectrum with a fast second order stark effect. In this study, the hyperfine splitting structure due to the nuclear quadropole coupling of ^{14}N was observed and structures assigned.

Rotational spectroscopy

Rotational spectroscopy is the investigation of interaction of radiation with rotating molecules. In explaining the behavior of rotating molecules, the classical thinking of rotating bodies can also be employed to think of quantum mechanical molecules. The first parameter that enables the rotation of a molecule is its moment of inertia. The moment of inertia *I*, for a diatomic molecule is given by

$$I = \mu r^2$$

where μ is the reduced mass of the system. The angular momentum for any particle rotating in space will be a combination of the moment of inertia and angular velocity vectors in all directions, and thus:

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{xy} & I_{yy} & I_{yz} \\ I_{xy} & I_{yz} & I_{zz} \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}$$

The matrix *I* is known as the moment of inertia tensor. It represents the addition of masses *m* at some distance *r* relative to the origin, which is the center of mass of the molecule.

A convenient set of axes is the principal axis system which has its axis oriented so that the off diagonal of the moment of inertia tensor, *I*, are zero. Molecular parameters in this system are therefore much easier to define, especially in a rotating

[15] Harmony, M.D., Fong, M.Y., *J.Chem.Phys.* **58,** (1973)

body since everything is now considered within the center of mass of the molecule. The principal axis is relatively easy to determine in a molecule that possesses symmetry C_n, such that $n \geq 2$. In this case, it holds that a molecular symmetry axis must coincide with any one of the principal axes, and a molecular symmetry plane, contains two of the principal axes and is perpendicular to the third.

For molecules that lack symmetry, the principal moments of inertia are harder to determine. The first step is expression of all the moments of inertia relative to the center of mass of the molecule, but arbitrarily oriented axes. This yields the moment of inertia tensor, *I*,

$$\begin{pmatrix} \sum m_i(y^2{}_i + z^2{}_i) & -\sum_i m_i x_i y_i & -\sum_i m_i x_i z_i \\ -\sum_i m_i y_i x_i & \sum m_i(x^2{}_i + z^2{}_i) & -\sum_i m_i y_i z_i \\ -\sum_i m_i z_i x_i & -\sum_i m_i z_i y_i & \sum m_i(x^2{}_i + y^2{}_i) \end{pmatrix}$$

The diagonal of the matrix represent the moments of inertia of the molecule,

$$I_{xx} = \sum m_i(y^2{}_i + z^2{}_i) = \sum m_i r^2{}_x$$

$$I_{yy} = \sum m_i(x^2{}_i + z^2{}_i) = \sum m_i r^2{}_y$$

$$I_{zz} = \sum m_i(x^2{}_i + y^2{}_i) = \sum m_i r^2{}_z$$

The off-diagonal elements of the molecule represent the products of inertia. Since the moment of inertia tensor is a symmetric matrix, there exists an orthogonal transformation matrix that transforms the said matrix into a diagonal form,

$$\begin{pmatrix} I_{xx} & 0 & 0 \\ 0 & I_{yy} & 0 \\ 0 & 0 & I_{zz} \end{pmatrix}$$

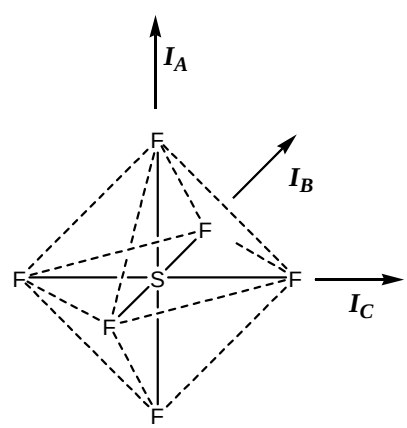
The matrix represents the principal axes, and the axes denoted I_A, I_B, and I_C in order of decreasing size, i.e.

$$I_A \leq I_B \leq I_C$$

<u>Molecules are classified according to their relative moments of inertia</u>

The distribution of the principal moments of inertia highly describes the rotational spectrum observed for the molecule. As a result spectroscopy has classified molecules according to their moments of inertia,

- A spherical top is molecule whose all three moments of inertia are the same. As a result there is no net dipole moment and as shall be discussed later, this means it is impossible to obtain a pure rotational spectrum from a spherical top molecule,



<u>Figure 4: A Spherical Top, I_A=I_B=I_C (SF_6)</u>

- A symmetric top molecule has two moments of inertia I_A and I_B or I_C and I_B equal. Hence, a linear molecular is a special case of the symmetric rotor since its two largest

moments of inertia I_B and I_C are equal. There are two types of symmetric tops; a prolate symmetric top is shaped like a cigar, and the $I_A < I_B = I_C$ for instance, NH_3. The other is the oblate top, disk shaped and have the $I_A = I_B < I_C$.

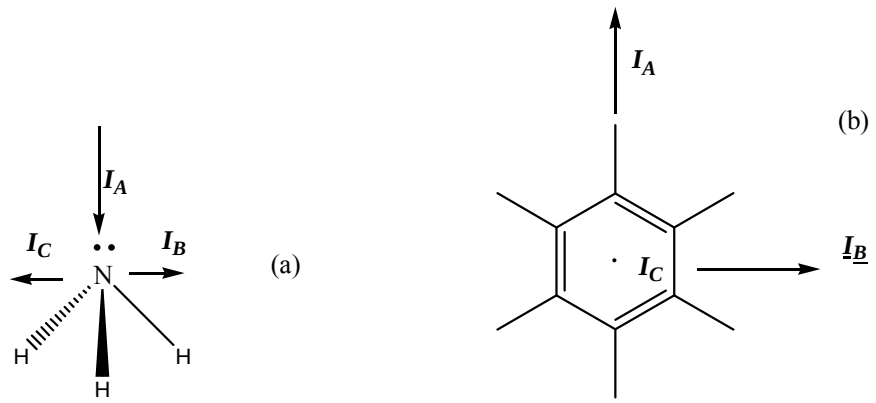


Figure 5:(a) Prolate top $I_A < I_B = I_C$ (NH_3) and, (b) Oblate $I_A = I_B < I_C$ (Benzene)

- By far the most common molecules are those with $I_A \neq I_B \neq I_c$. These are known as asymmetric molecules. The molecule investigated in this experiment, Cyanocyclobutane, is an asymmetric top molecule.

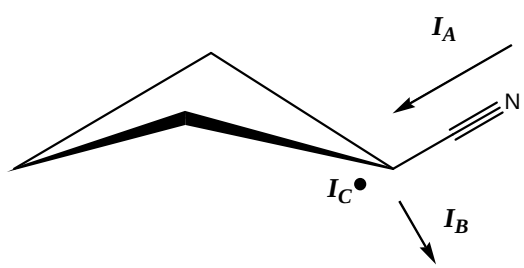


Figure 6: Assymetric top $I_A \neq I_B \neq I_C$ (Cyanocyclobutane)

A rotating molecule possesses kinetic energy associated with the moment of inertia, I, of the molecule and its angular velocity, ω,

$$E = \frac{1}{2} I \omega^2$$

Having described the moment of inertia, it is now possible to describe the energy of the molecule from its rotation. The energy possessed by any molecule is quantized, and the energy levels described by the time independent Schrodinger equation,

$$E\Psi = \hat{H}\Psi$$

where E, is the energy of the quantum system, H is the Hamiltonian operator, and Ψ(x, y, z) is a wave function that describes the time independent properties of the rotating molecule. The change in state of particle that arises from spectroscopic transitions, cannot be described by the time independent Schrodinger equation instead, the time dependent Schrodinger equation is employed,

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

The simplest case of a rotating body can be considered as two atoms in a diatomic molecule held together by an imaginary rigid bar, the rigid rotor. The frequencies of the rotation of the molecule can be defined by the classical mechanical treatment. To determine the energy, the classical interpretation is that of body rotating about its center of mass.

The classical parameters can now be converted to the quantum mechanical equivalents to yield an expression for the kinetic energy of the molecule, quantum mechanically, by first introducing the classical angular momentum, P, into the equation,

$$E = \frac{1}{2} \frac{P^2}{I}$$

and then substituting P for the operator ***ħJ,*** the energy expression replaced by the Hamiltonian operator gives,

$$H = (\hbar^2 / 2I)J^2$$

The energy states allowed for any transitions are obtained by solving the eigenvalue and the eigenfunction equations (in units of ħ) such that the operator J^2 satisfies the equation,

$$J^2\Psi_{JM} = J(J+1)\Psi_{JM}$$

Where *J*, is the rotational angular momentum number and can be any integer, *J* =0, 1, 2 …

Therefore, the energy of the rotating body is given by,

$$E = (\hbar^2 / 2I)J(J+1)$$

From this expression it is evident that the rotational energy levels depend inversely on the moment of inertia I. The coefficient of the J(J+1) –parameter in the energy level expression governs the difference between energy levels spacing and is known as the rotational constant, B. Mathematically,

$$B = \hbar^2 / 2I$$

B is expressed in wave numbers. Therefore, the common place spectroscopic expression detailing the energy level is using the rotational constants

$E / h = BJ(J+1)$ where J is an integer, J=0,1,2,3….

The results obtained from in the laboratory are computed as rotational constants initially and then 'worked backwards' to yield the moments of inertia and consequently, find the structure of the compound.

Selection rules

The intensity of any pure rotational transition observed, is governed by the transition dipole moment according to the equation

$$M=\int \psi_{J'M'} \mu \psi_{JM} d\tau.$$

Where usually, M^2 represents the intensity of the transition, μ is the dipole operator of the molecule and ψ is the rotational wavefunction. Therefore if the molecule has no overall dipole moment there are no observed transitions. Calculated selection rules on J and M, that shall not be discussed here, dictate that ΔJ=0, ±1 and ΔM=0, ±1.

The dipole moment can be projected to the principal axes of to yield the moment projected in all three axes. The projections of the overall dipole moment determine the type of transitions that are observed:

μ_a- a-type transitions, ΔK_a is Even (0,2,4…), ΔK_c is Odd (1,3,5...)

μ_b- b-type transitions, ΔK_a is Odd (1,3,5…), ΔK_c is Odd (1,3,5…)

μ_c- c-type transitions- ΔK_a is Odd (1,3,5…), ΔK_c is Even (0,2,4…)

Centrifugal Distortion

As the molecule rotates , centrifugal force pulls the molecule away from its center of mass and therefore, the rigid rotor approximation fails. The energy equation can be modified to include this distortion, resulting in an energy-level expression

$$F_v(J) = B_v J(J+1) - D_v[J(J+1)]^2 + \cdots. = [B - DJ(J+1)]J(J+1)$$

The parameter D, is called the *centrifugal distortion constant*. To get more accurate approximations of the structure additional distortion terms could be added to the equations

$$F(J) = BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3 + L[J(J+1)]^4 + M[J(J+1)]^5 + \cdots.$$

The rotational constant also depends on the vibration and electronic state. For a diatomic molecule, the average internuclear separation increases with increase in angular velocity according to due to the centrifugal interactions discussed above. Therefore, the rotational constant decreases because it is indirectly proportional to the internuclear separation, r, by

$$B_v = \frac{h^2}{8\pi^2\mu}\left\langle \frac{1}{r^2} \right\rangle$$

As a result the rotation energy levels also become dependent on v,

$$F_v(J) = B_v J(J+1) - D_v[J(J+1)]^2 + \cdots.$$

These constants must be accounted for when totaling the overall energy of the molecule.

<u>Hyperfine splitting</u>

Hyperfine splitting refers to spectra that arise due to small shifts in the energy levels of the molecule being investigated. Any atom that has a nuclear spin, I, greater than ½ possesses a non-spherical charge distribution around the nucleus. This gives the molecule a nuclear quadrupole moment. Consequently, the consideration of the nucleus as a point charge, which is considered when accounting for the regular distribution of energy levels, fails.

The magnitude of the charge deformation, Q, is given by,

$$eQ = \int \rho r^2 (3\cos^2\theta - 1) d\tau$$

where *e*, is the charge on the proton, ρ is the charge density in a volume element dτ at a distance *r*, from the center of the nucleus and making an angle *θ*, to the nuclear spin quantization axis.

The sign of Q indicates the shape of the deformation. Negative Q is due to the nucleus being flattened along the spin axis, while a positive Q results an elongated nucleus giving positive Q. An asymmetric charge distribution around the nucleus causes an asymmetric electric field at the nucleus, characterized by a tensor quantity called the Electric Field Gradient (EFG) ∇E. The electric quadrupole interaction between these two quantities gives rise to a splitting in the nuclear energy levels. The Hamiltonian expresses the interaction between the nuclear moment and the EFG,

$$H_{Eq} = -\frac{1}{6} eQ\nabla E$$

The rotational spectrum as a result of a hyperfine structure splits the total angular momentum quantum number *j,* into hyperfine structure components with F*,* the hyperfine component of values, $J + I, J + I - 1, \ldots J - I$, and the degeneracy of such a level is given by $2J + 1, 2\mathrm{I} + 1$.

Experimental

The microwave spectrometer employed to investigate the structure of Neon Cyanocylobutane was the Southern New England Microwave Consortium-owned pulsed nozzle microwave spectrometer. The spectrometer is made of two highly polished spherical mirrors in a vacuum chamber referred to as Fabry-Perot cavity, a supersonic nozzle located at the center of one of the mirrors, a microwave source, a diffusion pump to evacuate the chamber, and an antenna on the opposite side of the nozzle to introduce the microwave signal into the cavity.

The spherical mirrors are 35.6 cm in diameter and have a radius of curvature of 84cm. The radius of the mirrors and its radius of curvature determine the lower frequency limit of the spectrometry, by the equation[16],

$$\frac{a^2}{R\lambda} = 1$$

where a is the radius of the mirror, and R is the radius of curvature. By this equation, the lower frequency of the machine used in this experiment is 3 GHz. One of the mirrors is mobile and can move freely within the Fabry-Perot cavity. This allows control of the cavity to support the frequency of the microwave pulse introduced into the cavity, by simply moving the mirror in either direction.

The gas is introduced into the evacuated chamber in the form of pulsed jets from the nozzle located at the center of the mobile spherical mirror. Initially, it was observed that the common practice of preparing a tank of 1% of the monomer in a tank of noble gas, was not effective and produced very few and weak transitions.

[16] Aruman, E., Sagarika, Dev., *J. App. Spec,* **39,** 131-181, 2004

Instead, a U-tube with a few drops of the sample was used and the noble gas, Neon, gently pumped over the Cyanocyclobutane.

A microwave pulse is then introduced into the chamber after a delay of approximately 1ms. The microwaves reflect off the spherical mirrors and generate a standing wave. The interaction of the dipole moments of the rotating molecules, and the oscillating electromagnetic wave of the microwave radiation is at a maximum when the molecules are rotating as the same frequency as the standing wave in the cavity. The molecules absorb this radiation and then emit at a certain frequency. The emitted signal is amplified and detected by the signal detector, which is usually an A to D converter, as a time domain signal. The time domain signal is converted to a frequency dependent signal by Fourier transform calculated on the computer. An example of a peak is shown below,

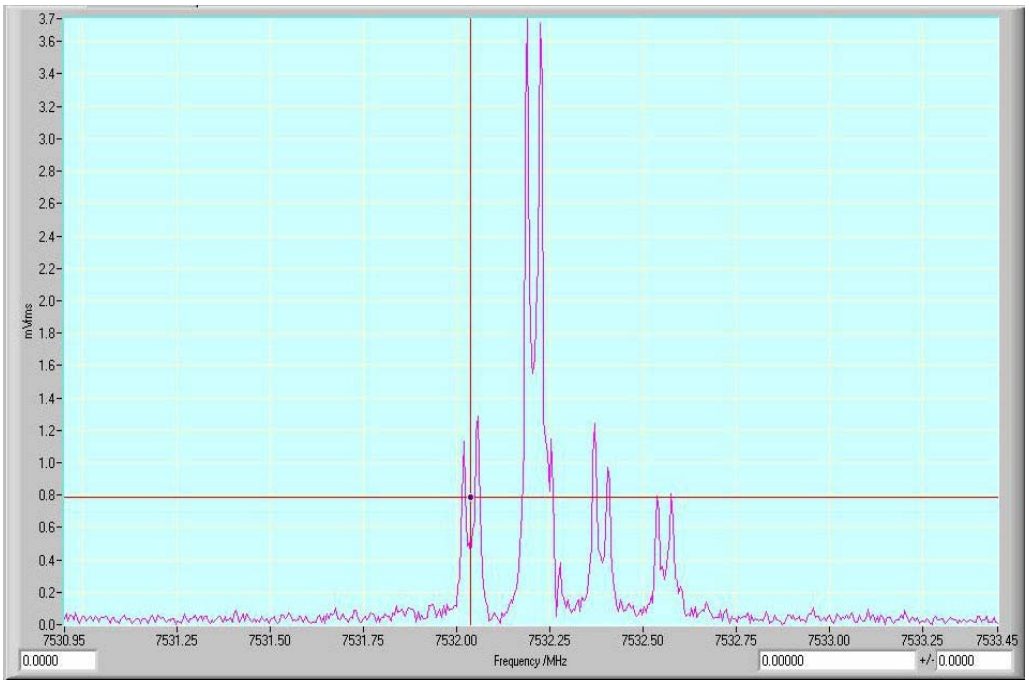


Figure 1. Neon Cyanocyclobutane peak observed at 7532.25 GHz .The observed smaller peaks are due to hyperfine splitting.

It is observed that the peak is seen as a doublet; this is due to the Doppler effect. The Doppler effect refers to the fact that since the microwave pulse is reflected between the two spherical mirrors to create a standing wave, the radiation has the effect of both the parallel and the anti-parallel interaction. The correct frequency is the average of the two peaks observed.

After collection of all the observed frequencies, the next step is to assign these frequencies to the quantum numbers that represent the rotational transitions observed. *Ab initio* calculations were performed and several computer programs used to assign the rotational transitions observed.

Ab initio calculations were performed using the Gaussian 03®[17] molecular determination program created by the Pople group at Carnegie-Mellon in 1970. The calculations were done using an augmented correlation-consistent, polarized double zeta valence-only basis set (Aug CC-pVDZ). The calculation was done to optimize the structure of the molecule.

The program MOMENT was used to project the relative positions of the Neon atoms. This program allows the determination of the rotational constants and the dipole moments of the molecule by inputting hypothetical coordinates of the atoms within the molecule. Therefore, the advantage of this is that the manual shifting of the position of the noble gas atom immediately provides rotational constants of the molecule.

[17] Pople et al

The program JB95[18], written at the National Institute of Standards and Technology, has a user interface that allows observed and simulated frequencies to be viewed on the same pane. The program has a tab that allows the user to change the moments of inertia and the rotational constants of the molecule while observing immediate effects on the predicted frequencies.

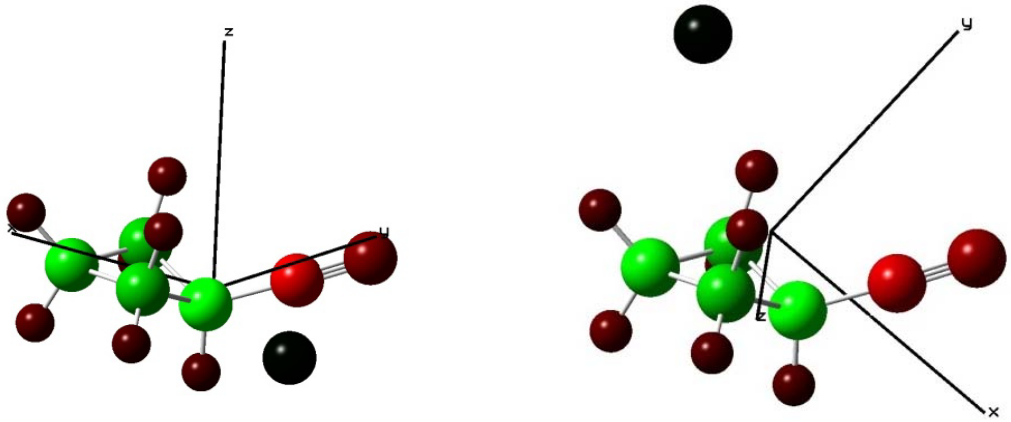
Herb Pickett's group of programs, SPFIT and SPCAT[19] were also invaluably employed to both predict and assign rotational transitions of the observed frequencies. By entering projected rotational constants and the principal dipole moments of a molecule, SPCAT can predict the quantum numbers and the high intensity frequencies expected for the molecule. The observed frequencies can be matched up with the projected frequencies and the SPFIT program iteratively calculates the rotational constants that would match the observed frequencies inputted into the program.

[18] David F. Plusquellic (2002), *User Guide to the* **Jb95** *Spectral Fitting Program*, [Online] http://physics.nist.gov/jb95

[19] H.M.Pickett, *J.Mol.Spectrosc.* **148**,371-377(1991)

Results and Discussion

The cyanocyclobutane monomer has been previously studied, [20]and the rotational constants observed and assigned.[21] The neon cyanocyclobutane complex however, had yet to be studied so this experiment presented a novel area in which to investigate. *Ab initio* results showed that the molecule had two possible position of the Neon atom,



(a) (b)

Legend

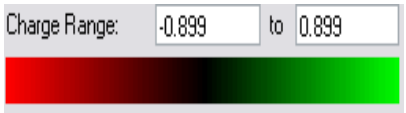


Figure 8: Result of the two *Ab Initio* calculations of Cyanocyclobutane.

[20] Harmony, M.D., Fong, M.Y., *J.Chem.Phys.* **58,** (1973)
[21] Caminati, W., Velino, B., Della Valle, R.G., *J. Mol. Spec.* **129**, 284-292 (1988)

Both calculations were ground state, convergent frequency and optimization methods and were done using the augmented, double zeta basis set. However, the interestingly marked difference in the structure of the complexes was due to the starting position of the Neon atom within the molecule. In (a), the Neon atom was placed under the ring, below the β-carbons of the monomer, while in (b) the Neon atom was placed above the β-carbons of the monomer.

The resulting complexes provided different rotational constants but similar dipole moments,

Complex (a)		Complex (b)	
Rotational constants(GHz)	A=2881.144	Rotational constants(GHz)	A= 2607.245
	B=1612.145		B=1526. 450
	C=1140. 361		C=1135.217
Dipole moment (Debye)	μ= 4.705	Dipole Moment (Debye)	μ= 4.723

Table 1: Ab Initio Rotational constants and Dipole moments.

In a Fourier Transform microwave spectrometer, intensity of the rotational transition is directly proportional to the dipole moment of the molecule. In this case, the strong dipole moment of the cyano group, led to the observations of over 2000 transitions of the molecule. Cyanocyclobutane rotational constants generated from

literature[22] were used to predict the monomer transitions, and eliminate these lines from the experimental spectrum. Additionally, scanning done on the Cyanocyclobutane complex with Argon in the Novick-Pringle lab, yielded the rotational transitions to this complex, which were used to further eliminate non-Neon complex lines. Still due again to the strong dipole moment of the molecule, there were 806 transitions associated with the Neon Cyanoclobutane complex. These lines also showed hyperfine splitting due to the nuclear quadrupole coupling splitting caused by the Nitrogen in the cyano group.

The positions of the neon atom in the ab initio structures of the complex provide an interesting subject of discussion. The behavior of a noble gas in a noble–gas ring compound complex has been postulated to be a function of the dipole moment of the molecule. Earlier experiments conducted in this group including the complexes Argon methylenecyclobutane (Dipole moment ≈ and showed little change in the position of argon with the respective change in the dipole moment of the molecule.[23]

The bulk of the complexes investigated in the group, were usually conducted using Argon as the noble gas; Argon is relatively inexpensive and therefore more commonly used. This experiment therefore provided an opportunity to examine how the lighter Neon (atomic mass=22) versus the heavy Argon (atomic mass=40) would behave in a complex small organic ring compounds. As a result of its smaller size, the neon atom also has a smaller van der Waals radius with the molecule and therefore will probably occupy a different position near the Cyanocyclobutane than does argon

[22] Durig R.J, Carreira L.A, *J. Mol. Chem.,* **46,** (1973)
[23] Pringle, et al Argon Methylcyclopentanone

atom. Furthermore, neon has a lower polarizability than argon and therefore the strength of the van der Waals interaction between the argon atom and the molecule should be stronger than the neon equivalent. This would of course, result in changes in the chemical properties of the molecule. Moreover, common intermolecular motions such a as ring puckering and in and out molecule plane movement of ring substituents in the monomer are also known to be influenced by the nature of the ring structure of noble gas complex. Ring puckering is sometimes quenched[24] with the introduction of a noble gas complex, while sometimes it is also not known to.

The different positions of neon in the complex would result in marked differences in the role of the neon atom in the complex. If the assigned structure is as presented in the structure Figure 8(a) with the neon atom below the β-carbon of the molecule, then the neon atom acts as a Lewis base; it is observed that the Neon atom is closest to the most positive part of the ring. The noble gas is within 3.0 Å van der Waals interaction distance with the cyano carbon and the α-carbon of the ring. Due to the strong pull of electrons by the nitrogen in the cyano group, the two carbon atoms are the most electron deficient atoms in the complex. In this interaction therefore, the electron rich noble gas acts as Lewis base, and stabilizes the complex by this interaction.

However, in the other position denoted in Figure 8 (b), the Neon is closest to the γ-carbon which is at a distance of ≈3.5 Å. With this position, the Neon avoids the most polarized parts of the ring which would be the cyano group and the carbons directly attached to it.

[24] Lin, W., Gayle, J.,Pringle, W., Novick, S. E., *J. Mol. Spec*. **251**, 210-216 (2008)

Apart from the *Ab Initio* calculations, the molecular was attempted to be fit by the programs mentioned above. The first step was the use Pickett SPCAT program to predict the rotational transitions of the structures obtained from the *Ab Initio* calculations. The strongest peaks predicted for the structure (a), were predicted to be the transitions, J=5→J=4, which are displayed below,

Transition	Log Intensity	J'	K_a'	K_c'	F'	J_a''	Ka''	K_c''	F''
11937.71	-2.635	5	0	5	4	4	1	4	3
11937.71	-3.9238	5	0	5	4	4	1	4	4
11937.71	-5.9195	5	0	5	4	4	1	4	5
11937.71	-2.5436	5	0	5	5	4	1	4	4
11937.71	-3.9238	5	0	5	5	4	1	4	5
11937.71	-2.4533	5	0	5	6	4	1	4	5
12179.24	-2.2609	5	0	5	4	4	0	4	3
12179.24	-3.5497	5	0	5	4	4	0	4	4
12179.24	-5.5454	5	0	5	4	4	0	4	5
12179.24	-2.1695	5	0	5	5	4	0	4	4
12179.24	-3.5497	5	0	5	5	4	0	4	5
12179.24	-2.0792	5	0	5	6	4	0	4	5
12049.01	-2.274	5	1	5	4	4	1	4	3
12049.01	-3.5628	5	1	5	4	4	1	4	4
12049.01	-5.5585	5	1	5	4	4	1	4	5
12049.01	-2.1826	5	1	5	5	4	1	4	4
12049.01	-3.5628	5	1	5	5	4	1	4	5

12049.01	-2.0923	5	1	5	6	4	1	4	5

Table 2: J=5→J=4 transitions for Figure 8(a)

The predicted spectrum however, did not match with the observed transitions. The same procedure was again used to predict the spectrum for the structure in Figure 8(b)

Transition	Log Intensity	J'	K_a'	K_c'	F'	J_a''	Ka''	K_c''	F''
12387.87	-3.0472	5	0	5	4	4	0	4	3
12387.87	-4.336	5	0	5	4	4	0	4	4
12387.87	-6.3317	5	0	5	4	4	0	4	5
12387.87	-2.9558	5	0	5	5	4	0	4	4
12387.87	-4.336	5	0	5	5	4	0	4	5
12387.87	-2.8655	5	0	5	6	4	0	4	5
12512.05	-3.3859	5	1	5	4	4	0	4	3
12512.05	-4.6747	5	1	5	4	4	0	4	4
12512.05	-6.6703	5	1	5	4	4	0	4	5
12512.05	-3.2945	5	1	5	5	4	0	4	4
12512.05	-4.6747	5	1	5	5	4	0	4	5
12512.05	-3.2042	5	1	5	6	4	0	4	5
12114.29	-3.4215	5	0	5	4	4	1	4	3
12114.29	-4.7103	5	0	5	4	4	1	4	4
12114.29	-6.706	5	0	5	4	4	1	4	5
12114.29	-3.3301	5	0	5	5	4	1	4	4

12114.29	-4.7103	5	0	5	5	4	1	4	5
12114.29	-3.2398	5	0	5	6	4	1	4	5
12238.47	-3.0618	5	1	5	4	4	1	4	3
12238.47	-4.3506	5	1	5	4	4	1	4	4
12238.47	-6.3462	5	1	5	4	4	1	4	5
12238.47	-2.9703	5	1	5	5	4	1	4	4
12238.47	-4.3506	5	1	5	5	4	1	4	5
12238.47	-2.8801	5	1	5	6	4	1	4	5

Table 3: J=5→J=4 transitions

It should be pointed out that due to the number of transitions observed the molecule is yet to be fully assigned. This is postulated to be due to the presence of significant peaks that are not from the Neon Cyanocyclobutane complex, this could have been due to the use of the U-tube method that was new to the lab could have let more impurities into the cavity. Previous fits observed proved to be quite accurate for local frequencies, within 1.5GHz, but failed as the range was increased. Nevertheless, significant progress was made in fitting the molecule. The best fit, obtained from the SPFIT program is shown below. The transitions included, are 5 of the 10 strongest lines in the observed spectrum and encapsulate a range of 5 GHz. The observed and predicted frequencies and the expected rotational transitions are shown below,

J’	K_a’	K_c’	F’	J’’	K_a’’	K_c’’	F’’	Exp. Freq.	Calc. Freq.	Diff.
3	0	3	3	2	0	2	2	7532.208	7528.100	4.108
3	1	2	2	2	1	1	1	8071.765	8071.123	0.642
3	1	3	3	2	0	2	2	8401.661	8405.346	-3.686

4	0	4	4	3	1	3	3	9009.360	9013.122	-3.762
5	0	5	5	4	0	4	4	12183.500	12181.127	2.373

Table 4: Current best fit

The observed constants for this fit are, A= 2.837 GHz, B=1.419 GHz and C=1138.630 GHz. These constants are closest to those of the first structure, Figure 8(a), deviating by an insignificant value on both the A and C constants, and by 12% from the B constant. The data therefore points to a structure with the neon atom close to the polarized part of the cyanocyclobutane ring and more specifically, to the more positive part of the ring.

Further work will therefore be conducted to complete this assignment and observe the motions of the Neon atom within the molecule. The Argon complex of the monomer is also in the process of being assigned, and this could shed more light into the noble gas-ring complex, especially so because of the strong dipole moment of the cyanocyclobutane monomer. The interaction of either inert gas with the nuclear quadrupole coupling, as compared to the observed negligible interaction observed in Argon Chlorocyclobutane by Subramanian et al[25] is also an area that further work into the molecule aims to ascertain.

[25] R. Subramanian, J.M. Szarko, W.C. Pringle and S.E. Novick, Rotational spectrum, nuclear quadrupole coupling constants, and structure of six isotopomers of the argon-chlorocyclobutane van der Waals complex *J. Mol. Struct.* **742** 165 (2005

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Supplemental Materials

Appendix 1:SPCAT Input files for the Best Fit

Cyanocb23.int

```
112 00001   2596.   0     20    -8.   -8.        14.0    5.0
    2      2.80   / b dipole
    1      3.80   / a dipole
    3      0.00   / c dipole
```

Cyanocb23.var

```
3    5    8    0    0.0000E+000    9.0000E+009    1.0000E+000 1.0000000000
'a'    4    1    0    10   0    1    1    1        0    1    0
          10000  2.836506220671103E+003 2.50901628E-003 / A0
          20000  1.419600874835955E+003 9.98697116E-004 / B0
          30000  1.138680691394983E+003 5.11836067E-004 / C0
-0.9239345-0.1857900-0.8026960-0.3344057-0.5963884 1.0000000
```

Appendix 2:SPFIT Input files for the Best Fit

Cyanocb23.lin

```
 5  0  5  5  4  0  4  4          12183.5006    .005    1.

 3  1  2  2  2  1  1  1           8071.7657    .005    1.

 3  0  3  3  2  0  2  2           7532.2080    .005    1.

 3  1  3  3  2  0  2  2           8401.6610    .005    1.

 4  0  4  4  3  1  3  3           9009.3600    .005    1.
```

Cyanocb23.par

```
 3    5    8    0    0.0000E+000    9.0000E+009    1.0000E+000 1.0000000000

'a'    4    1    0    10   0    1    1    1        0    1    0

          10000  2.836506220671103E+003 2.84951994E-003 / A0

          20000  1.419600874835955E+003 1.13544618E-002 / B0

          30000  1.138680691394983E+003 1.49751019E-003 / C0
```

Appendix 3: Observed Transitions for Neon Cyanocyclobutane and their relative intensities

Frequency	Intensity	Frequency	Intensity	Frequency	Intensity
5139.3599	0.2218	6453.1182	0.166	6909.1805	0.3183
5294.9685	0.1426	6455.6158	0.1748	6988.8248	0.1922
5400.7052	0.1957	6491.685	0.3668	6988.975	0.2035
5636.9267	0.2446	6504.3631	0.1739	7092.3977	0.1731
5716.3475	0.1216	6613.9322	0.1898	7092.6112	0.3152
5743.5008	0.1221	6683.8234	0.3508	7092.7461	0.2308
5775.7826	0.126	6683.8574	0.3107	7092.9297	0.1655
5777.3247	0.1651	6691.2004	0.3271	7147.2955	0.3285
5779.291	0.1384	6691.2018	0.2826	7147.4242	0.177
6133.3253	0.3368	6873.896	0.1532	7147.8017	0.7293
6133.3262	0.2575	6874.0197	0.1375	7147.803	1.1279
6133.3835	0.2096	6874.3622	0.4547	7147.8245	0.1656
6133.8851	0.4908	6874.4491	0.6028	7147.8603	1.0227
6133.8864	1.772	6874.4495	1.0751	7147.8609	2.9726
6133.9981	0.2848	6874.5586	2.0454	7147.8957	0.5276
6134.0019	0.3608	6874.559	0.327	7147.9306	1.8498
6134.0404	0.246	6874.5602	0.3954	7147.9411	0.5978
6134.0489	0.2596	6906.6534	0.2049	7147.9876	2.7701
6134.1163	0.2682	6906.6546	0.879	7147.9882	1.0615
6134.2469	0.3078	6906.6556	0.2085	7148.5663	0.1883
6134.5588	0.6098	6907.2838	0.5587	7150.845	0.1705
6134.5591	1.2571	6907.5912	0.4123	7150.9457	0.2555
6134.5608	0.1675	6907.8803	0.7514	7172.9736	0.1689
6134.7408	0.1628	6907.8806	2.4351	7172.9963	0.2994
6134.7905	0.2646	6907.8807	0.2801	7173.1057	0.1981
6134.9216	0.2019	6909.1463	0.3091	7194.5581	0.1751

Frequency	Intensity	Frequency	Intensity	Frequency	Intensity
7194.5608	0.2389	7319.3963	0.3314	7507.262	0.1774
7194.6888	0.6875	7324.6732	0.2671	7507.2652	0.6769
7212.6647	0.2148	7324.9092	0.5053	7507.3364	0.1841
7222.0	0.1783	7325.4236	0.2639	7507.3397	0.4569
7230.6208	0.2054	7332.422	0.3364	7523.2899	0.2209
7245.7814	0.1393	7354.8639	0.4908	7523.4158	0.1658
7246.3869	0.1599	7354.8641	0.2688	7523.4502	0.3022
7247.8277	0.1417	7364.1274	0.2039	7531.9052	0.1486
7248.7122	0.4244	7364.2975	0.165	7531.9074	0.347
7248.7125	0.5837	7387.081	0.3268	7532.0377	1.6952
7248.8823	0.2485	7387.4495	0.1583	7532.0378	0.2407
7248.8829	1.5431	7387.4515	0.4543	7532.0381	1.2302
7248.883	2.0921	7397.9369	0.194	7532.0384	0.3502
7248.9313	0.5677	7398.2525	0.2712	7532.2071	0.2127
7248.964	1.9199	7399.268	0.2932	7532.2074	1.1743
7248.9998	2.7411	7399.3883	0.2011	7532.2076	3.7998
7249.168	0.2643	7399.9092	0.1587	7532.2079	1.1767
7249.1685	1.8286	7411.1345	0.2239	7532.2082	0.2825
7249.1686	1.9258	7411.3249	0.165	7532.2469	0.3262
7249.3184	0.3289	7411.3559	0.3243	7532.3881	0.3036
7257.2145	0.1552	7417.6246	0.4041	7532.3883	1.1233
7257.4509	0.1677	7472.1176	0.1425	7532.3886	1.698
7296.5624	0.2411	7472.1919	0.1493	7532.5575	0.8106
7296.5636	0.2345	7472.1937	0.2299	7532.5581	0.4194
7316.8752	0.2047	7472.4902	0.1643	7532.5583	1.6142
7317.1111	0.4322	7507.1294	0.3017	7532.5594	3.2584
7317.6238	0.1903	7507.1564	0.2738	7532.7937	0.2133
7317.6923	0.2072	7507.1911	0.3435	7535.5937	0.2646
7319.3949	0.4409	-		7535.7999	0.1566

Frequency	Intensity	Frequency	Intensity	Frequency	Intensity
7535.8004	0.3304	8070.5633	1.7810	8308.5587	1.7447
7558.6892	0.248	8070.5638	0.2586	8308.9927	0.6358
7558.6901	0.2643	8070.5644	0.3553	8308.9928	1.932
7559.1991	0.2958	8071.0463	0.3573	8308.9933	0.4674
7567.4847	0.1877	8071.0465	0.6098	8308.9935	0.2115
7567.7778	0.4832	8071.0466	2.9760	8309.1174	1.0303
7568.2939	0.2416	8071.0863	2.6893	8309.1479	0.2963
7638.189	0.2055	8071.126	0.2293	8309.2908	0.3562
7638.2447	0.2254	8071.1266	1.6661	8309.7262	0.9665
7647.8855	0.2918	8071.1274	0.4035	8309.7268	1.2663
7647.9816	0.2471	8071.1671	0.9554	8309.7269	0.3055
7648.0347	0.4382	8071.2002	0.5184	8309.8509	0.1977
7648.0357	0.2079	8071.2006	0.395	8309.8515	0.9065
7695.048	0.1451	8071.3064	0.2242	8365.1669	0.1717
7695.0497	0.2154	8071.61	3.001	8365.1675	0.2824
7695.111	0.1317	8071.6102	0.1568	8365.1746	1.0381
7695.1327	0.1372	8071.6104	0.5325	8400.4405	0.1893
7796.3837	0.8376	8071.6106	0.5451	8401.0615	0.5736
7796.3853	0.1949	8071.7646	0.4154	8401.0681	1.0188
7823.6025	0.1842	8071.7655	0.678	8401.069	0.1628
7823.6354	1.4542	8071.8686	0.2691	8401.1039	0.349
7823.6357	0.1426	8114.2095	0.8104	8401.104	1.5876
7823.7517	0.9003	8114.2506	0.6139	8401.1119	0.6797
7823.7553	0.4591	8114.4356	1.4418	8401.218	0.9186
7823.7895	0.5509	8114.4382	0.1986	8401.2186	0.2568
7957.6038	0.2014	8114.5953	0.2987	8401.6165	0.69
7957.905	0.2444	8114.5959	0.8057	8401.6165	1.1562
7959.7994	0.1958	8308.2927	1.5421	8401.6168	0.3135
7959.8882	0.1353	8308.5585	0.3622	8401.6608	1.6501

Frequency	Intensity	Frequency	Intensity	Frequency	Intensity
8401.6609	0.4892	8621.3008	0.6739	9003.8126	0.58
8401.6614	0.3803	8621.3019	0.3233	9003.8127	1.3017
8401.7651	0.8173	8621.3044	2.312	9003.8581	0.9561
8401.7654	0.3679	8622.5391	0.6422	9003.8588	0.2429
8551.9422	0.2479	8636.4145	1.1812	9003.8589	0.7615
8575.5839	0.2982	8638.4011	0.2288	9003.9084	1.1655
8575.7937	0.1804	8638.4149	0.3329	9003.9151	0.207
8576.0454	0.2097	8638.4275	0.2535	9003.953	1.556
8576.1061	0.2491	8639.0644	0.3774	9003.9536	0.1758
8603.9212	0.931	8639.065	0.5825	9004.5208	0.1705
8603.9645	0.7814	8639.1519	0.6094	9008.3578	0.227
8603.9738	0.1834	8639.5378	1.554	9008.982	1.8791
8604.007	1.1644	8639.538	0.4104	9009.0123	0.6772
8604.0507	0.8027	8639.5383	0.2718	9009.0254	1.2587
8604.0521	0.1673	8639.5388	1.7156	9009.3479	1.1034
8604.1411	0.23	8640.7733	0.4865	9009.3595	0.9055
8604.1411	1.3715	8640.7743	0.3559	9009.3596	0.3854
8604.162	0.2158	8667.9233	0.1481	9009.3739	1.6825
8604.1841	1.4375	8719.2174	0.3242	9088.8533	0.9492
8604.1846	0.196	8719.2178	0.8315	9089.2926	0.2364
8615.3709	0.2821	8719.2179	3.0099	9089.9892	2.1468
8615.4071	0.3029	8719.218	1.2988	9089.99	0.7528
8618.0819	0.3503	8719.2182	0.1656	9091.0367	0.5004
8618.13	0.2864	8834.4508	0.3208	9091.0368	0.2213
8620.1804	1.19	8899.6196	0.2876	9101.6458	0.616
8620.1813	0.316	8988.4718	1.2847	9101.6784	0.6581
8620.83	0.19	8988.4727	0.294	9101.7241	0.5705
8620.8301	0.8871	9003.7365	1.4996	9101.7574	0.2896
8620.9171	0.7378	9003.7796	0.912	9101.8051	0.2752

Frequency	Intensity	Frequency	Intensity	Frequency	Intensity
9101.8095	0.3663	9245.947	0.3296	9458.8424	1.0756
9101.8613	0.6502	9246.3633	0.1572	9458.8427	1.4035
9166.2768	0.163	9246.3808	0.1675	9599.3291	0.2748
9166.2913	0.8002	9246.3883	0.1862	9604.0512	0.7101
9166.2994	0.1937	9247.0078	0.1868	9651.2523	0.3615
9166.7154	0.2268	9247.0737	0.2285	9670.9435	0.1563
9166.7452	0.2696	9247.0742	0.886	9671.0011	0.2315
9167.3606	0.3241	9247.0747	0.3416	9711.1063	0.887
9167.4288	0.6545	9248.1067	0.1736	9711.1407	0.2349
9167.4298	0.2768	9248.1517	0.2208	9711.1552	0.6197
9167.4299	0.7848	9406.1914	0.3866	9712.3836	0.2465
9167.441	0.1397	9406.1914	0.2959	9712.3847	0.6445
9168.477	0.2164	9406.2523	0.1894	9712.434	0.4379
9168.4772	0.2747	9426.0041	1.2687	9712.4345	0.3485
9168.6219	0.2076	9426.0043	0.2306	9713.0862	0.4192
9211.0259	0.1798	9426.1821	1.1683	9713.1215	0.2113
9211.0312	0.5972	9426.1835	0.4609	9713.136	0.2818
9211.4579	0.1826	9426.3017	0.3024	9780.4569	1.8018
9211.4606	0.2553	9426.3024	1.0713	9780.4575	0.5601
9211.4774	0.1953	9426.4806	1.4885	9780.6269	0.2189
9211.4904	0.1882	9426.4813	0.3264	9780.627	2.2064
9212.1431	0.1535	9426.4822	0.2416	9780.6272	0.6007
9212.1693	0.6147	9458.2092	0.2229	9780.8271	0.3318
9212.1695	0.3	9458.5942	0.7138	9780.8279	2.8074
9212.1696	2.504	9458.6124	0.1799	9780.992	1.3559
9212.188	0.1473	9458.6666	0.6143	9780.998	0.2216
9213.2173	0.8303	9458.6667	3.04	9780.9984	0.839
9213.2191	0.197	9458.7818	2.0828	9781.033	2.0949
9245.9017	0.3276	9458.8353	0.203	9781.121	0.3825

Frequency	Intensity	Frequency	Intensity	Frequency	Intensity
9803.7779	0.1539	9974.6534	0.3745	10152.9134	0.7559
9912.4098	0.2576	9974.7466	4.765	10152.9655	0.2495
9912.7856	0.1953	9974.7467	0.8954	10152.9661	0.7778
9916.4466	0.1678	9974.7467	0.2314	10153.4096	1.589
9918.1343	0.1795	9974.7469	1.495	10153.41	0.207
9918.1745	0.1686	9975.4864	0.1802	10153.4104	0.7663
9972.3303	0.845	9975.4867	1.0484	10153.4106	0.2489
9972.3304	1.1077	9975.4868	0.3689	10154.1107	0.2015
9972.4109	0.7738	10119.838	0.2261	10154.1114	0.4969
9972.7976	0.9005	10150.5414	0.3558	10435.9438	0.4574
9972.8614	2.9351	10150.543	0.6155	10436.5375	0.2701
9972.8618	2.8591	10151.006	0.78	10436.5376	0.4806
9972.8618	0.4297	10151.0066	0.3455	10437.9655	0.6051
9972.8622	0.3688	10151.0068	1.6497	10438.459	0.3004
9973.6058	0.4283	10151.7138	0.4563	10438.5574	0.4234
9973.6061	1.043	10151.7144	0.2116	10438.5576	0.2636
9974.2142	1.4248	10152.9134	0.1877	10575.4619	0.1959
9974.2147	0.6202	9974.2658	0.2437	10576.1735	0.33
9974.2658	0.2437				
9974.3036	0.8715				