

CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF
FLUOROiodoACETONITRILE AND CHLOROPENTAFLUOROACETONE

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This work focuses on finding the complete iodine and nitrogen nuclear electric quadrupole coupling tensors for fluoroiodoacetonitrile using chirped-pulse Fourier transform microwave spectroscopy. Fluoroiodoacetonitrile contains two hyperfine nuclei, iodine ($I=5/2$) and nitrogen ($I=1$) and the spectra were observed with great resolution. A total of 499 transitions were observed for this molecule. The a, b and c rotational constants were obtained. A study of chloropentafluoroacetone was also done using chirped-pulse Fourier transform microwave spectroscopy. The two chlorine isotopes for this molecule, Cl-35 and Cl-37 were observed and 326 and 170 transitions were recorded, respectively.

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CHAPTER 1

INTRODUCTION

1.1 Microwave Spectroscopy

Originally microwave spectroscopy was used to determine the structure of a molecule, including the bond length, bond angle, dipole moment and hyperfine structures arising from the coupling of nuclear and magnetic quadrupole moments.

Microwave spectroscopy is a branch of spectroscopy that uses a radiation source to measure the transitions between quantized rotational energy levels. The microwave region is found from the 30 cm to 0.3 mm (3-30 GHz) region of the electromagnetic spectrum.[3]

Balle and Flygare developed pulsed nozzle Fourier transform microwave spectroscopy (PNFTMW) to study the conformers of organic molecules, weakly bound complexes, free radicals and reaction intermediates with great resolution and high sensitivity. A number of preparative techniques such as heating, dc discharge, and laser ablation technology have been applied to study solid and liquid species with high vapor pressures. The weakly bound complexes between metallic compounds and inert gases as well as weak interactions between some biomolecules have been studied. [1]

The application of microwave spectroscopy in detecting spectral lines of molecules in the interstellar medium has been useful for astronomical investigations [3].

1.2 Theory and Background

Broadly, there are three kinds' transition energy levels in spectroscopy: electronic, vibrational and rotational. The frequency range corresponding to energy between rotational

levels is generally in the microwave region. Microwaves are in the range of frequency from 300 MHz to 300GHz. Microwave spectroscopy is also called rotational spectroscopy.

In quantum mechanics, the angular momentum of the molecular rotation is quantized. Solids and liquids have high densities and they collide with each other when the molecules are close to each other. Gases with less density have a molecular rotation that is free. The study of microwave spectroscopy is generally carried out in the gas phase [1].

The energy levels of molecules can be given by the Schrodinger equation:[1]

$$H\psi = E\psi$$

And ψ is the eigenfunction and E is the eigenvalue of the Hamiltonian operators, H . The Hamiltonian operator is the operator that corresponds to the sum of the kinetic and potential energy of a system. This Schrodinger equation can be written as an eigenvalue equation of the form:[2]

$$(\text{Operator})(\text{Function}) = (\text{constant factor}) \times (\text{same function})$$

A Hamiltonian operator for a freely rigid rotor molecule can be given by the formula:[1]

$$H_r = \frac{P_a^2}{2I_a} + \frac{P_b^2}{2I_b} + \frac{P_c^2}{2I_c}$$

P refers to the angular momentum, P_a , P_b and P_c are the components of the angular momentum about the principal axes, $h^2J(J+1)/4\pi^2$, h is the Planck constant, J is the quantum number of the angle momentum, which is an integral number ($J= 0,1,2,\dots$). The formula $h^2J(J+1)/4\pi^2$ follows:

$H_r = AJ_a + BJ_b + CJ_c$. A, B and C are the principal rotational constants and J_a , J_b and J_c are the components of the rotational angular momentum operator.

The selection rules for the molecular rotational transitions are found to be:

$$\Delta J = J' - J'' = 0, \pm 1$$

1.3 Moment of Inertia

In order to understand the pure rotation spectra of a molecule, it is important to understand the moment of inertia, I , of a molecule. The moment of inertia of a molecule is defined as the product of the mass of each atom within the system with the square of its distance from the rotational axis through the center of mass of the molecule. [2]

$$I = \sum m_i r_i^2$$

r_i is the perpendicular distance of the atom i from the axis of rotation. Clearly, the moment of inertia depends upon various factors like the mass and molecular geometry, so rotational spectroscopy will give information regarding the bond length and bond angles. The rotational properties can be expressed in terms of the moments of inertia about three perpendicular axes set in the molecule. The moment of inertia for linear molecules around the internuclear axis is zero. [2]

The components of the moment of inertia tensor in the space fixed x, y, z axis system are given by: [3]

$$I = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{xy} & I_{yy} & I_{yz} \\ I_{xz} & I_{yz} & I_{zz} \end{pmatrix}$$

The diagonal elements or the moment of inertia are defined as:

$$I_{xx} = \sum_i m_i (y_i^2 + z_i^2)$$

$$I_{yy} = \sum_i m_i (x_i^2 + z_i^2)$$

$$I_{zz} = \sum_i m_i (x_i^2 + y_i^2)$$

The off-diagonal elements, or product of inertia, are given by

$$I_{yx} = I_{xy} = -\sum_i m_i x_i y_i$$

$$I_{zx} = I_{xz} = -\sum_i m_i x_i z_i$$

$$I_{zy} = I_{yz} = -\sum_i m_i y_i z_i$$

Rotational spectroscopy is performed in the molecule-fixed orientation with axes labeled a, b and c. This is just a movement of the space-fixed orientation giving tensor components I_a , I_b and I_c which are put in order such that $I_a \leq I_b \leq I_c$. These values may be obtained by diagonalizing the above inertia tensor.

When deriving quantum mechanical properties of molecular rotors, it is important to express the angular momenta and rotational energy. The classical angular momentum of a rigid system of particles is given by:[3]

$$P = I \cdot \omega$$

where ω is the angular velocity and I is the moment of inertia tensor which in dyadic notation is written as

$$I = I_{xx}ii + I_{xy}jj + I_{xz}ik + I_{yx}ji + I_{yy}jj + I_{yz}jk$$

$$+ I_{zx}ki + I_{zy}kj + I_{zz}kk$$

When taking into consideration different principal axes, x, y and z, the components of angular momentum become

$$P_x = I_x \omega_x \quad P_y = I_y \omega_y \quad P_z = I_z \omega_z$$

The kinetic energy can be given by:

$$E = \frac{1}{2} \omega \cdot I \cdot \omega \\ = \frac{1}{2} (I_{xx} \omega_x^2 + I_{yy} \omega_y^2 + I_{zz} \omega_z^2 + 2I_{xy} \omega_x \omega_y + 2I_{xz} \omega_x \omega_z + 2I_{yz} \omega_y \omega_z)$$

1.4 Rigid Rotors

Molecules are considered to be rigid rotors when they do not distort under the stress of rotation. There are four types of rotors namely; linear, symmetric, asymmetric and spherical rotors. The two molecules that form the bases of this work are both asymmetric.

1.4.1 Linear Rotors

The nuclei are regarded as mass points, and the rotation occurs about an axis perpendicular to the line of atoms and there is zero angular momentum around the line. The rotational terms of a linear molecule are therefore

$$F(J) = BJ(J+1) \quad J=0,1,2,\dots$$

1.4.2 Symmetric Rotors

Two moments of inertia are equal but different from the third in a symmetric rotor. The unique axis of the molecule is its principle axis. The unique moment of inertia is written as $I_{||}$

and the other two as I_{\perp} . If $I_{\parallel} > I_{\perp}$ the rotor is oblate and if $I_{\parallel} < I_{\perp}$ the rotor is prolate. The classical expression for the energy of a symmetric rotor is:

$$E = \frac{J_b^2 + J_c^2}{2I_{\perp}} + \frac{J_a^2}{2I_{\parallel}}$$

This expression can be written in terms of $J^2 = J_a^2 + J_b^2 + J_c^2$

$$E = \frac{J^2 - J_a^2}{2I_{\perp}} + \frac{J_a^2}{2I_{\parallel}} = \frac{J^2}{2I_{\perp}} + \left(\frac{1}{2I_{\parallel}} - \frac{1}{2I_{\perp}} \right) J_a^2$$

A quantum expression can be generated by replacing J^2 by $J(J+1)h^2$, where J is the angular momentum quantum number. According to the quantum theory of angular momentum, the component of angular momentum about any axis is restricted to the values Kh , with $K=0, \pm 1, \dots, \pm J$. J_a^2 is replaced by $K^2 h^2$.

It follows that the rotational terms are

$$F(J, K) = BJ(J+1) + (A-B)K^2 \quad J=0, 1, 2, \dots \quad K=0, \pm 1, \dots, \pm J \quad \text{-----1}$$

with

$$A = h^2/4\pi^2 I_{\parallel} \quad B = h^2/4\pi^2 I_{\perp}$$

The above first equation shows the dependence of the energy level on the two distinct moments of inertia of the molecule. When $K=0$, there is no component of angular momentum about the principal axis, and the energy levels depend only on I_{\perp} . When $K = \pm J$, the angular momentum arises when there is a rotation around the principal axis, and the energy levels are determined largely by I_{\parallel} . Opposite values of K means that the rotation is opposite and does not depend on the energy, therefore the sign of K does not also affect the energy as well.

1.4.3 Asymmetric Top Rotors

When no two principal moments of inertia are equal then the rotor is considered an asymmetric top. The asymmetric top is treated largely as a deviation from the symmetric case. As the asymmetric rotor starts to deviate from the prolate and the oblate symmetric top, a general picture of the behavior of the energy levels of an asymmetric top can be predicted.

The energy for this is given by:

$$W = \frac{P_x^2}{2I_a} + \frac{P_y^2}{2I_b} + \frac{P_z^2}{2I_c} = \frac{4\pi^2 A}{h} \frac{P_x^2}{h} + \frac{4\pi^2 B}{h} \frac{P_y^2}{h} + \frac{4\pi^2 C}{h} \frac{P_z^2}{h}$$

For an asymmetric rotor the constants A, B and C are all different. When B=C, this gives a symmetric prolate top. And when B=A, this gives an oblate top. If B differs from A or from C by a small amount, the rotor can be called a slightly asymmetric top.

In order to understand the degree of asymmetry, various parameters can be used. One of these is Ray's asymmetry parameter, given by:

$$K = \frac{2B-A-C}{A-C}$$

This becomes -1 for a prolate symmetric top (B=C) and 1 for an oblate symmetric top (B=A), varying between these two values for asymmetric cases. The most asymmetric top has k=0. [3] The energy level difference of the asymmetric top from the symmetric top which corresponds to -K and +K, are separated in the asymmetric rotor and are degenerate in the symmetric rotor. There are (2J+1) distinct rotational sublevels for each value of J in a asymmetric rotor and J+1 distinct sublevels in a symmetric rotor [3].

For a symmetric top, the total angular momentum J and its projection M on an axis fixed in space are constants of the motion and are considered to be “good” quantum numbers which can be used to specify the state of the rotor [4].

The quantum mechanical Hamiltonian describing the rotation of a rigid asymmetric body is given by:

$$H = AP_a^2 + BP_b^2 + CP_c^2$$

where A , B and C are the rotational constants and P_a , P_b and P_c are the angular momentum operators. Using the equation for Ray’s asymmetry parameter and the equation $P^2 = P_a^2 + P_b^2 + P_c^2$ then it has been shown by Ray that the Hamiltonian becomes:

$$H = \frac{1}{2}(A+C) P^2 + \frac{1}{2}(A-C) H(k)$$

where $H(k) = P_a^2 + kP_b^2 - P_c^2$

The eigenvalues of $H(k)$, depend only on the inertial asymmetry parameter k and not on the individual rotational constants.[3]

The general selection rule for rotational transitions in an asymmetric top is that $\Delta J = 0, \pm 1$. The $\Delta J = -1$ transitions are designated as P-branch; the $\Delta J = 0$, as Q-branch; and the $\Delta J = +1$, as R-branch transition.[3]

1.4.4 Centrifugal Distortion

Centrifugal distortion plays an important role in the microwave spectra of asymmetric rotors. Small shifts of the order of 1MHz or less are produced by symmetric tops and the centrifugal distortions change the rotational frequencies many hundreds of megacycles in asymmetric rotors. This occurs due to the fact that microwave transitions take place in

asymmetric rotors between states of large angular momentum and of large rotational energies. Transitions between small J states are seen in light symmetric tops, whereas transitions between states of larger J are observed for heavier symmetric molecules. The moment of inertia is so large for heavy symmetric molecules that the rotational energies in these states are still rather small.

The centrifugal distortion can stretch the bond in a diatomic molecule and increase the moment of inertia. The rotational constant can be reduced by centrifugal distortion and the energy levels become closer than in rigid rotors. [2]

The formula

$$F(J) = BJ(J+1) - D_J J^2(J+1)^2$$

is obtained by subtracting a term from the energy. The parameter D_J is the centrifugal distortion constant. For a diatomic molecule, the centrifugal distortion constant is related to the vibrational wavenumber of the bond.

For an asymmetric rotor, Watson has developed a reduced Hamiltonian in which the centrifugal distortion terms are represented by Δ_J , Δ_{JK} , Δ_K , δ_J and δ_K .

1.4.5 Nuclear Electric Quadrupole Coupling

An asymmetric distribution of nucleons results in a nuclear quadrupole moment and a distribution of electronic charge about the nucleus give rise to an electric field gradient at the nucleus. The field gradients are fixed in direction in solids and pure nuclear quadrupole spectra analogous to nuclear magnetic resonance can be observed. The field gradient at the nucleus

depends on the rotational state of the molecule and the nuclear quadrupole interaction is different for each rotational state in gases.

When a nuclear spin I is coupled with a molecular rotational angular momentum J , a resultant vector F is formed. F can be represented as the total angular momentum of the molecule with nuclear coupling and J is the total angular momentum excluding the nuclear spin. J^2 is a constant of motion and F , M_F , J and I are good quantum numbers.[3]

The new angular momentum quantum numbers are given by

$$F=J+1, J+I-1, J+I-2, \dots, |J-I|$$

The quadrupole Hamiltonian which includes the terms I, J ; e as the charge of an electron, Q the quadrupolar moment, and q_j as the electric field gradient. The Hamiltonian is given by: [3]

$$H_Q = eQq_j / 2J(2J-1)I(2I-1) [3(I \cdot J)^2 + 3/2I \cdot J - I^2 J^2]$$

The quantity q_j depends on the particular type of molecule, whether it is linear, symmetric or asymmetric rotor. The total angular momentum is defined as the vector sum of the rotational angular momentum and the nuclear spin vector, or $\mathbf{F} = \mathbf{J} + \mathbf{I}$. This gives

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

and

$$\mathbf{I} \cdot \mathbf{J} = 1/2(F^2 - J^2 - I^2)$$

1.4.6 Quadrupole Coupling by More Than One Nucleus in a Rotating Molecule

The rotational hyperfine structure of a molecule can be complicated if there are two or more nuclei with quadrupole coupling. This will be further explained as in the case of Fluoroiodoacetonitrile in chapter 3. The nucleus that is coupled can affect the rotational axes and change the field gradient which interacts with other coupling nuclei. In frozen type

molecules, the quadrupole interaction of one nucleus is independent of other type of molecules. When there are two or more coupling nuclei in the same molecule, the coupling constants χ are obtained by measuring the pure quadrupole resonance in the solid state. The coupling constants in gaseous molecules are different from solid molecules. [3]

The complications involved with the presence of a dual nuclear coupling can be easily resolved, when the coupling of one nucleus is large as compared with that of the second nucleus.

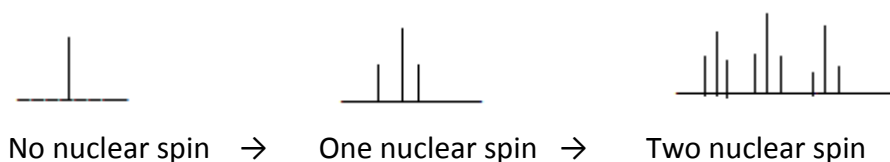


Figure 1.1: Nuclear spins.

1.5 Instrumental Theory

The basic theory for microwave Fourier transform spectroscopy is based on the work of the Bloch type equations. Flygare and Ekker's explain the theory by applying it to practical experiments. A number of rotational two-level system with resonance frequencies ω_j connected by dipole transition moments $k_j = (2/h) |\langle a | \mu | b \rangle_j|$ is taken into consideration. This system is irradiated by a beam of intense microwave pulses with carrier frequency $\omega_p/2\pi$, pulse length τ , and period T. The frequency side bands in the spectrum are separated by $1/T$ Hz around the carrier frequency. The spectrum is assumed to be narrow and above the cutoff frequency of the waveguide. This is done so that there are no distortions of the pulses due to the various characteristics of the waveguide. [5]

The microwave pulses induce a macroscopic polarization of the sample which is a function of time and the location z along the waveguide. The decoherence of this macroscopic polarization is collected as a function of time, digitized and Fourier transformed into a frequency domain.[5]

The time domain pulsed Fourier transform microwave spectrometer has greatly enhanced its sensitivity and resolution when compared to a standard microwave spectrograph that operates in the frequency domain. Sensitivity of microwave spectroscopy is important when studying various complex molecules. With the development of the time dependent theory, the behavior of absorption and emission of two-level quantum mechanical systems shows the measurement of rotational transitions in the time domain which is similar to the NMR experiments performed. Most of the transient microwave experiments are performed by moving a transition into or out of resonance by switching the stark field in a conventional stark cell [5].

In the work performed by Flygare, a high-power pulse train is passed through the absorption cell. Most of the detection of the signals takes place in the absence of any microwave power from the master oscillator, therefore a balanced bridge is eliminated and an empty waveguide or any other suitable device can be used for an absorption cell. This does not affect the signal-to-noise ratio [5].

CHAPTER 2

EXPERIMENT AND INSTRUMENTATION

2.1 Chirped-Pulse Fourier Transform Microwave Spectrometer

The chirped-pulse FTMW spectrometer consists of three basic components: (1) chirp microwave pulse generation, (2) microwave excitation pulse and molecular beam sample interaction region and (3) FID detection. The two main components of a CP-FTMW, the arbitrary waveform generators (AWGs) and digital oscilloscopes are discussed in detail.

In order to perform broadband FTMW spectroscopy, a microwave source is required that can produce phase-reproducible linear frequency sweeps over an 11 GHz frequency range in about 1 μ s. Short sweep durations are important as the sample can be polarized on a time scale faster than that of rotational free induction decay (FID). The FID decays with a Gaussian profile in about 10 μ s and are dominated by Doppler broadening. A high phase stability of the microwave source is required to average the FID signal in the time domain.[8]

2.1.1 Arbitrary Waveform Generator (AWG)

The original CP-FTMW spectrometer used a 4.2 Gsample/s for the production of chirped pulse. The phase stability of the internal clock in the 4.2 Gsample/s AWG is not enough for performing time-domain signal averaging of the 11 GHz bandwidth molecular emission signal. A phase-locked dielectric resonator oscillator is used as an external clock for the AWG. The phase-locked resonator oscillator works at frequency of 3.96 GHz. When comparing this with the Nyquist frequency range, the 3.96 Gsample/s AWG operates at a frequency range of

1.98GHz. For a AWG performing at a lower bandwidth, a bandwidth multiplication circuit is used to produce pulse that covers a range of 11 GHz bandwidth.

By using a high-speed AWG, the production of chirped pulse can be greatly simplified. For instance, a 20 Gsamples/s AWG (Tektronix AWG 7102) can be used to create a chirped pulse with a linear frequency sweep from 500 MHz to 10 GHz.

2.1.2 Digital Oscilloscopes

The bandwidth extension of the linear frequency sweep can occur in two stages. By first using an active frequency quadrupler, the bandwidth of the microwave pulse can be increased by a factor of 4. The output that is produced from the frequency quadrupler is filtered in a high pass filter with a 25 GHz cutoff frequency to remove the residual power leakage and lower harmonics of the sweep that appear on the output of the quadrupler. The frequency multiplied sweep is changed by 19.8 GHz in a broadband mixer. The oscillator used for the broadband mixer is provided by the frequency doubled output of the 9.9 GHz phase-locked oscillator source. The mixer output is amplified in a broadband microwave amplifier and sent to an active frequency doubler to increase the sweep bandwidth by a factor of 8 overall after the two multiplier stages. The output of this doubler is passed to a second high pass filter that has a 26 GHz cutoff frequency. The sweep is then down converted to the 7.5-18.5 GHz range by using a broadband mixer with the 19.8 GHz signal as the local oscillator. The pulse is preamplified in a low-noise, solid-state amplifier and sent through a programmable attenuator before being directed to the input of a high-power microwave amplifier.

For amplification, a 5 W solid-state amplifier is used and pulsed traveling wave tube amplifiers with peak powers of 300 W are also used. The amplifiers are known to have great phase stability in successive pulses to permit time-domain averaging of the FID.

Two digital oscilloscopes are used to digitize the broadband FID signal. The 40 Gsample/s oscilloscope that is used for detection helps in down converting to the dc-12 GHz frequency range. The downconverted FID signal passes through a low pass filter that removes the local oscillator signal that can leak through the mixer. The latest generation digital oscilloscope offers 50 Gsample/s digitization rates with hardware bandwidths up to 20 GHz. This type of oscilloscope is used to directly digitize the FID.

2.2 Spectrometer Operation

In order to have an optimal performing spectrometer, it is important to have a linear sweep excitation, high microwave peak power and digital signal processing of rotational free induction decay (FID). The linear sweep excitation and high microwave peak power helps in the optimal polarization of the molecular sample being studied. Digital signalization improves the frequency resolution at the baseline. [8]

2.2.1 Linear Sweep Excitation

Fast passage excitation is a method that can be used to excite the molecular sample. In the measurement by Brown, et al, the sweep duration of the chirped pulse is much slower compared to the time scale of the transient molecular emission. Khodos et al, described better ways to analyze the transient signals in an experiment where the sweep duration is slow

compared to the molecular emission. With the use of an Arbitrary waveform generator, it is possible to perform broadband chirped pulse excitation in a time scale shorter compared to the transient emission time.

The chirped pulse provides a separation of the bandwidth and the pulse duration, and this ultimately helps to control the frequency range of the excitation and the amount of energy acting on the sample. The linear frequency sweep pulse helps in polarizing the molecular sample. The signal that is produced from the chirped pulse excitation can be given by the form:

$$S \propto \omega \cdot \mu^2 \cdot E_{\text{pulse}} \cdot \Delta N_0 \cdot (\pi/\alpha)^{\frac{1}{2}}$$

where ω is the frequency, μ is the transition dipole moment, E_{pulse} the electric field strength and ΔN_0 the population difference at equilibrium which remains unchanged by the pulse. [8]

2.2.2 Power Requirements for Broadband FTMW Spectroscopy

The power requirements in a CP-FTMW depend on the pulse duration, bandwidth and other properties like the dipole moment. When comparing the Balle-Flygare cavity FTMW spectrometer to the CP-FTMW, more peak power is required by the CP-FTMW spectrometer to polarize the sample because the CP-FTMW spectrometer lacks the amplification power that the Fabry-Perot cavity provides. Also, the peak power is inversely related to the cavity Q. The small cavity FTMW spectrometer generally has cavity Q on the order of 10, 000. The CP-FTMW spectrometer (Q=1) requires a factor of 10, 000 or greater power in order to excite the transition. Another reason why CP-FTMW requires greater power is due to the fact the cavity FTMW spectrometer covers a bandwidth of 1 MHz with each microwave pulse and the CP-

FTMW spectrometer covers 11GHz. This leads to another factor of 11, 000 power requirement.

[8]

2.2.3 Digital Signal Processing of the Broadband FID

Signal leakage in the frequency domain spectrum is a current problem in the CP-FTMW spectrometer. The frequency side lobes of the CP-FTMW can cover a large spectral region near the baseline. It can be difficult at times to observe weak rotational transitions that have transitions close to strong transitions with these side lobes. This problem is common when measuring the rotational spectrum of isotopes that have low abundance. [8]

2.3 Supersonic Expansion

A supersonic expansion of gases takes place when a gas in a reservoir at thermal equilibrium is expanded through a nozzle into vacuum. Tremendous cooling of translational and rotational degrees of freedom occurs during supersonic expansion of gases. Vibrational degrees of freedom are much less cooled. Molecules do not undergo much collision when their distance amongst each other increases especially when there is not enough background pressure. This generally occurs due to translational cooling and when the particle density decreases. The carrier gas usually used in microwave spectroscopy is helium or argon. Carrier gases are more cooled during expansion than when the gas passes a beam. [10]

Flygare and co-workers used a method to measure rotational transitions that combined the principles of pulsed Fourier transform microwave spectroscopy in a Fabry-Perot cavity with

a pulse supersonic jet that is travelling across the microwave field. A decrease in the Doppler linewidth, limits the resolution in static microwave spectroscopy. [10]

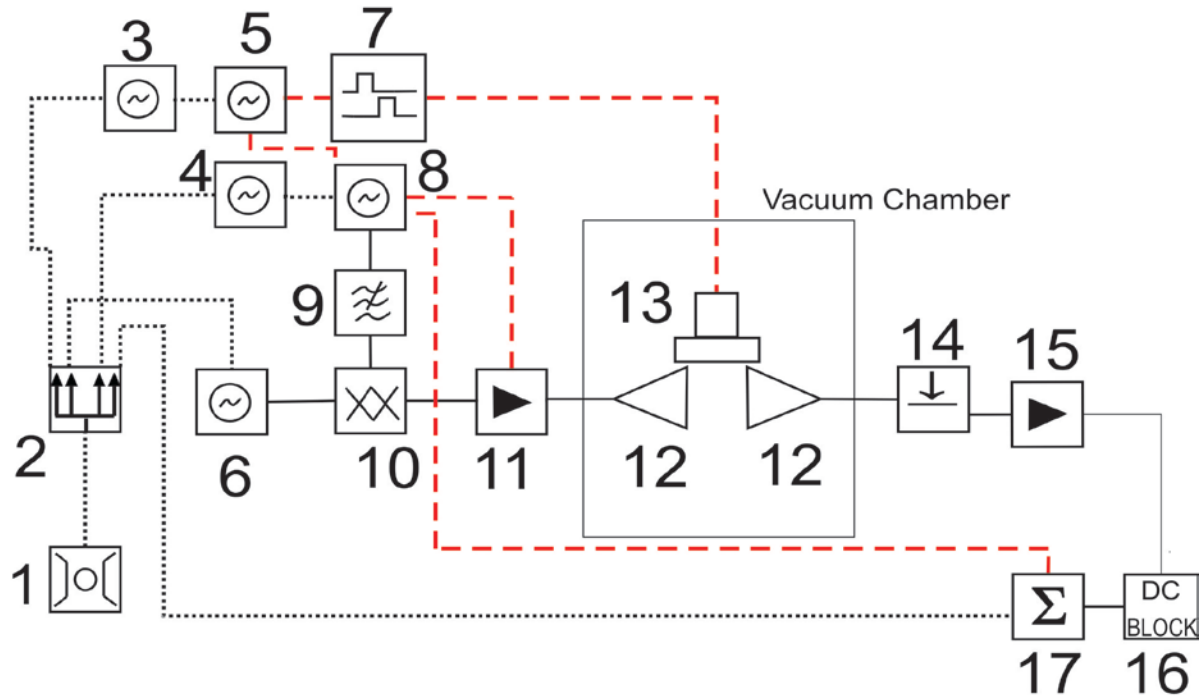


Figure 2.1: Chirped-pulse Fourier transform spectrometer.

Solid lines are microwave frequencies for use in experiment. Dotted lines are reference frequencies. Dashed lines are timing control connections. Components are 1. Stanford Research Systems 10 MHz Rb Standard Model FS725, 2. 10 MHz Distribution Amplifier, Wenzel Associates 600-15888, 3. Nexyn Corporation 640 MHz Phase Locked Oscillator, NXPLOS-0064-023814. Nexyn Corporation 3.96 GHz Phase Locked Oscillator, NXPLOS-0396-02381, 5. Tektronix AWG2041 Arbitrary Waveform Generator, 6. Microwave Synthesizer, HP 8341A, 7. Berkeley Nucleonics Corporation Pulse Generator, 8. Tektronix AWG 710B 4.2 GS/s Arbitrary Waveform Generator, 9. Low Pass Filter, Minicircuits VLF-1800+, 10. Mixer, Miteq DB0418LW1, 11. 5W Power Amplifier, Microwave PowerL0818-37, 12. Horn Antennae, Amplifier Research AR 4004, 13. Series 9 Solenoid Valve, Parker-Hannifin, 14. SPST Switch 0.5-18.0 GHz, Advanced Technical Materials AMT31517D, 15. Low Noise Amplifier, Miteq AMF-6F-0800-1800-14-10P, 16. DC-250 MHz Block 17. Oscilloscope, Tektronic.

CHAPTER 3

CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF FLUOROiodoACETONITRILE

3.1 Introduction

Only a few molecules that are asymmetric and contain two hyperfine structure-generating nuclei such as Iodine ($I=5/2$) and nitrogen ($I=1$) have been completely analyzed that have high resolution spectra recorded. The spectral assignment can become complex due to the presence of asymmetry and two quadrupolar nuclei. Nitrogen possesses a small quadrupole moment so the task of successfully resolving nitrogen hyperfine structure becomes less favorable for a heavy asymmetric molecule.[9]

A "high throughput" characterization technique can be achieved by a chirped-pulse Fourier transform microwave spectroscopy [11]. The technique has several nice features and, at the same time, maintains many of the strengths of the more traditional form of FTMW spectroscopy. With regard to molecular characterization, these features and strengths include (i) line center measurements with precision of less than 10 kHz, (ii) quite reasonable resolution with achievable line widths of less than 80 kHz. (iii) a pulsed molecular source ensuring a cold rotational temperature and therefore a more sparse, easily assignable rotational spectrum. (iv) rapid data acquisition, allowing several gigahertz of spectra to be recorded, with signal averaging, in matter of minutes or hours and (v) reliable relative intensities for observed transitions, which again further aid in spectral assignments.

Fluoroiodoacetonitrile is chiral, a prototype molecule with asymmetry. One nucleus is present with a large quadrupole moment, iodine and a second nucleus is present with a small

quadrupole moment, nitrogen. A dense spectrum is obtained in the 8-16 GHz region.

3.2 Experiment

Fluoroiodoacetonitrile (97% minimum) was purchased from Synquest Laboratories and used without further purification. A solenoid valve is used to produce pulses of gas from a reservoir held at 1000-2000 Torr into a vacuum chamber at 10^{-5} Torr. The sample was loaded in a $\frac{1}{4}$ in. diameter vacuum tube 20-30cm upstream of the solenoid valve [9].

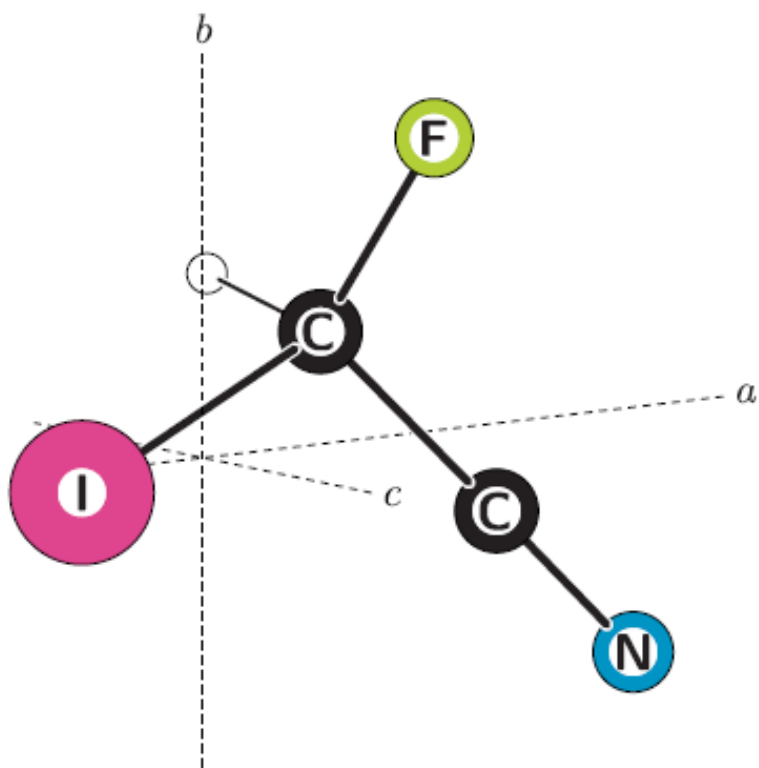


Figure 3.1: The calculated structure of fluoroiodoacetonitrile [9].

Argon was bubbled through the sample on its way from the reservoir to the solenoid valve. The instrument used in this work has been described in chapter 2. Briefly, the instrument utilizes fast ($< 5 \mu\text{s}$) linear frequency sweeps of microwave radiation to induce a macroscopic polarization in those molecules having rotational transitions with 2 GHz span of frequencies

inside the 8-18GHz region. An oscillating electric field is produced as the polarized molecules decohere and it is received via a broadband horn antenna. Free induction decay is recorded on a digital oscilloscope (TDS6124C, Tektronix). In these experiments 10,000 averaging cycles were used, and the free induction decays were directly digitized as opposed to utilizing a mixing down stage. Line widths obtained were 80 kHz and an uncertainty of 10 kHz was measured.

3.3 Quantum Chemistry Calculations

Quantum chemistry calculations were done to aid this experimental investigation. These calculations have been performed to determine the molecular structure, iodine and nitrogen nuclear quadrupole coupling constants and the molecular dipole moments. Gaussian 03 was used for all the calculations [14]. An assumption that the errors are largely systematic and can be corrected is made when performing the calculations for the molecular structure and the nuclear quadrupole coupling constant [15]-[17]. An MP2/6-311+G(d,p) optimized bond lengths r_{opt} versus known experimental r_e bond lengths calculation was done to determine the CN bond length. Linear regression equations were also derived for CC and CF bond lengths [18]. The molecular structure of CHIFCN was derived by MP2/6-311+G (d,p). For CI, the bond length is the optimized value, and for CH, $r_e(\text{\AA}) = 1.001r_{\text{opt}}$, where $r_{\text{opt}} = \text{MP2/6-31G (d,p)}$. [17]

The electric field gradients (q_{ij}) at the iodine nucleus were calculated at the B1LYP/6-311G (d,p) level of theory, transformed from Gaussian 03 "standard orientation" axes to inertial a, b and c axes, and converted to nuclear quadrupole coupling constants by $X_{ij} = (eQ_{\text{eff}}/h)q_{ij}$, where $eQ_{\text{eff}}/h = -173.815(271) \text{ MHz/a.u.}$ [18] The electric field gradient for nitrogen was calculated at the B3PW91/6-311+G(df, pd) level, transformed to a, b and c axes,

and converted to coupling constants with $eQ_{\text{eff}}/h=4.5586(40)$ MHz/a.u.[18]-[19] The calculated quadrupole coupling constants are given in Table 3.3 . Also the calculated electric dipole moments done at the B1LYP/6-311G (df,p) level of theory and transformed to inertial axes are given in Table 3.3.

B1LYP is Becke's one-parameter hybrid functional [20] with Lee-Yang-Parr correlation [21] as implemented by Adamo and Barone[22]. B3PW91 is Becke's three-parameter hybrid [23] with Perdew-Wang correlation [24]. For iodine, a 6-311G (d) basis [25] was downloaded from the Environmental molecular sciences laboratory basis set library [26], [27]. To build 6-311G(df) an f polarization function with exponent 0.40 was added; to build 6-311+G(d) and 6-311+G(df), diffuse function s and p, each with exponent 0.02, were added.

3.4 Results and Analyses

The AABS (assignment and analysis of broadband spectra) package [28] from the Programs for Rotational Spectroscopy website [29] was used for spectral assignments. This package uses the powerful SPFIT/SPCAT [30], [31] software for fitting spectroscopic constants to assigned transitions and for producing spectral predictions.

As previously mentioned, the asymmetry of the molecule caused the spectral assignment to be challenging. The molecule coupled with the large hyperfine splitting's due to the iodine nucleus, caused the harmonic series of ${}^aR_{0,1}$ transitions to become difficult to identify. A total of 499 transitions were observed. A series of ${}^bQ_{1,-1}$ transitions was identified and assigned, which enhanced the determination of the rotational constants and then allowed

numerous other types of transition series, ${}^aQ_{0,1}$, ${}^cR_{1,0}$ to be identified and assigned.

Fluoroiodoacetonitrile consists of two quadrupolar nuclei, ${}^{127}\text{I}$ ($I=5/2$) and ${}^{14}\text{N}$ ($I=1$).

The Hamiltonian, H , was constructed in the coupled basis $\mathbf{I}(I) + \mathbf{J} = \mathbf{F}_1$, $\mathbf{F} = \mathbf{F}_1 + \mathbf{I}(\text{N})$ and had the form

$$H = H_R + H_Q(I) + H_Q(N) + H_{SR}(I)$$

where

H_R = operator appropriate to a semirigid rotor.

H_Q = operator describing the nuclear quadrupole coupling of I/N nuclear spin and framework angular momentum vectors \mathbf{I} and \mathbf{J} , respectively.

$H_{SR}(I) = \mathbf{I}_1 \cdot \mathbf{M}_1 \cdot \mathbf{J}$. This describes the magnetic spin-rotation coupling of the two vectors in terms of the iodine nuclear spin-rotation coupling tensor. The forms of H_R , H_Q and H_{SR} are well known [3].

The spectroscopic constants obtained are given in Table 3.4.

3.5 Discussion

3.5.1 Algebraic Signs of the Off Diagonal Components of the Iodine and Nitrogen Quadrupole Coupling Tensors

The complete quadrupole coupling tensors for iodine and nitrogen has been experimentally determined. It is not very common to determine all of the off-diagonal components of the quadrupole coupling tensors for a molecule containing two quadrupolar nuclei with molecular coordinates, unrelated through symmetry. Caution is required with regards to the signs of the off-diagonal nuclear quadrupole coupling tensor components [34]. A real contribution is made to the off-diagonal components of the Hamiltonian matrix by one of the off-diagonal components of the nuclear electric quadrupole coupling tensors, while an

imaginary contribution is made by the other two off diagonal nuclear electric quadrupole tensors. When the signs of the off diagonal nuclear quadrupole coupling tensor components are changed, a complex conjugate Hamiltonian matrix is obtained, which will ultimately give identical eigenvalues when diagonalized. Only the magnitude and the product of the signs of the off-diagonal nuclear quadrupole coupling tensor components can be determined from the actual experiment that is performed.

Sixty-four possible sign combinations for the off-diagonal components are present for two quadrupolar nuclei (I and N). The following sign combinations are obtained according to Bauder et al.:

$$\begin{aligned}\prod^{(I)} &= \text{sign}(\chi_{ab}^{(I)} \chi_{ac}^{(I)} \chi_{bc}^{(I)}) \\ \prod^{(N)} &= \text{sign}(\chi_{ab}^{(N)} \chi_{ac}^{(N)} \chi_{bc}^{(N)}) \\ \prod_{ab} &= \text{sign}(\chi_{ab}^{(I)} \chi_{ab}^{(N)}) \\ \prod_{ac} &= \text{sign}(\chi_{ac}^{(I)} \chi_{ac}^{(N)}) \\ \prod_{bc} &= \text{sign}(\chi_{bc}^{(I)} \chi_{bc}^{(N)})\end{aligned}$$

The four of the 16 possible sign combinations which are obtained from the 64 combinations, gives identical spectra, which are shown in table IV. Spectral fits using off-diagonal components with signs not consistent with the signs of $\prod^{(I)}$, $\prod^{(N)}$, \prod_{ab} , \prod_{ac} , \prod_{bc} shown in Table IV, gave standard deviations that were an order of magnitude larger than those obtained with sign combinations, consistent with those examples in Table 3.5.

The sign combinations 1 in Table 3.5 matched the signs of the calculated off-diagonal quadrupole coupling tensor components as shown in Table 3.3. The sign combination 1 was one of the 16 possible combinations required experimentally and was produced from the quantum chemical calculations.

3.5.2 Iodine Nuclear Quadrupole Coupling Tensor

The iodine nuclear quadrupole tensor for CHFICN is shown in table V and this tensor is rotated into the principal axes of the quadrupole tensor, and another similar molecule like CH₂ICN [35]. The C-I bond axis for both these molecules lies very close to the principal z-axis that is $\pm 1^\circ$. This allows us to compare the χ_{zz} values.

In the bromine analogs such as CH₂BrCN and CHBrFCN, the magnitude of $\chi_{zz} (^{79}\text{Br})$ decreases [12],[36], while an increase in magnitude of $\chi_{zz} (\text{I})$ in the order CH₂ICN < CHFICN is observed. Calculations have been performed to indicate that $\chi_{zz} (\text{I})$ decreases in the order of CH₂ICN > CHFICN, consistent with the Br series.

Therefore it can be seen that there is a decrease in the electric field gradient, q_{zz} at the Br/I centers upon fluorination of the -CH₂CN group. It can be concluded that the electronegativity of CH₂CN is less than that of -CHFICN.

3.5.3 Nitrogen Nuclear Electric Quadrupole Coupling Tensor

The nitrogen nuclear quadrupole coupling tensor for CHFICN in the principal axes system is compared with other compounds as shown in Table 3.7. The angle formed between the z and a axes is close to the angle between the CN bond axes and the a axis. The χ_{zz} decreases in magnitude in the order of CF₃CN \approx CHF₂CN > CH₂FCN \approx CHFICN \approx CHBrFCN > CH₂BrCN > CH₃CN.

The $\chi_{zz} (\text{N})$ in fluoroacetonitriles arises even though it differs in contributions from various mesomeric forms[37]. Contributions from H⁺CH₂C=N⁻ mesomer are important in CH₃CN than similar contributions from the F⁺CF₂C=N⁻ mesomer in CF₃CN. A more ionic nitrogen

environment will produce a more spherical electron distribution about the nitrogen nucleus which reduces the magnitude of the electric field gradient, and also reduces the nitrogen nuclear quadrupole coupling tensor. Data for nuclear quadrupole coupling has been used to establish a group electronegativity scale. The following experimentally determined series is put forward in order of decreasing group electronegativity: $\text{—CF}_3 \approx \text{—CHF}_2 > \text{—CH}_2\text{F} \approx \text{—CHF} \approx \text{—CHBrF} > \text{—CH}_2\text{Br} > \text{—CH}_3$

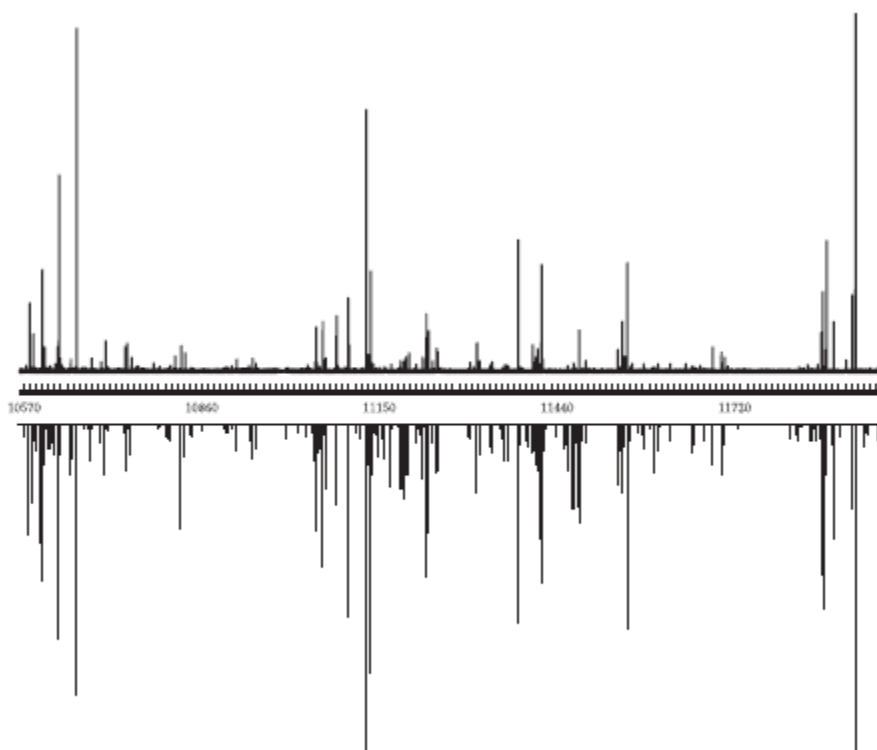


Figure 3.2: A 2 GHz scan of the pure rotational spectrum of fluoroiodoacetonitrile recorded using the CP-FTMW spectrometer. The spectrum showed required 10,000 averaging cycles to record (~ 2 h). The inverted spectrum shows the spectrum obtained with the fitted parameters in Table 3.4 together with the calculated dipole moments given in Table 3.3. [9]

Table 3.1: Calculated structural parameters for fluoroiodoacetonitrile.

Bond	Length	Angle	Calculated
r(C—C)	1.457 Å	(I, C, C)	110.3°
r(C—N)	1.157 Å	(H, C, C)	110.8°
r(C—I)	2.166 Å	(F, C, C)	110.0°
r(C—F)	1.360 Å	(C, C, N)	178.4°
r(C—H)	1.089 Å	(I, C, F)	110.2°
		(I, C, H)	106.5°
		(H, C, F)	109.1°

Table 3.2: Calculated rotational constants for fluoroiodoacetonitrile.

Parameter	Calculated
A / MHz	5420.70
B / MHz	1543.61
C / MHz	1238.19

Table 3.3: Calculated molecular dipole moments and iodine and nitrogen nuclear electric quadrupole coupling tensors in the a, b and c axes.

Parameter	Iodine	Nitrogen
χ_{aa} (MHz)	-1721.2	-0.869
χ_{bb} (MHz)	801.8	-1.031
χ_{cc} (MHz)	919.4	1.900
χ_{ab} (MHz)	813.1	-3.180
χ_{ac} (MHz)	667.7	-0.757
χ_{bc} (MHz)	-144.4	-1.309
μ_a (D)	1.74	
μ_b (D)	1.18	
μ_c (D)	1.65	
μ_{total} (D)	2.67	

Table 3.4: Spectroscopic parameters for fluoroiodoacetonitrile.

Parameter	Value
A(MHz)	5371.7732(11) ^a
B(MHz)	1572.530 01(29)
C(MHz)	1253.302 75(27)
Δ_J (kHz)	0.3912(41)
Δ_{JK} (kHz)	-1.672(22)
Δ_K (kHz)	11.49(24)
δ_J (kHz)	0.1144(18)
δ_K (kHz)	1.002(83)
χ_{aa} (I) (MHz)	-1692.0710(52)
χ_{bb} (I) (MHz)	787.9365(76)
χ_{cc} (I) (MHz)	904.1345(56)
$ \chi_{ab} $ (I) ^b (MHz)	838.393(12)
$ \chi_{ac} $ (I) ^b (MHz)	682.369(33)
$ \chi_{bc} $ (I) ^b (MHz)	155.74(15)
χ_{aa} (N) (MHz)	-0.7741(53)
χ_{bb} (N) (MHz)	-1.1183(72)
χ_{cc} (N) (MHz)	1.8924(49)
$ \chi_{ab} $ (N) ^b (MHz)	3.148(14)
$ \chi_{ac} $ (N) ^b (MHz)	0.836(40)
$ \chi_{bc} $ (N) ^b (MHz)	1.46(20)
C_{aa} (I) (kHz)	5.03(38)
C_{bb} (I) (kHz)	5.70(25)
C_{cc} (I) (kHz)	5.27(20)
N^c	499
rms ^d	0.7883

^aNumbers in parentheses give standard errors (1σ , 67% confidence level) in units of the least significant figure.

^bSee text for a discussion concerning the signs of the off diagonal components of the quadrupole coupling tensor.

^cNumber of observed transitions used in the fit.

^dRoot mean square deviation of the fit, $\Sigma[((\text{obs}-\text{calc})/\text{error})^2]/N$ lin

Table 3.5: Four sign combinations of the off-diagonal quadrupole coupling constants of iodine and nitrogen producing the same spectrum.

No.	$\text{Sign}(\chi_{ab}^{(0)})$	$\text{Sign}(\chi_{ac}^{(0)})$	$\text{Sign}(\chi_{bc}^{(0)})$	$\Pi^{(0)}$	$\text{Sign}(\chi_{ab}^{(0)})$	$\text{Sign}(\chi_{ac}^{(0)})$	$\text{Sign}(\chi_{bc}^{(0)})$	$\Pi(\text{N})$	Π_{ab}	Π_{ac}	Π_{bc}
1 ^a	+	+	-	-	-	-	-	-	-	-	+
2	+	-	+	-	-	+	+	-	-	-	+
3	-	+	+	-	+	-	+	-	-	-	+
4	-	-	-	-	+	+	-	-	-	-	+

^aThis is the combination of signs produced from the quantum chemical calculation and is the combination of signs used in the fit.

Table 3.6: Comparison of the principal axes ¹²⁷Iodine quadrupole coupling tensor in fluoroiodoacetonitrile with iodoacetonitrile.

	CHFICN	CH ₂ ICN ^a
X _{xx} (MHz)	1004.55(14) ^b	1043
X _{yy} (MHz)	1106.03(13)	1043
X _{zz}	-2110.581(25)	-2086
η_x^c	0.048 08(9)	0
$\theta_{za}^{(0)}$ (°) ^d	21.1648(9)	30.5
$\theta_{Cl,a}^{(0)}$ (°) ^e	21.5	29.8

^aTaken from ref. 35. A second order quadrupole theory analysis was formed; no uncertainties given

^bNumbers in parentheses give the uncertainties in units of the least significant figure.

^cThe asymmetry of the χ tensor in the principal axes system, $\eta_x = (\chi_{xx} - \chi_{yy}) / \chi_{zz}$

^dThe angle between the z and a axes.

^eThe angle between the C-I bond and the a axis obtained from the calculated structure. Our calculated structure for iodoacetonitrile produces A=20 379.4 MHz, B= 1721.7 MHz, and C= 1603.7 MHz, compared to the experimental values (Ref.35) of A= 20 037(3) MHz, B= 17 47.9(4) MHz, and C=1622.8(4) MHz respectively.

Table 3.7: Comparison of the principal axes nitrogen quadrupole coupling tensor fluoroiodoacetonitrile with related compounds.

	CHFICN	CH ⁷⁹ BrFCN ^a	CH ₂ ⁷⁹ BrCN ^b	CF ₃ CN ^c	CHF ₂ CN ^c	CH ₂ FCN ^c	CH ₃ CN ^d
X_{xx} (MHz)	1.87(10) ^e	2.00(21)	2.2966(2)	2.328(8)	2.2357(87)	1.8180(40)	2.112 36(40)
X_{yy} (MHz)	2.65(17)	2.49(19)	2.0160(6)	2.328(8)	2.3990(90)	2.7098(36)	2.112 36(40)
X_{zz} (MHz)	-4.517(73)	-4.49(14)	- 4.3126(22)	- 4.656(15)	-4.6347(87)	-4.5278(36)	-4.224 73(80)
η^f	0.171(45)	0.108(63)	-0.065 07(53)	0 ^g	0.0352(27)	0.1970(12)	0 ^g
θ_{za} (°)^h	49.05(59)	42.93(50)	34.4274(77)	0 ^g	11.254(20)	19.680(14)	0 ^g
θ_{CN, a} (°)ⁱ	47.8	43.0	34.0	0 ^g	10.2	18.9	0 ^g

^aReference 13.

^bReference 36.

^cReference 37.

^dReference 38.

^eNumbers in parentheses are the uncertainties in units of the least significant figure.

^fThe asymmetry of the χ tensor in the principal axes system, $\eta = (\chi_{xx} - \chi_{yy}) / \chi_{zz}$

^gBy symmetry.

^hThe angle between the z and a axes.

ⁱThe angle between the C≡N bond and the a axis.

Table 3.8: Transition frequencies and assignments for fluoroiodoacetonitrile.

										Obs.	o-c	error	
1	4	0	4	7	8	3	0	3	6	7	11128.5490	0.0017	0.010
2	4	0	4	7	7	3	0	3	6	6	11128.4562	-0.0047	0.010
3	4	1	4	7	8	3	1	3	6	7	10655.7109	-0.0117	0.010
4	4	1	3	7	8	3	1	2	6	7	11927.6850	-0.0011	0.010
5	4	1	3	6	6	3	1	2	5	5	11926.9122	0.0003	0.010
6	4	1	3	6	7	3	1	2	5	6	11926.6746	0.0004	0.010
7	4	1	3	2	3	3	1	2	1	2	11921.4427	-0.0014	0.010
8	4	0	4	6	6	3	0	3	5	5	11135.5130	0.0000	0.010
9	4	0	4	6	7	3	0	3	5	6	11135.6559	-0.0052	0.010
10	4	0	4	2	3	3	0	3	1	2	11080.0423	-0.0021	0.010
11	4	0	4	2	1	3	0	3	1	1	11080.2542	-0.0028	0.010
12	4	0	4	2	2	3	0	3	1	1	11079.7761	-0.0014	0.010
13	4	0	4	4	5	3	0	3	3	4	11057.7416	-0.0128	0.010
14	4	0	4	4	4	3	0	3	3	3	11057.6158	0.0015	0.010
15	4	1	4	6	6	3	1	3	5	5	10627.0059	0.0003	0.010
16	4	1	4	4	4	3	1	3	3	3	10579.0838	-0.0057	0.010
17	4	1	4	4	5	3	1	3	3	4	10579.3571	0.0057	0.010
18	4	1	4	3	4	3	1	3	2	3	10585.0408	0.0003	0.010
19	4	1	4	3	2	3	1	3	2	1	10585.2086	-0.0038	0.010
20	4	1	4	3	3	3	1	3	2	2	10584.7435	-0.0018	0.010
21	4	1	4	5	5	3	1	3	4	4	10599.4428	-0.0009	0.010
22	4	1	4	5	6	3	1	3	4	5	10599.7165	0.0133	0.010
23	4	1	4	4	4	3	1	3	4	4	10703.0081	-0.0048	0.010
24	4	1	4	4	5	3	1	3	4	5	10703.1173	-0.0051	0.010
25	4	1	4	3	3	3	1	3	3	3	10738.0391	0.0069	0.010
26	4	1	4	3	4	3	1	3	3	4	10738.2513	0.0039	0.010
27	4	1	4	2	3	3	1	3	2	3	10745.5837	0.0001	0.010
28	4	1	4	2	2	3	1	3	2	2	10745.1251	0.0041	0.010
29	4	0	4	3	3	3	0	3	2	2	11046.8192	-0.0088	0.010
30	4	0	4	3	4	3	0	3	2	3	11047.0169	-0.0065	0.010
31	4	0	4	3	2	3	0	3	2	1	11047.1053	-0.0110	0.010
32	4	2	3	6	7	3	2	2	5	6	11226.6747	0.0038	0.010
33	4	2	3	5	5	3	2	2	4	4	11230.0472	0.0010	0.010
34	4	2	3	5	6	3	2	2	4	5	11230.3468	0.0159	0.010
35	4	0	4	3	4	3	0	3	3	4	11243.4358	0.0063	0.010
36	4	0	4	3	3	3	0	3	3	3	11243.2978	0.0083	0.010
37	4	2	3	4	4	3	2	2	3	3	11309.0388	-0.0016	0.010
38	4	2	3	4	5	3	2	2	3	4	11309.5558	-0.0045	0.010
39	4	2	3	4	3	3	2	2	3	2	11309.7104	-0.0040	0.010
40	4	2	3	4	4	3	2	2	4	4	11313.1936	-0.0028	0.010
41	4	2	3	4	5	3	2	2	4	5	11313.7131	0.0041	0.010
42	4	2	3	4	3	3	2	2	4	3	11313.8636	0.0019	0.010
43	4	3	2	4	5	3	3	1	3	4	11355.1904	0.0089	0.010
44	4	3	1	4	5	3	3	0	3	4	11359.5948	-0.0056	0.010

										Obs.	o-c	error	
45	4	2	3	7	8	3	2	2	6	7	11376.3420	-0.0029	0.010
46	4	2	3	3	4	3	2	2	2	3	11404.9157	0.0030	0.010
47	4	2	3	3	3	3	2	2	2	2	11404.2385	-0.0006	0.010
48	4	2	3	2	3	3	2	2	2	3	11406.7265	-0.0066	0.010
49	4	2	3	2	3	3	2	2	1	2	11408.1842	0.0053	0.010
50	4	2	3	3	4	3	2	2	3	4	11410.3263	-0.0029	0.010
51	4	2	2	5	5	3	2	1	4	4	11413.6699	0.0134	0.010
52	4	2	2	5	6	3	2	1	4	5	11413.7398	-0.0104	0.010
53	4	2	2	6	7	3	2	1	5	6	11414.5709	0.0011	0.010
54	4	2	2	4	4	3	2	1	3	3	11467.0305	-0.0134	0.010
55	4	2	2	4	5	3	2	1	3	4	11467.1487	-0.0128	0.010
56	3	1	3	6	6	2	0	2	5	5	11475.6630	-0.0022	0.010
57	3	1	3	6	7	2	0	2	5	6	11476.0411	0.0071	0.010
58	3	1	3	2	3	2	0	2	2	3	11487.0202	-0.0057	0.010
59	4	2	2	3	3	3	2	1	2	2	11539.1781	-0.0026	0.010
60	4	2	2	3	4	3	2	1	2	3	11539.3042	0.0137	0.010
61	3	1	3	5	5	2	0	2	4	4	11545.9225	-0.0032	0.010
62	3	1	3	5	6	2	0	2	4	5	11546.4959	-0.0019	0.010
63	3	1	3	4	4	2	0	2	4	4	11549.8030	0.0002	0.010
64	3	1	3	4	5	2	0	2	4	5	11550.1007	0.0071	0.010
65	4	2	2	7	8	3	2	1	6	7	11554.7381	0.0115	0.010
66	3	1	3	3	4	2	0	2	3	4	11580.9812	0.0109	0.010
67	4	2	2	2	3	3	2	1	2	3	11599.6124	0.0049	0.010
68	2	2	0	3	4	2	1	1	4	5	11624.7440	0.0054	0.010
69	2	2	0	3	3	2	1	1	4	4	11624.5548	-0.0089	0.010
70	4	3	2	2	3	3	3	1	1	2	11659.7472	0.0055	0.010
71	4	3	1	2	3	3	3	0	1	2	11664.1139	-0.0044	0.010
72	2	2	1	4	5	2	1	1	4	5	11694.1291	-0.0033	0.010
73	4	1	3	6	7	3	1	2	6	7	11708.2693	-0.0048	0.010
74	4	1	3	6	6	3	1	2	6	6	11708.3978	-0.0005	0.010
75	2	2	0	4	5	2	1	1	4	5	11713.4706	-0.0033	0.010
76	4	1	3	5	6	3	1	2	4	5	11873.8429	-0.0068	0.010
77	4	1	3	4	5	3	1	2	4	5	11980.7227	-0.0034	0.010
78	2	1	1	5	4	1	0	1	4	3	10057.9548	0.0003	0.010
79	2	1	1	5	6	1	0	1	4	5	10058.0412	-0.0124	0.010
80	2	1	1	5	5	1	0	1	4	4	10058.4405	-0.0020	0.010
81	5	2	3	8	8	5	1	4	8	8	10169.8723	0.0061	0.010
82	5	2	3	8	9	5	1	4	8	9	10170.0224	0.0112	0.010
83	4	2	3	2	3	4	1	3	2	3	10182.4033	0.0076	0.010
84	5	2	3	4	5	5	1	4	4	5	10188.0991	-0.0018	0.010
85	5	2	3	5	6	5	1	4	5	6	10238.6035	-0.0033	0.010
86	5	2	3	7	8	5	1	4	7	8	10249.9035	0.0113	0.010
87	5	2	3	7	7	5	1	4	7	7	10249.7224	-0.0056	0.010
88	5	2	3	6	7	5	1	4	6	7	10268.9044	-0.0131	0.010
89	4	2	3	7	7	4	1	3	7	7	10275.2165	0.0073	0.010
90	4	2	3	7	8	4	1	3	7	8	10275.3771	0.0190	0.010
91	2	1	1	3	3	1	0	1	3	3	10313.9292	0.0043	0.010

											Obs.	o-c	error
92	2	1	1	3	4	1	0	1	3	4	10314.1170	0.0107	0.010
93	4	2	3	6	6	4	1	3	6	6	10362.1588	-0.0046	0.010
94	4	2	3	6	7	4	1	3	6	7	10362.5352	0.0024	0.010
95	4	2	3	4	4	4	1	3	4	4	10380.7762	0.0023	0.010
96	4	2	3	4	5	4	1	3	4	5	10381.2788	-0.0033	0.010
97	4	2	3	4	3	4	1	3	4	3	10381.4351	0.0019	0.010
98	4	2	3	5	5	4	1	3	5	5	10404.3243	-0.0001	0.010
99	4	2	3	5	6	4	1	3	5	6	10404.7780	-0.0023	0.010
100	4	2	3	5	4	4	1	3	5	4	10404.8719	-0.0130	0.010
101	2	1	1	2	2	1	0	1	3	3	10434.1995	0.0033	0.010
102	2	1	1	2	3	1	0	1	3	4	10434.4973	0.0069	0.010
103	2	1	1	2	1	1	0	1	3	2	10434.6866	0.0070	0.010
104	4	2	2	7	7	4	1	3	7	7	10544.1314	0.0021	0.010
105	4	2	2	7	8	4	1	3	7	8	10544.3037	0.0104	0.010
106	4	1	4	5	4	3	1	3	4	4	10599.9074	0.0086	0.010
107	4	1	4	2	3	3	1	3	1	2	10626.8929	0.0007	0.010
108	4	1	4	2	2	3	1	3	1	1	10626.5534	0.0038	0.010
109	4	1	4	6	7	3	1	3	5	6	10627.1858	0.0139	0.010
110	4	1	4	6	5	3	1	3	5	5	10627.6798	0.0080	0.010
111	4	2	2	4	5	4	1	3	4	5	10628.6215	0.0033	0.010
112	4	2	2	6	6	4	1	3	6	6	10646.0624	-0.0100	0.010
113	4	2	2	6	7	4	1	3	6	7	10646.3995	0.0166	0.010
114	4	2	2	5	6	4	1	3	5	6	10680.0878	-0.0056	0.010
115	4	2	2	5	5	4	1	3	5	5	10679.9602	-0.0025	0.010
116	3	2	2	1	2	3	1	2	1	2	10695.6695	0.0086	0.010
117	3	2	2	2	3	3	1	2	1	2	10697.1089	0.0022	0.010
118	4	1	4	3	2	3	1	3	3	2	10738.3349	-0.0049	0.010
119	3	2	2	6	6	3	1	2	6	6	10826.5009	0.0060	0.010
120	3	2	2	6	7	3	1	2	6	7	10826.6897	-0.0095	0.010
121	4	0	4	6	7	3	0	3	6	7	10833.0524	0.0162	0.010
122	3	2	1	2	3	3	1	2	2	3	10900.5420	0.0036	0.010
123	3	2	1	6	6	3	1	2	6	6	10917.0159	0.0050	0.010
124	3	2	1	6	7	3	1	2	6	7	10917.2592	0.0064	0.010
125	3	2	2	2	3	3	1	2	3	4	10948.3919	0.0033	0.010
126	3	2	2	2	2	3	1	2	3	3	10948.2965	-0.0042	0.010
127	2	2	1	1	2	2	1	1	2	3	10999.9982	0.0082	0.010
128	3	2	1	3	4	3	1	2	3	4	11032.7205	0.0136	0.010
129	3	2	2	6	6	3	1	2	5	5	11045.0054	-0.0030	0.010
130	3	2	2	4	4	3	1	2	4	4	11048.1928	0.0009	0.010
131	3	2	2	5	5	3	1	2	5	5	11062.4259	0.0001	0.010
132	4	0	4	5	6	3	0	3	5	6	11100.4600	-0.0183	0.010
133	4	0	4	5	5	3	0	3	5	5	11100.3833	-0.0063	0.010
134	4	0	4	5	5	3	0	3	5	4	11100.2598	-0.0100	0.010
135	4	0	4	5	5	3	0	3	4	4	11098.8537	-0.0027	0.010
136	5	0	5	5	4	4	1	4	4	3	11132.0745	-0.0040	0.010
137	5	0	5	6	7	4	1	4	5	6	11137.7904	-0.0067	0.010
138	3	2	1	4	5	3	1	2	4	5	11140.1758	-0.0172	0.010

											Obs.	o-c	error
139	5	0	5	4	4	4	1	4	3	3	11150.0009	-0.0061	0.010
140	5	0	5	4	5	4	1	4	3	4	11150.1480	-0.0018	0.010
141	3	2	1	5	6	3	1	2	5	6	11158.4944	0.0071	0.010
142	5	0	5	7	8	4	1	4	6	7	11169.1342	0.0041	0.010
143	5	0	5	7	7	4	1	4	6	6	11169.2926	-0.0012	0.010
144	4	3	2	6	6	3	3	1	5	5	11184.2194	0.0023	0.010
145	4	3	2	6	7	3	3	1	5	6	11184.3175	0.0067	0.010
146	4	3	1	6	6	3	3	0	5	5	11188.5598	0.0049	0.010
147	4	3	1	6	7	3	3	0	5	6	11188.6535	0.0077	0.010
148	5	0	5	8	9	4	1	4	7	8	11192.3042	0.0130	0.010
149	5	0	5	8	8	4	1	4	7	7	11192.4977	0.0115	0.010
150	4	3	2	5	6	3	3	1	4	5	11194.0454	-0.0045	0.010
151	4	3	1	5	6	3	3	0	4	5	11198.3987	-0.0046	0.010
152	5	1	5	3	4	3	2	2	2	3	11209.9582	0.0094	0.010
153	5	1	5	3	3	3	2	2	2	2	11210.1584	0.0175	0.010
154	4	2	3	5	5	3	2	2	5	4	11220.3857	0.0139	0.010
155	4	2	3	5	6	3	2	2	5	6	11220.6713	-0.0012	0.010
156	4	0	4	4	4	3	0	3	4	4	11220.7713	0.0071	0.010
157	4	0	4	4	5	3	0	3	4	5	11220.8617	-0.0104	0.010
158	2	2	1	5	4	2	1	1	5	4	11226.0011	0.0030	0.010
159	3	1	3	5	5	2	0	2	5	5	11237.1218	0.0131	0.010
160	3	1	3	5	6	2	0	2	5	6	11237.2376	-0.0076	0.010
161	2	2	0	5	6	2	1	1	5	6	11245.7304	0.0022	0.010
162	2	2	0	5	5	2	1	1	5	5	11245.8044	-0.0074	0.010
163	3	1	3	2	3	2	0	2	1	2	11298.2101	0.0026	0.010
164	3	1	3	2	2	2	0	2	1	1	11298.3225	-0.0065	0.010
165	2	2	1	2	3	2	1	1	3	4	11331.1398	-0.0004	0.010
166	2	2	1	2	2	2	1	1	3	3	11331.0392	0.0031	0.010
167	3	1	3	3	3	2	0	2	2	2	11333.5599	-0.0140	0.010
168	3	1	3	3	4	2	0	2	2	3	11333.8112	-0.0077	0.010
169	2	2	0	2	3	2	1	1	3	4	11351.4627	0.0038	0.010
170	2	2	0	2	2	2	1	1	3	3	11351.3293	0.0085	0.010
171	2	2	1	5	5	2	1	1	4	4	11361.2365	0.0015	0.010
172	2	2	0	5	6	2	1	1	4	5	11380.7506	0.0014	0.010
173	2	2	0	5	5	2	1	1	4	4	11381.0093	0.0085	0.010
174	4	2	2	5	5	3	2	1	5	5	11400.0301	-0.0099	0.010
175	4	2	3	3	3	3	2	2	3	3	11409.6454	0.0040	0.010
176	3	1	3	1	2	2	0	2	1	2	11416.9040	0.0051	0.010
177	3	1	3	4	5	2	0	2	3	4	11457.1861	-0.0130	0.010
178	4	3	2	3	4	3	3	1	2	3	11538.6097	-0.0064	0.010
179	4	3	1	3	4	3	3	0	2	3	11543.0588	0.0041	0.010
180	4	3	1	3	3	3	3	0	2	2	11543.1359	-0.0111	0.010
181	2	2	1	4	5	2	1	1	5	6	11559.1032	-0.0082	0.010
182	2	2	1	4	4	2	1	1	5	5	11558.9298	-0.0052	0.010
183	2	2	1	3	4	2	1	1	4	5	11604.8114	0.0030	0.010
184	2	2	1	3	3	2	1	1	4	4	11604.6575	-0.0007	0.010
185	4	1	3	5	4	3	1	2	5	4	11878.4183	-0.0026	0.010

											Obs.	o-c	error
186	2	2	0	5	5	2	1	2	5	5	12193.4965	0.0021	0.010
187	3	1	3	5	5	2	1	2	4	4	7957.1696	0.0028	0.010
188	3	1	3	5	6	2	1	2	4	5	7957.4672	-0.0021	0.010
189	3	1	3	4	5	2	1	2	4	5	7961.0560	-0.0091	0.010
190	4	0	4	3	4	3	1	3	2	3	8010.3226	0.0056	0.010
191	4	0	4	3	3	3	1	3	2	2	8010.0184	-0.0062	0.010
192	5	0	5	8	8	4	1	3	7	7	8016.2543	0.0035	0.010
193	5	0	5	8	9	4	1	3	7	8	8016.9720	0.0055	0.010
194	4	0	4	6	7	3	1	3	5	6	8018.5198	-0.0010	0.010
195	4	0	4	6	6	3	1	3	5	5	8018.6497	-0.0023	0.010
196	3	1	3	6	6	2	1	2	5	5	8036.5933	-0.0035	0.010
197	3	1	3	6	7	2	1	2	5	6	8036.7340	0.0000	0.010
198	3	1	3	3	3	2	1	2	3	3	8042.7444	0.0055	0.010
199	3	1	3	3	4	2	1	2	3	4	8042.9220	0.0013	0.010
200	3	1	3	2	2	2	1	2	2	2	8058.1409	-0.0035	0.010
201	3	1	3	2	3	2	1	2	2	2	8058.0179	-0.0052	0.010
202	3	1	3	2	3	2	1	2	2	3	8058.3497	-0.0048	0.010
203	4	0	4	2	3	3	1	3	1	2	8070.4885	0.0081	0.010
204	4	0	4	7	8	3	1	3	6	7	8075.2572	0.0139	0.010
205	4	0	4	7	7	3	1	3	6	6	8075.4500	-0.0016	0.010
206	3	1	3	1	2	2	1	2	1	2	8076.0297	0.0022	0.010
207	3	0	3	5	4	2	0	2	5	4	8120.0361	-0.0167	0.010
208	3	0	3	5	6	2	0	2	5	6	8120.1105	0.0054	0.010
209	3	0	3	5	5	2	0	2	5	5	8120.2437	-0.0041	0.010
210	3	1	3	1	2	2	1	2	2	2	8176.7242	0.0096	0.010
211	3	1	3	1	2	2	1	2	2	3	8177.0388	-0.0071	0.010
212	3	1	3	2	2	2	1	2	3	3	8196.0233	-0.0023	0.010
213	3	1	3	2	3	2	1	2	3	4	8196.1210	-0.0065	0.010
214	6	1	5	9	9	6	0	6	9	9	8230.5332	0.0049	0.010
215	6	1	5	9	10	6	0	6	9	10	8229.7420	-0.0174	0.010
216	3	0	3	3	3	2	0	2	2	2	8253.5879	-0.0080	0.010
217	3	0	3	3	4	2	0	2	2	3	8253.9103	-0.0030	0.010
218	3	0	3	3	2	2	0	2	2	1	8254.1513	-0.0042	0.010
219	3	0	3	2	3	2	0	2	1	2	8261.4983	-0.0026	0.010
220	6	1	5	6	7	6	0	6	6	7	8264.2735	-0.0082	0.010
221	6	1	5	8	9	6	0	6	8	9	8269.0193	-0.0144	0.010
222	3	0	3	4	5	2	0	2	3	4	8337.9468	0.0000	0.010
223	3	2	1	5	6	2	2	0	4	5	8354.7346	-0.0063	0.010
224	3	2	2	3	3	2	2	1	3	4	8361.9520	0.0125	0.010
225	3	2	2	3	3	2	2	1	3	3	8362.0529	0.0021	0.010
226	3	0	3	1	2	2	0	2	1	2	8407.3337	-0.0010	0.010
227	3	0	3	6	7	2	0	2	5	6	8422.7164	-0.0135	0.010
228	3	0	3	5	5	2	0	2	4	4	8429.0630	-0.0019	0.010
229	3	0	3	5	6	2	0	2	4	5	8429.3654	0.0078	0.010
230	3	2	1	4	5	2	2	0	3	4	8429.7552	-0.0054	0.010
231	3	2	1	4	4	2	2	0	3	3	8430.0134	-0.0039	0.010
232	3	0	3	4	4	2	0	2	4	4	8430.5998	0.0017	0.010

											Obs.	o-c	error
233	3	0	3	4	5	2	0	2	4	5	8430.8480	0.0066	0.010
234	3	2	1	3	2	2	2	0	3	2	8431.6364	-0.0058	0.010
235	3	2	1	3	4	2	2	0	3	4	8431.7522	0.0019	0.010
236	3	2	1	3	3	2	2	0	3	3	8431.9973	-0.0036	0.010
237	3	0	3	2	2	2	0	2	2	2	8450.0670	0.0097	0.010
238	3	0	3	2	3	2	0	2	2	3	8450.3145	-0.0048	0.010
239	3	0	3	2	2	2	0	2	2	1	8450.5722	-0.0004	0.010
240	3	0	3	3	4	2	0	2	3	4	8501.0626	-0.0019	0.010
241	3	2	2	6	6	2	2	1	5	5	8593.5576	-0.0037	0.010
242	3	2	2	6	7	2	2	1	5	6	8593.8091	0.0107	0.010
243	3	0	3	1	1	2	0	2	2	2	8595.8776	0.0100	0.010
244	3	0	3	1	2	2	0	2	2	3	8596.1512	-0.0019	0.010
245	3	2	2	3	2	2	2	1	2	1	8602.8918	0.0085	0.010
246	3	2	2	3	4	2	2	1	2	3	8603.0041	-0.0062	0.010
247	3	2	2	3	3	2	2	1	2	2	8603.1632	-0.0027	0.010
248	3	2	2	2	3	2	2	1	2	3	8608.4300	0.0031	0.010
249	3	2	2	5	5	2	2	1	5	5	8610.9796	0.0009	0.010
250	3	2	2	5	6	2	2	1	5	6	8611.2316	-0.0036	0.010
251	3	2	1	6	6	2	2	0	5	5	8664.3068	-0.0045	0.010
252	6	2	5	9	9	6	1	5	9	9	8666.5293	-0.0111	0.010
253	3	2	1	3	2	2	2	0	2	1	8672.2150	-0.0050	0.010
254	3	2	1	3	4	2	2	0	2	3	8672.4229	-0.0036	0.010
255	3	2	1	3	3	2	2	0	2	2	8672.7361	-0.0010	0.010
256	3	2	1	2	3	2	2	0	2	3	8679.2620	0.0034	0.010
257	3	2	1	5	5	2	2	0	5	5	8687.1940	-0.0026	0.010
258	3	2	1	5	6	2	2	0	5	6	8687.4800	0.0141	0.010
259	6	2	5	7	7	6	1	5	7	7	8733.5747	-0.0090	0.010
260	6	2	5	7	8	6	1	5	7	8	8733.8840	-0.0103	0.010
261	3	1	2	5	5	2	1	1	5	5	8774.5922	-0.0066	0.010
262	3	1	2	5	6	2	1	1	5	6	8774.7046	-0.0022	0.010
263	3	2	2	1	2	2	2	1	1	2	8817.7511	0.0038	0.010
264	3	2	2	2	3	2	2	1	1	2	8819.1897	-0.0032	0.010
265	2	1	2	3	2	1	0	1	2	1	8841.1267	0.0011	0.010
266	2	1	2	3	4	1	0	1	2	3	8841.2717	0.0000	0.010
267	2	1	2	3	3	1	0	1	2	2	8841.5546	-0.0035	0.010
268	3	1	2	3	2	2	1	1	2	1	8870.6248	-0.0041	0.010
269	3	1	2	3	4	2	1	1	2	3	8870.7952	0.0008	0.010
270	3	1	2	3	3	2	1	1	2	2	8871.0314	-0.0008	0.010
271	3	1	2	4	5	2	1	1	3	4	8881.6822	-0.0204	0.010
272	3	1	2	4	4	2	1	1	3	3	8881.8453	-0.0090	0.010
273	3	2	1	2	3	2	2	0	1	2	8890.7637	-0.0048	0.010
274	3	2	1	1	2	2	2	0	1	2	8893.8497	0.0014	0.010
275	3	1	2	5	6	2	1	1	4	5	8909.7374	0.0096	0.010
276	3	1	2	4	5	2	1	1	4	5	8914.3180	0.0118	0.010
277	3	1	2	2	3	2	1	1	1	2	8918.9911	-0.0005	0.010
278	2	1	2	4	5	1	0	1	4	5	8951.5446	0.0035	0.010
279	2	1	2	4	4	1	0	1	4	4	8951.6330	-0.0005	0.010

											Obs.	o-c	error
280	2	1	2	2	3	1	0	1	2	3	8979.0498	0.0050	0.010
281	2	1	2	2	2	1	0	1	2	2	8979.4199	-0.0194	0.010
282	3	1	2	3	4	2	1	1	3	4	8991.1654	-0.0130	0.010
283	3	1	2	3	3	2	1	1	3	3	8991.2927	-0.0108	0.010
284	3	1	2	6	6	2	1	1	5	5	8993.1071	-0.0052	0.010
285	3	1	2	2	3	2	1	1	2	3	9009.7918	-0.0029	0.010
286	3	1	2	2	2	2	1	1	2	2	9009.9977	0.0104	0.010
287	3	1	2	1	2	2	1	1	1	2	9031.2702	-0.0028	0.010
288	2	1	2	1	2	1	0	1	2	3	9080.0856	0.0222	0.010
289	2	1	2	5	6	1	0	1	4	5	9111.0855	0.0204	0.010
290	2	1	2	5	5	1	0	1	4	4	9110.7606	0.0006	0.010
291	3	1	2	1	2	2	1	1	2	3	9122.0784	0.0022	0.010
292	3	1	2	2	2	2	1	1	3	2	9130.1848	0.0086	0.010
293	2	1	2	4	4	1	0	1	3	3	9309.7970	-0.0010	0.010
294	2	1	2	4	5	1	0	1	3	4	9310.0246	0.0135	0.010
295	2	1	2	3	4	1	0	1	3	4	9351.9354	0.0087	0.010
296	2	1	2	3	3	1	0	1	3	3	9352.0244	-0.0018	0.010
297	5	2	4	5	6	5	1	4	4	5	9411.2843	0.0048	0.010
298	6	0	6	6	6	5	1	4	5	5	9454.0138	0.0024	0.010
299	6	0	6	7	8	5	1	4	6	7	9460.4171	-0.0090	0.010
300	6	0	6	7	6	5	1	4	6	5	9460.5353	0.0061	0.010
301	6	0	6	8	8	5	1	4	7	7	9472.0946	0.0008	0.010
302	6	0	6	8	9	5	1	4	7	8	9472.8309	-0.0076	0.010
303	6	0	6	8	7	5	1	4	7	6	9472.9396	-0.0023	0.010
304	2	1	2	2	3	1	0	1	3	4	9489.7099	0.0102	0.010
305	2	1	2	2	1	1	0	1	3	2	9489.4857	-0.0003	0.010
306	5	2	4	3	3	5	1	4	3	3	9490.3446	-0.0034	0.010
307	5	2	4	3	4	5	1	4	3	4	9490.5720	-0.0016	0.010
308	5	2	4	3	2	5	1	4	3	2	9490.6567	-0.0135	0.010
309	6	0	6	9	9	5	1	4	8	8	9517.8656	0.0009	0.010
310	6	0	6	4	5	5	1	4	3	4	9520.0401	-0.0070	0.010
311	5	2	4	8	8	5	1	4	8	8	9524.7255	0.0005	0.010
312	5	2	4	8	9	5	1	4	8	9	9525.0799	-0.0219	0.010
313	5	2	4	8	7	5	1	4	8	7	9525.1575	0.0125	0.010
314	5	2	4	4	5	5	1	4	4	5	9527.7041	-0.0083	0.010
315	5	2	4	5	6	5	1	4	5	6	9566.2979	-0.0191	0.010
316	5	2	4	7	7	5	1	4	7	7	9599.6834	-0.0025	0.010
317	5	2	4	7	8	5	1	4	7	8	9600.0400	0.0002	0.010
318	5	2	4	6	6	5	1	4	6	6	9621.5684	-0.0001	0.010
319	5	2	4	6	7	5	1	4	6	7	9621.9485	0.0180	0.010
320	6	0	6	5	5	5	1	4	5	5	9649.2308	0.0004	0.010
321	6	0	6	5	6	5	1	4	5	6	9649.8938	-0.0031	0.010
322	6	0	6	5	4	5	1	4	5	4	9650.0400	-0.0071	0.010
323	2	1	1	3	4	1	0	1	2	3	9803.4534	0.0021	0.010
324	7	2	5	5	6	7	1	6	5	6	9869.7250	0.0096	0.010
325	7	2	5	6	7	7	1	6	6	7	9895.7090	-0.0046	0.010
326	6	2	4	4	5	6	1	5	4	5	9899.4063	0.0010	0.010

											Obs.	o-c	error
327	7	2	5	7	6	7	1	6	7	6	9912.3252	0.0005	0.010
328	7	2	5	9	10	7	1	6	9	10	9920.8537	-0.0079	0.010
329	7	2	5	8	9	7	1	6	8	9	9922.1769	-0.0093	0.010
330	2	1	1	4	5	1	0	1	4	5	9923.0312	-0.0014	0.010
331	2	1	1	4	4	1	0	1	4	4	9923.2580	0.0044	0.010
332	2	1	1	2	2	1	0	1	2	1	9923.5951	-0.0198	0.010
333	2	1	1	2	3	1	0	1	2	3	9923.8356	0.0000	0.010
334	2	1	1	2	1	1	0	1	2	2	9924.0387	0.0040	0.010
335	6	2	4	9	10	6	1	5	9	10	9925.4142	0.0089	0.010
336	6	2	4	5	6	6	1	5	5	6	9936.4806	-0.0059	0.010
337	6	2	4	8	9	6	1	5	8	9	9971.7777	-0.0001	0.010
338	6	2	4	6	7	6	1	5	6	7	9974.9125	-0.0020	0.010
339	6	2	4	7	8	6	1	5	7	8	9992.9498	-0.0075	0.010
340	2	1	1	1	2	1	0	1	2	3	10014.6606	0.0219	0.010
341	4	1	3	3	3	3	1	2	3	3	12030.5523	0.0047	0.010
342	4	1	3	3	4	3	1	2	3	4	12030.6679	-0.0070	0.010
343	4	1	3	2	3	3	1	2	2	3	12033.7229	-0.0026	0.010
344	2	2	1	2	3	2	1	2	1	2	12054.5270	-0.0011	0.010
345	2	2	1	5	4	2	1	2	5	4	12172.8232	-0.0054	0.010
346	2	2	1	5	6	2	1	2	5	6	12173.0013	0.0051	0.010
347	2	2	1	5	5	2	1	2	5	5	12173.7287	0.0002	0.010
348	2	2	0	5	4	2	1	2	5	4	12192.5404	0.0014	0.010
349	2	2	0	5	6	2	1	2	5	6	12192.7187	0.0018	0.010
350	2	2	1	3	3	2	1	2	2	2	12396.1665	-0.0023	0.010
351	2	2	1	3	4	2	1	2	2	3	12396.6081	-0.0033	0.010
352	2	2	1	3	2	2	1	2	2	1	12396.9056	-0.0203	0.010
353	2	2	0	3	4	2	1	2	2	3	12416.5458	0.0041	0.010
354	2	2	1	4	5	2	1	2	3	4	12623.7081	-0.0003	0.010
355	2	2	0	4	4	2	1	2	3	3	12642.8579	-0.0021	0.010
356	2	2	0	4	5	2	1	2	3	4	12643.0410	-0.0090	0.010
357	3	2	1	2	3	3	1	3	1	2	12678.0882	0.0102	0.010
358	3	2	1	1	2	3	1	3	1	2	12681.1519	-0.0057	0.010
359	3	2	2	6	5	3	1	3	6	5	12729.9440	0.0007	0.010
360	3	2	2	6	7	3	1	3	6	7	12730.0619	0.0013	0.010
361	3	2	2	6	6	3	1	3	6	6	12730.6934	0.0004	0.010
362	3	2	1	3	4	3	1	3	2	3	12789.9338	-0.0034	0.010
363	3	2	1	6	5	3	1	3	6	5	12820.5108	0.0076	0.010
364	3	2	1	6	7	3	1	3	6	7	12820.6165	0.0024	0.010
365	3	2	1	6	6	3	1	3	6	6	12821.2063	-0.0025	0.010
366	3	2	1	3	4	3	1	3	3	4	12943.1526	0.0084	0.010
367	3	2	2	4	5	3	1	3	4	5	12973.0310	-0.0009	0.010
368	3	2	2	5	6	3	1	3	5	6	12986.2910	0.0049	0.010
369	3	2	2	5	5	3	1	3	5	5	12986.6749	0.0081	0.010
370	3	2	1	4	5	3	1	3	4	5	13064.9078	-0.0177	0.010
371	3	2	1	3	4	3	1	3	4	5	13066.9160	0.0006	0.010
372	3	2	1	3	3	3	1	3	4	4	13067.1566	0.0156	0.010
373	3	2	1	4	5	3	1	3	5	6	13068.5330	0.0116	0.010

											Obs.	o-c	error
374	3	2	1	5	6	3	1	3	5	6	13082.2363	-0.0009	0.010
375	3	2	1	5	5	3	1	3	5	5	13082.6490	-0.0016	0.010
376	3	1	2	5	4	2	0	2	5	4	13160.9072	-0.0008	0.010
377	3	1	2	5	6	2	0	2	5	6	13160.9919	-0.0033	0.010
378	3	1	2	5	5	2	0	2	5	5	13161.3481	-0.0016	0.010
379	5	1	5	3	4	4	1	4	2	3	13169.9870	0.0028	0.010
380	5	1	5	3	3	4	1	4	2	2	13170.4971	-0.0001	0.010
381	5	1	5	4	3	4	1	4	3	2	13174.9417	0.0107	0.010
382	5	1	5	4	5	4	1	4	3	4	13175.0519	0.0115	0.010
383	5	1	5	4	4	4	1	4	3	3	13175.3405	0.0148	0.010
384	5	1	5	5	4	4	1	4	4	3	13213.2657	-0.0102	0.010
385	5	1	5	6	7	4	1	4	6	7	13215.3074	0.0015	0.010
386	5	1	5	6	6	4	1	4	5	5	13238.9649	-0.0029	0.010
387	5	1	5	7	7	4	1	4	6	6	13239.0756	-0.0046	0.010
388	5	1	5	6	7	4	1	4	5	6	13239.1848	0.0061	0.010
389	5	1	5	7	8	4	1	4	6	7	13239.3180	0.0022	0.010
390	3	1	2	3	3	2	0	2	2	2	13244.0326	-0.0047	0.010
391	3	1	2	3	4	2	0	2	2	3	13244.2588	0.0025	0.010
392	3	1	2	3	2	2	0	2	2	1	13244.4398	-0.0162	0.010
393	5	1	5	8	9	4	1	4	7	8	13271.0804	-0.0143	0.010
394	3	1	2	1	2	2	0	2	1	2	13306.7182	-0.0016	0.010
395	5	1	5	3	4	4	1	4	3	4	13330.5195	-0.0077	0.010
396	5	1	5	4	3	4	1	4	4	3	13333.8364	-0.0002	0.010
397	5	1	5	4	5	4	1	4	4	5	13333.9433	0.0070	0.010
398	5	1	5	4	4	4	1	4	4	4	13334.2589	-0.0094	0.010
399	4	2	3	3	3	4	1	4	2	3	13364.2481	-0.0060	0.010
400	4	2	3	3	3	4	1	4	2	2	13364.5920	-0.0034	0.010
401	4	2	3	3	4	4	1	4	2	3	13364.9423	-0.0059	0.010
402	3	1	2	6	5	2	0	2	5	4	13379.2989	0.0020	0.010
403	3	1	2	6	7	2	0	2	5	6	13379.3950	-0.0002	0.010
404	3	1	2	6	6	2	0	2	5	6	13379.6016	-0.0061	0.010
405	3	1	2	6	6	2	0	2	5	5	13379.8620	-0.0012	0.010
406	3	1	2	4	5	2	0	2	3	4	13381.9435	0.0117	0.010
407	3	1	2	4	4	2	0	2	3	3	13382.0399	-0.0015	0.010
408	3	1	2	2	3	2	0	2	2	3	13383.2601	0.0032	0.010
409	4	2	3	4	4	4	1	4	3	3	13424.3698	-0.0003	0.010
410	4	2	3	7	6	4	1	4	7	6	13450.5705	0.0074	0.010
411	4	2	3	7	8	4	1	4	7	8	13450.6899	0.0070	0.010
412	4	2	3	7	7	4	1	4	7	7	13451.4585	0.0138	0.010
413	3	1	2	4	5	2	0	2	4	5	13474.8207	-0.0055	0.010
414	5	0	5	7	8	4	0	4	7	8	13482.2581	-0.0118	0.010
415	4	2	3	5	6	4	1	4	4	5	13500.2233	-0.0170	0.010
416	4	2	3	6	5	4	1	4	6	5	13585.6935	0.0115	0.010
417	4	2	3	6	7	4	1	4	6	7	13585.7853	0.0001	0.010
418	4	2	3	6	6	4	1	4	6	6	13586.3000	-0.0108	0.010
419	4	2	2	3	4	4	1	4	2	3	13590.4790	0.0027	0.010
420	4	2	2	3	3	4	1	4	2	2	13590.7765	-0.0059	0.010

											Obs.	o-c	error
421	4	2	3	5	6	4	1	4	5	6	13603.6529	-0.0065	0.010
422	4	1	4	3	4	3	0	3	2	3	13621.7566	0.0096	0.010
423	4	1	4	3	3	3	0	3	2	2	13621.5381	-0.0108	0.010
424	4	1	4	2	3	3	0	3	1	2	13636.4520	-0.0042	0.010
425	4	1	4	4	4	3	0	3	3	3	13659.0729	0.0052	0.010
426	4	1	4	4	5	3	0	3	3	4	13659.2435	-0.0135	0.010
427	4	1	4	7	7	3	0	3	6	6	13708.6622	0.0136	0.010
428	4	1	4	7	8	3	0	3	6	7	13709.0176	-0.0089	0.010
429	4	1	4	5	5	3	0	3	4	4	13718.6580	0.0095	0.010
430	4	2	2	7	6	4	1	4	7	6	13719.4960	-0.0058	0.010
431	4	2	2	7	8	4	1	4	7	8	13719.6222	0.0041	0.010
432	4	2	2	7	7	4	1	4	7	7	13720.3809	0.0161	0.010
433	5	0	5	6	7	4	0	4	6	7	13722.5699	-0.0052	0.010
434	5	0	5	4	4	4	0	4	3	3	13724.7369	0.0090	0.010
435	5	0	5	4	5	4	0	4	3	4	13724.8881	0.0146	0.010
436	5	0	5	5	5	4	0	4	4	4	13733.4532	0.0118	0.010
437	5	0	5	5	6	4	0	4	4	5	13733.5832	0.0077	0.010
438	5	0	5	3	3	4	0	4	2	2	13742.4808	-0.0103	0.010
439	5	0	5	3	4	4	0	4	2	3	13742.6453	0.0108	0.010
440	4	1	4	6	6	3	0	3	5	5	13743.8608	-0.0055	0.010
441	4	1	4	6	7	3	0	3	5	6	13744.3048	-0.0072	0.010
442	5	0	5	6	6	4	0	4	5	5	13757.6230	-0.0030	0.010
443	5	0	5	6	7	4	0	4	5	6	13757.7598	0.0018	0.010
444	5	0	5	8	9	4	0	4	7	8	13772.7707	0.0001	0.010
445	5	0	5	7	7	4	0	4	6	6	13777.6399	-0.0073	0.010
446	5	0	5	7	8	4	0	4	6	7	13777.7812	0.0002	0.010
447	4	1	4	3	4	3	0	3	3	4	13818.1378	-0.0152	0.010
448	4	1	4	4	5	3	0	3	4	5	13822.3663	-0.0083	0.010
449	4	1	4	4	4	3	0	3	4	4	13822.2174	-0.0002	0.010
450	4	2	2	4	4	4	1	4	4	4	13831.1726	0.0006	0.010
451	5	0	5	5	6	4	0	4	5	6	13855.4495	-0.0034	0.010
452	4	2	2	6	7	4	1	4	6	7	13869.6294	-0.0057	0.010
453	4	2	2	6	6	4	1	4	6	6	13870.2183	-0.0015	0.010
454	4	2	2	5	5	4	1	4	5	5	13879.3551	-0.0149	0.010
455	4	2	2	5	6	4	1	4	5	6	13878.9748	0.0021	0.010
456	5	0	5	4	4	4	0	4	4	4	13910.4037	0.0006	0.010
457	5	0	5	4	5	4	0	4	4	5	13910.5389	-0.0096	0.010
458	5	2	4	7	7	4	2	3	7	7	13930.0821	-0.0068	0.010
459	5	2	4	5	4	4	2	3	4	3	13984.2396	0.0151	0.010
460	5	2	4	5	6	4	2	3	4	5	13984.4023	0.0090	0.010
461	5	2	4	5	5	4	2	3	4	4	13984.9862	0.0138	0.010
462	5	2	4	8	8	4	2	3	7	7	14100.9587	-0.0028	0.010
463	5	2	4	8	9	4	2	3	7	8	14101.2179	0.0063	0.010
464	5	3	3	6	7	4	3	2	5	6	14107.2182	0.0118	0.010
465	5	3	3	7	8	4	3	2	6	7	14122.7653	0.0068	0.010
466	5	2	4	3	4	4	2	3	2	3	14132.2887	0.0089	0.010
467	5	3	2	7	8	4	3	1	6	7	14137.6155	0.0047	0.010

											Obs.	o-c	error
468	5	3	3	5	4	4	3	2	4	3	14160.6422	0.0085	0.010
469	6	0	6	4	3	4	2	3	3	2	14163.5231	-0.0138	0.010
470	6	0	6	4	4	4	2	3	3	3	14163.6395	-0.0167	0.010
471	5	2	3	5	6	4	2	2	4	5	14409.3631	0.0161	0.010
472	5	2	3	6	5	4	2	2	5	4	14410.7206	-0.0115	0.010
473	5	2	3	7	8	4	2	2	6	7	14428.5411	0.0031	0.010
474	5	2	3	8	9	4	2	2	7	8	14477.1853	-0.0002	0.010
475	5	2	3	3	4	4	2	2	2	3	14497.5099	-0.0130	0.010
476	5	1	4	4	5	4	1	3	3	4	14794.9647	-0.0065	0.010
477	5	1	4	4	4	4	1	3	3	3	14795.1280	0.0020	0.010
478	5	1	4	5	5	4	1	3	4	4	14799.4845	-0.0082	0.010
479	5	1	4	6	7	4	1	3	5	6	14821.9174	0.0021	0.010
480	5	1	4	3	4	4	1	3	2	3	14824.1053	0.0034	0.010
481	5	1	4	3	3	4	1	3	2	2	14824.2075	-0.0008	0.010
482	5	1	4	7	7	4	1	3	6	6	14824.8919	0.0015	0.010
483	5	1	4	7	8	4	1	3	6	7	14825.0203	-0.0083	0.010
484	5	2	3	4	5	5	1	5	4	5	15010.9045	0.0077	0.010
485	5	1	5	8	8	4	0	4	7	7	15851.2198	0.0001	0.010
486	5	1	5	8	9	4	0	4	7	8	15851.5769	0.0028	0.010
487	6	1	6	7	7	5	1	5	6	6	15857.6771	0.0122	0.010
488	6	1	6	6	6	5	1	5	5	5	15859.5853	0.0045	0.010
489	6	1	6	9	10	5	1	5	8	9	15873.8386	0.0168	0.010
490	6	1	6	5	6	5	1	5	4	5	15909.3242	-0.0109	0.010
491	6	1	6	8	9	5	1	5	7	8	15911.2982	0.0167	0.010
492	6	1	6	8	8	5	1	5	7	7	15911.4422	-0.0065	0.010
493	4	2	3	3	4	4	1	3	3	4	10322.6436	0.0172	0.010
494	4	1	4	6	7	3	1	3	6	7	10388.3846	0.0013	0.010
495	4	2	2	5	6	4	1	3	4	5	10573.2071	-0.0100	0.010
496	4	1	4	5	6	3	1	3	5	6	10603.3113	0.0123	0.010
497	7	1	6	9	9	6	2	4	8	8	10631.3011	-0.0035	0.010
498	4	2	3	6	7	3	2	2	6	7	11244.1043	-0.0033	0.010
499	8	0	8	1	11	7	1	6	1	10	11416.5022	-0.0041	0.010
			1					0					

Parameters in fit:

10000	A /MHz	5371.7732(13)	1
20000	B /MHz	1572.53001(37)	2
30000	C /MHz	1253.30275(34)	3
200	DelJ /kHz	0.3912(52)	4
1100	DelJK /kHz	-1.672(27)	5
2000	DelK /kHz	11.49(29)	6
40100	delJ /kHz	0.1144(23)	7
41000	delk /kHz	1.00(10)	8
110010000	Xaa /MHz	-1692.0710(65)	9
-110020000	Xbb /MHz	1692.0710(65) = -1.00000 *	9

110030000	Xcc /MHz	904.1345(70)		10
-110020000	Xbb /MHz	-904.1345(70)	= -1.00000 *	10
110610000	Xab /MHz	838.393(15)		11
110410000	Xac /MHz	682.369(41)		12
110210000	Xbc /MHz	-155.74(19)		13
220010000	Xaa /MHz	-0.7741(67)		14
-220020000	Xbb /MHz	0.7741(67)	= -1.00000 *	14
220030000	Xcc /MHz	1.8924(61)		15
-220020000	Xbb /MHz	-1.8924(61)	= -1.00000 *	15
220610000	Xab /MHz	-3.148(18)		16
220410000	Xac /MHz	-0.836(50)		17
220210000	Xbc /MHz	-1.46(25)		18
10010000	Maa /MHz	0.00503(48)		19
10020000	Maa /MHz	0.00570(31)		20
10030000	Maa /MHz	0.00527(25)		21

MICROWAVE AVG = -0.000062 MHz, IR AVG = 0.00000

MICROWAVE RMS = 0.007884 MHz, IR RMS = 0.00000

END OF ITERATION 1 OLD, NEW RMS ERROR = 0.78837, 0.78837

Distinct frequency lines in fit: 499

CHAPTER 4

CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF CHLOROPENTAFLUOROACETONE

4.1 Introduction

A study on the molecule chloropentafluoroacetone was done using chirped-pulse Fourier transform microwave spectroscopy. The two isotopes of chlorine, Cl-35 and Cl-37 were observed and 326 and 170 transitions were recorded, respectively. Chloropentafluoroacetone is a prolate type molecule in which B and C constants are in close agreement with each other.

Perfluorination is the act of replacing all the hydrogens with all the fluorines in a molecule. In the case of carbonyls, perfluorination is known to cause destabilization of the carbonyl carbons. Electron withdrawal from the carbonyl carbon by the carbonyl oxygen is opposed by the perfluoroalkyl group.

One could attempt to quantify this destabilizing effect by tagging the carbonyl carbon with, say, a chlorine center, and record the Cl NQCC. We have recently studied several acyl chlorides and perfluoroacyl chlorides.

The tensor, $\chi_{zz}(\text{Cl})$ for acyl chlorides is approximately -60 MHz and for perfluoroacyl chlorides is approximately -65 MHz. We have started mono- and di-chlorinating elsewhere in carbonyl compounds to further sample the electron distributions, i.e. $\text{ClF}_2(\text{C}=\text{O})\text{Cl}$.

4.2 Experimentation

The same spectrometer is used to study chloropentafluoroacetone as described for the previous molecule.

4.3 Quantum Chemistry Calculations

In order to assist with the quantum chemical calculations of chlorine in chloropentafluoroacetone, an MP2/6-311+G(3df) optimization with approximate r_e C-C, CF, and C=O and CCl bond lengths and by MP2/aug-cc-pVTZ optimization with approximate r_e C-C, CF and C=O and CCl bond lengths is done. For the C-C bond length, for example, linear regression analysis of MP2/6-311+G(3df) optimized bond lengths r_{opt} versus known experimental r_e bond lengths for a number of molecules yields $r_e(\text{\AA}) = 0.95172 \times r_{opt} + 0.07134$. In a similar manner, the C-C bond length obtained by the linear regression analysis of MP2/aug-cc-pVTZ yields $r_e(\text{\AA}) = 0.95547 \times r_{opt} + 0.06568$.

Table 4.1: ^{35}Cl nqcc's in chloropentafluoroacetone ($\text{CF}_2\text{Cl-C(=O)-CF}_3$) (MHz). Calculation was made on structures given by (1) MP2/6-311+G(3df) optimization and (2) MP2/aug-cc-pVTZ optimization, each with approximate r_e bond lengths.[39]

^{35}Cl	Calc (1)	Calc (2)	Expt [1]
χ_{aa}	12.08	12.99	13.206(24)
χ_{bb}	-12.93	-14.50	-15.011(32)
χ_{cc}	0.84	1.50	1.805(21)
χ_{ab}	-36.48	-36.29	-32.6(70)
χ_{ac}	-28.93	-27.97	-31.8(72)
χ_{bc}	-43.97	-44.15	-43.89(57)
RMS	1.47 (15%)	0.36(3.6%)	
RSD	0.49(1.1%)	0.49(1.1%)	
χ_{xx}	35.93	35.79	34(7)
χ_{yy}	39.39	39.36	40(7)
χ_{zz}	-75.32	-75.15	-75(6)
ETA	0.0460	0.0474	0.1(1)
$\phi_{z\text{CCl}}$	1.70	1.74	

Table 4.2: ^{37}Cl nqcc's in chloropentafluoroacetone ($\text{CF}_2\text{Cl-C(=O)-CF}_3$) (MHz). Calculation was made on structures given by (1) MP2/6-311+G(3df) optimization and (2) MP2/aug-cc-pVTZ optimization, each with approximate r_e bond lengths. [39]

^{37}Cl	Calc (1)	Calc (2)	Expt [1]
χ_{aa}	8.49	9.22	9.413(37)
χ_{bb}	-13.03	-14.17	-14.430(49)
χ_{cc}	4.54	4.94	5.017(32)
χ_{ab}	-30.40	-30.20	-34.0(97)
χ_{ac}	-21.71	-21.02	-16(21)
χ_{bc}	-33.43	-33.52	-33.0(11)
RMS	1.00(10%)	0.19(2.0%)	
RSD	0.44(1.1%)	0.44(1.1%)	
χ_{xx}	28.32	28.21	
χ_{yy}	31.04	31.02	
χ_{zz}	-59.36	-59.22	
ETA	0.0460	0.0474	
$\phi_{z,\text{CCl}}$	1.70	1.74	

Table 4.3: Selected parameters for chloropentafluoroacetone. r(1)= MP2/6-311+G(3df) optimization and r(2)= MP2/aug-cc-pVTZ optimization, each with approximate r_e bond lengths. [39]

Bond	Length r(1)	Length r(2)	Angle r(1)	Angle r(2)
C(1)-O	1.1943 Å	1.1945 Å		
C(1)-C(3)	1.5441 Å	1.5441 Å		
C(1)-C(4)	1.5402 Å	1.5394 Å		
C(4)-Cl	1.7574 Å	1.7574 Å		
C(3)-C(1)-C(4)			116.50°	116.72°
C(3)-C(1)-O			121.78°	121.65°
C(4)-C(1)-O			121.67°	121.62°
C(1)-C(4)-Cl			108.72°	108.49°
Cl-C(4)-C(1)-O			91.68°	92.48°

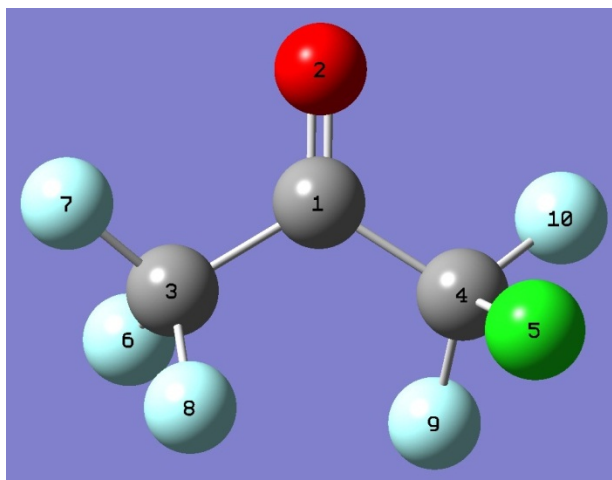


Figure 4.1: Point Group C_1

Table 4.4: Rotational constants for chloropentafluoroacetone. $r(1)$ = MP2/6-311+G(3df) optimization and $r(2)$ = MP2/aug-cc-pVTZ optimization, each with approximate r_e bond lengths. [39]

Parameter	$r(1)$	$r(2)$
A/MHz	1777.7	1776.9
B/MHz	861.3	862.6
C/MHz	826.6	826.5

Table 4.5: Transition frequencies and assignments for the observed Cl-35 isotope in chloropentafluoroacetone.

									Exp Freq	Calc. Freq	Diff	Exp Err	Est Err Avg
1	3	3	1	4	2	2	0	4	9683.39158	9683.40065	-0.00907	0.02500	0.00000
2	3	3	0	4	2	2	1	4	9684.4513	9684.45855	-0.00725	0.02500	0.00000
3	3	3	1	3	2	2	0	2	9686.20396	9686.20746	-0.0035	0.02500	0.00000
4	3	3	1	4	2	2	0	3	9686.54039	9686.5399	0.00049	0.02500	0.00000
5	3	3	1	2	2	2	0	1	9686.97948	9686.9773	0.00218	0.02500	0.00000
6	3	3	0	3	2	2	1	2	9687.2766	9687.27785	-0.00125	0.02500	0.00000
7	3	3	1	5	2	2	0	4	9687.46425	9687.46508	-0.00083	0.02500	0.00000
8	3	3	0	4	2	2	1	3	9687.71799	9687.7172	0.00079	0.02500	0.00000
9	3	3	0	2	2	2	1	1	9688.05316	9688.05133	0.00183	0.02500	0.00000
10	3	3	0	5	2	2	1	4	9688.52495	9688.52398	0.00097	0.02500	0.00000
11	3	3	0	3	2	2	1	3	9689.60979	9689.61011	-0.00032	0.02500	0.00000
12	3	3	1	2	2	2	0	2	9690.35917	9690.35818	0.00099	0.02500	0.00000
13	3	3	0	2	2	2	1	2	9691.42189	9691.42299	-0.0011	0.02500	0.00000
14	4	2	3	5	3	1	2	4	9372.8043	9372.80198	0.00232	0.02500	0.00000
15	4	2	3	4	3	1	2	3	9374.69299	9374.68873	0.00426	0.02500	0.00000
16	4	2	3	6	3	1	2	5	9376.23872	9376.23734	0.00138	0.02500	0.00000
17	4	2	3	3	3	1	2	2	9377.6028	9377.59385	0.00895	0.02500	0.00000
18	6	0	6	5	5	1	5	4	9287.01252	9287.01242	0.0001	0.02500	0.00000
19	6	0	6	8	5	1	5	7	9287.35889	9287.35813	0.00076	0.02500	0.00000
20	6	0	6	6	5	1	5	5	9288.70333	9288.70447	-0.00114	0.02500	0.00000
21	6	0	6	7	5	1	5	6	9289.11823	9289.1171	0.00113	0.02500	0.00000
22	5	1	5	6	4	0	4	5	9015.88296	9015.88131	0.00165	0.02500	0.00000
23	5	1	5	5	4	0	4	4	9016.72842	9016.72601	0.00241	0.02500	0.00000
24	5	1	5	7	4	0	4	6	9018.0807	9018.0795	0.0012	0.02500	0.00000
25	5	1	5	4	4	0	4	3	9018.85357	9018.85117	0.0024	0.02500	0.00000
26	3	2	2	4	2	1	1	3	7757.65683	7757.65491	0.00192	0.02500	0.00000
27	3	2	2	3	2	1	1	2	7760.86515	7760.86268	0.00247	0.02500	0.00000
28	3	2	2	5	2	1	1	4	7761.85688	7761.85542	0.00146	0.02500	0.00000
29	5	1	5	7	4	1	4	6	8250.92842	8250.9218	0.00662	0.02500	0.00000

										Exp Freq	Calc. Freq	Diff	Exp Err	Est Err Avg
30	7	1	7	8	6	2	4	7		8271.12532	8271.13486	-0.00954	0.02500	0.00000
31	7	1	7	7	6	2	4	6		8271.73913	8271.73964	-0.00051	0.02500	0.00000
32	7	1	7	9	6	2	4	8		8273.45766	8273.45106	0.0066	0.02500	0.00000
33	7	1	7	6	6	2	4	5		8273.97406	8273.97867	-0.00461	0.02500	0.00000
34	5	0	5	6	4	0	4	5		8325.49771	8325.49783	-0.00012	0.02500	0.00000
35	5	0	5	7	4	0	4	6		8325.6895	8325.70394	-0.01444	0.02500	0.00000
36	5	0	5	4	4	0	4	3		8325.95287	8325.95264	0.00023	0.02500	0.00000
37	5	2	3	4	4	2	2	3		8365.08427	8365.08112	0.00315	0.02500	0.00000
38	5	2	3	7	4	2	2	6		8365.22232	8365.21784	0.00448	0.02500	0.00000
39	5	2	3	5	4	2	2	4		8365.92602	8365.92793	-0.00191	0.02500	0.00000
40	5	2	3	6	4	2	2	5		8366.04364	8366.04121	0.00243	0.02500	0.00000
41	10	5	5	11	10	4	6	11		8407.05816	8407.05732	0.00084	0.02500	0.00000
42	10	5	5	10	10	4	6	10		8407.18611	8407.17982	0.00629	0.02500	0.00000
43	10	5	5	12	10	4	6	12		8407.92946	8407.93087	-0.00141	0.02500	0.00000
44	10	5	6	10	10	4	7	10		8408.05762	8408.0559	0.00172	0.02500	0.00000
45	10	5	6	12	10	4	7	12		8408.80262	8408.80059	0.00203	0.02500	0.00000
46	10	5	6	9	10	4	9	7		8408.92495	8408.9305	-0.00555	0.02500	0.00000
47	11	5	6	13	11	4	7	13		8401.39309	8401.39979	-0.0067	0.02500	0.00000
48	11	5	7	13	11	4	8	13		8403.26116	8403.25173	0.00943	0.02500	0.00000
49	9	5	4	10	9	4	5	10		8411.68489	8411.68626	-0.00137	0.02500	0.00000
50	9	5	4	9	9	4	5	9		8411.83919	8411.84852	-0.00933	0.02500	0.00000
51	9	5	5	10	9	4	6	10		8412.05786	8412.06499	-0.00713	0.02500	0.00000
52	9	5	5	9	9	4	6	9		8412.22105	8412.22607	-0.00502	0.02500	0.00000
53	9	5	4	11	9	4	5	11		8412.72806	8412.72832	-0.00026	0.02500	0.00000
54	9	5	4	8	9	4	5	8		8412.90348	8412.89931	0.00417	0.02500	0.00000
55	9	5	5	11	9	4	6	11		8413.09943	8413.10263	-0.0032	0.02500	0.00000
56	9	5	5	8	9	4	6	8		8413.28159	8413.27347	0.00812	0.02500	0.00000
57	8	5	3	9	8	4	4	9		8414.91233	8414.91172	0.00061	0.02500	0.00000
58	8	5	4	8	8	4	5	8		8415.14578	8415.1555	-0.00972	0.02500	0.00000
59	8	5	3	10	8	4	4	10		8416.10958	8416.11331	-0.00373	0.02500	0.00000
60	8	5	4	10	8	4	5	10		8416.23555	8416.24037	-0.00482	0.02500	0.00000

									Exp Freq	Calc. Freq	Diff	Exp Err	Est Err Avg
61	8	5	3	7	8	4	4	7	8416.40821	8416.42948	-0.02127	0.02500	0.00000
62	8	5	4	7	8	4	5	7	8416.56228	8416.57385	-0.01157	0.02500	0.00000
63	8	5	3	7	8	4	4	7	8416.40821	8416.42948	-0.02127	0.02500	0.00000
64	8	5	4	7	8	4	5	7	8416.56228	8416.57385	-0.01157	0.02500	0.00000
65	7	5	3	8	7	4	4	8	8417.09297	8417.08254	0.01043	0.02500	0.00000
66	6	5	1	7	6	4	2	7	8418.24833	8418.23751	0.01082	0.02500	0.00000
67	5	5	0	5	5	4	1	5	8419.49465	8419.49243	0.00222	0.02500	0.00000
68	6	5	1	8	6	4	2	8	8420.42588	8420.41744	0.00844	0.02500	0.00000
69	5	5	0	7	5	4	1	7	8421.65737	8421.65454	0.00283	0.02500	0.00000
70	5	5	0	4	5	4	1	4	8422.51159	8422.51173	-0.00014	0.02500	0.00000
71	5	1	4	4	4	1	3	3	8433.40116	8433.40241	-0.00125	0.02500	0.00000
72	5	1	4	5	4	1	3	4	8433.56436	8433.56356	0.0008	0.02500	0.00000
73	8	2	6	7	7	3	5	6	8839.35023	8839.35479	-0.00456	0.02500	0.00000
74	8	2	6	10	7	3	5	9	8839.65676	8839.65577	0.00099	0.02500	0.00000
75	8	2	6	8	7	3	5	7	8841.36016	8841.36261	-0.00245	0.02500	0.00000
76	8	2	6	9	7	3	5	8	8841.69724	8841.69555	0.00169	0.02500	0.00000
77	5	1	5	5	4	0	4	5	9015.69792	9015.70197	-0.00405	0.02500	0.00000
78	7	1	6	6	6	2	5	5	9363.85838	9363.85468	0.0037	0.02500	0.00000
79	7	1	6	9	6	2	5	8	9364.28789	9364.29155	-0.00366	0.02500	0.00000
80	7	1	6	7	6	2	5	6	9366.49175	9366.49404	-0.00229	0.02500	0.00000
81	7	1	6	8	6	2	5	7	9366.99757	9366.99929	-0.00172	0.02500	0.00000
82	4	2	3	4	3	1	2	4	9372.3355	9372.33981	-0.00431	0.02500	0.00000
83	4	2	3	3	3	1	2	3	9373.40524	9373.41505	-0.00981	0.02500	0.00000
84	4	2	2	3	3	1	3	3	9609.33865	9609.34195	-0.0033	0.02500	0.00000
85	4	2	2	3	3	1	3	2	9609.98856	9609.99042	-0.00186	0.02500	0.00000
86	4	2	2	6	3	1	3	5	9610.09606	9610.09671	-0.00065	0.02500	0.00000
87	4	2	2	4	3	1	3	3	9610.93179	9610.93995	-0.00816	0.02500	0.00000
88	4	2	2	5	3	1	3	4	9611.62206	9611.62643	-0.00437	0.02500	0.00000
89	4	2	2	5	3	1	3	5	9611.81994	9611.82666	-0.00672	0.02500	0.00000
90	8	1	8	9	7	2	5	8	9726.20312	9726.20057	0.00255	0.02500	0.00000
91	8	1	8	8	7	2	5	7	9726.81476	9726.82812	-0.01336	0.02500	0.00000

										Exp Freq	Calc. Freq	Diff	Exp Err	Est Err Avg
92	8	1	8	10	7	2	5	9		9729.00227	9728.99936	0.00291	0.02500	0.00000
93	8	1	8	7	7	2	5	6		9729.52316	9729.52387	-0.00071	0.02500	0.00000
94	6	0	6	7	5	0	5	6		9979.49956	9979.50059	-0.00103	0.02500	0.00000
95	6	0	6	6	5	0	5	5		9979.66154	9979.67711	-0.01557	0.02500	0.00000
96	6	0	6	8	5	0	5	7		9979.74443	9979.73369	0.01074	0.02500	0.00000
97	6	0	6	5	5	0	5	4		9979.9094	9979.91094	-0.00154	0.02500	0.00000
98	6	2	5	5	5	2	4	4		10011.18992	10011.18798	0.00194	0.02500	0.00000
99	6	2	5	7	5	2	4	6		10011.52847	10011.52172	0.00675	0.02500	0.00000
100	6	3	4	5	5	3	3	4		10020.95954	10020.96421	-0.00467	0.02500	0.00000
101	6	3	4	8	5	3	3	7		10021.16109	10021.16164	-0.00055	0.02500	0.00000
102	6	3	4	6	5	3	3	5		10021.84803	10021.85108	-0.00305	0.02500	0.00000
103	6	3	3	8	5	3	2	7		10022.23854	10022.24749	-0.00895	0.02500	0.00000
104	6	3	3	7	5	3	2	6		10023.132	10023.1359	-0.0039	0.02500	0.00000
105	6	2	4	7	5	2	3	6		10048.10803	10048.11513	-0.0071	0.02500	0.00000
106	6	5	2	5	5	5	1	4		10017.17721	10017.17361	0.0036	0.02500	0.00000
107	6	5	2	8	5	5	1	7		10017.97412	10017.97296	0.00116	0.02500	0.00000
108	6	4	3	5	5	4	2	4		10018.77688	10018.77481	0.00207	0.02500	0.00000
109	6	4	2	8	5	4	1	7		10019.20366	10019.21011	-0.00645	0.02500	0.00000
110	6	5	2	6	5	5	1	5		10019.5654	10019.56868	-0.00328	0.02500	0.00000
111	6	4	2	6	5	4	1	5		10020.27812	10020.28703	-0.00891	0.02500	0.00000
112	6	3	4	7	5	3	3	6		10022.03975	10022.03451	0.00524	0.02500	0.00000
113	6	3	3	6	5	3	2	5		10022.95029	10022.94858	0.00171	0.02500	0.00000
114	6	2	4	8	5	2	3	7		10047.56415	10047.55484	0.00931	0.02500	0.00000
115	6	1	5	8	5	1	4	7		10116.59553	10116.59225	0.00328	0.02500	0.00000
116	10	3	8	11	9	4	5	10		10173.01639	10173.01394	0.00245	0.02500	0.00000
117	10	3	8	10	9	4	5	9		10172.89024	10172.89017	0.00007	0.02500	0.00000
118	10	3	7	12	9	4	6	11		10205.10874	10205.11486	-0.00612	0.02500	0.00000
119	9	2	8	11	8	3	5	10		10257.46063	10257.45945	0.00118	0.02500	0.00000
120	9	2	8	9	8	3	5	8		10257.73597	10257.73816	-0.00219	0.02500	0.00000
121	10	6	4	11	10	5	5	11		10285.29701	10285.28996	0.00705	0.02500	0.00000
122	10	6	5	10	10	5	6	10		10285.47606	10285.48636	-0.0103	0.02500	0.00000

									Exp Freq	Calc. Freq	Diff	Exp Err	Est Err Avg
123	10	6	4	12	10	5	5	12	10286.3543	10286.34699	0.00731	0.02500	0.00000
124	9	6	3	10	9	5	4	10	10287.49925	10287.49774	0.00151	0.02500	0.00000
125	9	6	4	9	9	5	5	9	10287.7108	10287.70966	-0.00114	0.02500	0.00000
126	9	6	3	11	9	5	4	11	10288.75332	10288.74897	0.00435	0.02500	0.00000
127	7	6	1	8	7	5	2	8	10289.9329	10289.93471	0.00181	0.02500	0.00000
128	6	6	0	7	6	5	1	7	10290.32762	10290.33118	0.00356	0.02500	0.00000
129	8	6	2	7	8	5	3	7	10290.83388	10290.83656	0.00268	0.02500	0.00000
130	7	6	1	9	7	5	2	9	10291.90823	10291.91207	0.00384	0.02500	0.00000
131	7	6	1	6	7	5	2	6	10292.30463	10292.30492	0.00029	0.02500	0.00000
132	6	6	0	8	6	5	1	8	10292.94382	10292.94672	0.0029	0.02500	0.00000
133	6	6	0	5	6	5	1	5	10293.5681	10293.5659	-0.0022	0.02500	0.00000
134	6	1	6	7	5	0	5	6	10588.90664	10588.90518	-0.00146	0.02500	0.00000
135	6	1	6	6	5	0	5	5	10589.50595	10589.50568	-0.00027	0.02500	0.00000
136	6	1	6	8	5	0	5	7	10590.85256	10590.8534	0.00084	0.02500	0.00000
137	6	1	6	5	5	0	5	4	10591.4072	10591.40612	-0.00108	0.02500	0.00000
138	9	2	7	8	8	3	6	7	10592.68411	10592.69206	0.00795	0.02500	0.00000
139	9	2	7	11	8	3	6	10	10592.93792	10592.93688	0.00104	0.02500	0.00000
140	9	2	7	9	8	3	6	8	10594.61715	10594.6222	-0.00505	0.02500	0.00000
141	9	2	7	10	8	3	6	9	10594.91177	10594.90795	0.00382	0.02500	0.00000
142	5	2	4	4	4	1	3	4	10968.64458	10968.65962	-0.01504	0.02500	0.00000
143	5	2	4	5	4	1	3	5	10968.76891	10968.75948	0.00943	0.02500	0.00000
144	5	2	4	6	4	1	3	5	10969.31165	10969.30955	0.0021	0.02500	0.00000
145	5	2	4	5	4	1	3	4	10970.57145	10970.56761	0.00384	0.02500	0.00000
146	5	2	4	7	4	1	3	6	10972.30761	10972.30681	0.0008	0.02500	0.00000
147	5	2	4	4	4	1	3	3	10973.33463	10973.33292	0.00171	0.02500	0.00000
148	7	0	7	6	6	1	6	5	11017.07874	11017.07657	0.00217	0.02500	0.00000
149	7	0	7	9	6	1	6	8	11017.32501	11017.32395	0.00106	0.02500	0.00000
150	7	0	7	7	6	1	6	6	11018.49043	11018.49014	0.00029	0.02500	0.00000
151	7	0	7	8	6	1	6	7	11018.78211	11018.78009	0.00202	0.02500	0.00000
152	9	1	9	10	8	2	6	9	11134.31945	11134.31015	0.0093	0.02500	0.00000
153	8	1	7	7	7	2	6	6	11163.87899	11163.87462	0.00437	0.02500	0.00000

	Exp Freq									Calc. Freq	Diff	Exp Err	Est Err Avg
154	8	1	7	10	7	2	6	9	11164.26088	11164.25863	0.00225	0.02500	0.00000
155	8	1	7	8	7	2	6	7	11166.3061	11166.30626	-0.00016	0.02500	0.00000
156	8	1	7	9	7	2	6	8	11166.68092	11166.68095	-0.00003	0.02500	0.00000
157	4	3	2	5	3	2	1	4	11353.31095	11353.31106	-0.00011	0.02500	0.00000
158	4	3	2	4	3	2	1	3	11353.804	11353.80539	-0.00139	0.02500	0.00000
159	4	3	2	6	3	2	1	5	11354.62881	11354.62832	0.00049	0.02500	0.00000
160	4	3	2	3	3	2	1	2	11355.07304	11355.07383	-0.00079	0.02500	0.00000
161	4	3	1	5	3	2	2	4	11358.96732	11358.96837	-0.00105	0.02500	0.00000
162	4	3	1	4	3	2	2	3	11359.32352	11359.3238	-0.00028	0.02500	0.00000
163	4	3	1	6	3	2	2	5	11360.04218	11360.04079	0.00139	0.02500	0.00000
164	4	3	1	3	3	2	2	2	11360.43933	11360.437	0.00233	0.02500	0.00000
165	5	2	3	4	4	1	4	3	11372.79422	11372.79363	0.00059	0.02500	0.00000
166	5	2	3	7	4	1	4	6	11373.12734	11373.12655	0.00079	0.02500	0.00000
167	5	2	3	5	4	1	4	4	11374.48228	11374.48393	-0.00165	0.02500	0.00000
168	5	2	3	6	4	1	4	5	11375.10162	11375.10462	-0.003	0.02500	0.00000
169	7	1	7	9	6	1	6	8	11544.73841	11544.73365	0.00476	0.02500	0.00000
170	7	0	7	8	6	0	6	7	11628.19008	11628.18614	0.00394	0.02500	0.00000
171	7	0	7	7	6	0	6	6	11628.3204	11628.31898	0.00142	0.02500	0.00000
172	7	0	7	9	6	0	6	8	11628.44592	11628.44282	0.0031	0.02500	0.00000
173	7	0	7	6	6	0	6	5	11628.57625	11628.57283	0.00342	0.02500	0.00000
174	7	2	6	9	6	2	5	8	11677.09992	11677.08975	0.01017	0.02500	0.00000
175	7	6	1	9	6	6	0	8	11687.68395	11687.68962	-0.00567	0.02500	0.00000
176	7	5	3	6	6	5	2	5	11688.33777	11688.33942	-0.00165	0.02500	0.00000
177	7	5	3	9	6	5	2	8	11688.72212	11688.72496	-0.00284	0.02500	0.00000
178	7	5	3	7	6	5	2	6	11689.83189	11689.83324	-0.00135	0.02500	0.00000
179	7	2	5	8	6	2	4	7	11734.51942	11734.52139	-0.00197	0.02500	0.00000
180	7	1	7	8	6	0	6	7	12154.14873	12154.14381	0.00492	0.02500	0.00000
181	7	1	7	7	6	0	6	6	12154.57552	12154.5827	-0.00718	0.02500	0.00000
182	7	1	7	9	6	0	6	8	12155.85403	12155.85252	0.00151	0.02500	0.00000
183	7	1	7	6	6	0	6	5	12156.26384	12156.26326	0.00058	0.02500	0.00000
184	12	7	5	13	12	6	6	13	12155.49907	12155.48982	0.00925	0.02500	0.00000

	Exp Freq									Calc. Freq	Diff	Exp Err	Est Err Avg
185	12	7	5	12	12	6	6	12	12155.62619	12155.61091	0.01528	0.02500	0.00000
186	11	7	4	11	11	6	5	11	12157.93075	12157.92472	0.00603	0.02500	0.00000
187	11	7	4	13	11	6	5	13	12158.79048	12158.79393	-0.00345	0.02500	0.00000
188	10	7	3	11	10	6	4	11	12159.49582	12159.4966	-0.00078	0.02500	0.00000
189	10	7	3	10	10	6	4	10	12159.64043	12159.63648	0.00395	0.02500	0.00000
190	8	7	1	9	8	6	2	9	12161.48663	12161.49132	-0.00469	0.02500	0.00000
191	9	7	2	11	9	6	3	11	12162.16447	12162.16623	-0.00176	0.02500	0.00000
192	8	7	1	10	8	6	2	10	12163.31144	12163.30696	0.00448	0.02500	0.00000
193	8	7	1	7	8	6	2	7	12163.62274	12163.62385	-0.00111	0.02500	0.00000
194	7	7	0	9	7	6	1	9	12164.19783	12164.20137	-0.00354	0.02500	0.00000
195	6	2	5	7	5	1	4	6	12547.60173	12547.603	-0.00127	0.02500	0.00000
196	6	2	5	6	5	1	4	5	12548.53776	12548.53811	-0.00035	0.02500	0.00000
197	6	2	5	8	5	1	4	7	12550.35124	12550.35304	-0.0018	0.02500	0.00000
198	6	2	5	5	5	1	4	4	12551.11552	12551.11848	-0.00296	0.02500	0.00000
199	8	0	8	7	7	1	7	6	12744.24219	12744.24158	0.00061	0.02500	0.00000
200	8	0	8	10	7	1	7	9	12744.42262	12744.42217	0.00045	0.02500	0.00000
201	8	0	8	8	7	1	7	7	12745.40144	12745.40334	-0.0019	0.02500	0.00000
202	8	0	8	9	7	1	7	8	12745.60543	12745.60702	-0.00159	0.02500	0.00000
203	9	1	8	8	8	2	7	7	12975.30699	12975.30638	0.00061	0.02500	0.00000
204	9	1	8	11	8	2	7	10	12975.60491	12975.60634	-0.00143	0.02500	0.00000
205	9	1	8	9	8	2	7	8	12977.52463	12977.52666	-0.00203	0.02500	0.00000
206	9	1	8	10	8	2	7	9	12977.84131	12977.84425	-0.00294	0.02500	0.00000
207	5	3	3	6	4	2	2	5	13016.35572	13016.35787	-0.00215	0.02500	0.00000
208	5	3	3	5	4	2	2	4	13016.84773	13016.84743	0.0003	0.02500	0.00000
209	5	3	3	7	4	2	2	6	13017.62964	13017.62929	0.00035	0.02500	0.00000
210	5	3	3	4	4	2	2	3	13018.06282	13018.0622	0.00062	0.02500	0.00000
211	5	3	2	6	4	2	3	5	13033.17405	13033.17432	-0.00027	0.02500	0.00000
212	5	3	2	5	4	2	3	4	13033.49024	13033.48879	0.00145	0.02500	0.00000
213	5	3	2	7	4	2	3	6	13034.02877	13034.02701	0.00176	0.02500	0.00000
214	5	3	2	4	4	2	3	3	13034.36766	13034.36668	0.00098	0.02500	0.00000
215	6	2	4	5	5	1	5	4	13169.29392	13169.29701	-0.00309	0.02500	0.00000

									Exp Freq	Calc. Freq	Diff	Exp Err	Est Err Avg
216	6	2	4	8	5	1	5	7	13169.76075	13169.75959	0.00116	0.02500	0.00000
217	6	2	4	6	5	1	5	5	13171.54646	13171.54753	-0.00107	0.02500	0.00000
218	6	2	4	7	5	1	5	6	13172.1285	13172.12605	0.00245	0.02500	0.00000
219	8	1	8	8	7	1	7	7	13189.59251	13189.60554	-0.01303	0.02500	0.00000
220	4	4	1	4	3	3	0	3	13228.13958	13228.1286	0.01098	0.02500	0.00000
221	4	4	0	4	3	3	1	3	13228.13958	13228.15356	-0.01398	0.02500	0.00000
222	4	4	1	5	3	3	0	4	13228.44376	13228.43054	0.01322	0.02500	0.00000
223	4	4	0	5	3	3	1	4	13228.44376	13228.45221	-0.00845	0.02500	0.00000
224	4	4	1	3	3	3	0	2	13228.63556	13228.62457	0.01099	0.02500	0.00000
225	4	4	0	3	3	3	1	2	13228.63556	13228.64394	-0.00838	0.02500	0.00000
226	4	4	1	6	3	3	0	5	13228.94958	13228.93639	0.01319	0.02500	0.00000
227	4	4	0	6	3	3	1	5	13228.94958	13228.95906	-0.00948	0.02500	0.00000
228	8	0	8	9	7	0	7	8	13271.5591	13271.56469	-0.00559	0.02500	0.00000
229	8	0	8	8	7	0	7	7	13271.66946	13271.66706	0.0024	0.02500	0.00000
230	8	0	8	10	7	0	7	9	13271.82552	13271.83187	-0.00635	0.02500	0.00000
231	8	0	8	7	7	0	7	6	13271.92727	13271.93201	-0.00474	0.02500	0.00000
232	8	7	1	10	7	7	0	9	13357.40413	13357.40646	-0.00233	0.02500	0.00000
233	8	6	2	7	7	6	1	6	13357.97576	13357.97437	0.00139	0.02500	0.00000
234	8	6	2	10	7	6	1	9	13358.30171	13358.30087	0.00084	0.02500	0.00000
235	8	5	4	9	7	5	3	8	13360.65089	13360.64896	0.00193	0.02500	0.00000
236	8	4	5	7	7	4	4	6	13361.91696	13361.91451	0.00245	0.02500	0.00000
237	8	4	5	9	7	4	4	8	13362.67507	13362.67386	0.00121	0.02500	0.00000
238	8	3	6	9	7	3	5	8	13365.4963	13365.50281	-0.00651	0.02500	0.00000
239	8	3	5	9	7	3	4	8	13370.3833	13370.3951	-0.0118	0.02500	0.00000
240	8	2	6	10	7	2	5	9	13424.57171	13424.57031	0.0014	0.02500	0.00000
241	8	1	8	9	7	0	7	8	13715.54427	13715.54476	-0.00049	0.02500	0.00000
242	8	1	8	8	7	0	7	7	13715.87387	13715.86926	0.00461	0.02500	0.00000
243	8	1	8	10	7	0	7	9	13717.023	13717.0202	0.0028	0.02500	0.00000
244	8	1	8	7	7	0	7	6	13717.33035	13717.32854	0.00181	0.02500	0.00000
245	7	2	6	8	6	1	5	7	14108.31291	14108.31407	-0.00116	0.02500	0.00000
246	7	2	6	7	6	1	5	6	14109.01582	14109.01478	0.00104	0.02500	0.00000

									Exp Freq	Calc. Freq	Diff	Exp Err	Est Err Avg
247	7	2	6	9	6	1	5	8	14110.85303	14110.85054	0.00249	0.02500	0.00000
248	7	2	6	6	6	1	5	5	14111.49845	14111.50178	-0.00333	0.02500	0.00000
249	11	2	9	13	10	3	8	12	14171.09236	14171.08651	0.00585	0.02500	0.00000
250	11	2	9	10	10	3	8	9	14170.86002	14170.86438	-0.00436	0.02500	0.00000
251	9	0	9	8	8	1	8	7	14465.06128	14465.05933	0.00195	0.02500	0.00000
252	9	0	9	11	8	1	8	10	14465.1974	14465.19087	0.00653	0.02500	0.00000
253	9	0	9	9	8	1	8	8	14465.99473	14465.99142	0.00331	0.02500	0.00000
254	9	0	9	10	8	1	8	9	14466.13845	14466.1324	0.00605	0.02500	0.00000
255	6	3	4	7	5	2	3	6	14672.3492	14672.35117	-0.00197	0.02500	0.00000
256	6	3	4	6	5	2	3	5	14672.76986	14672.77058	-0.00072	0.02500	0.00000
257	6	3	4	8	5	2	3	7	14673.57279	14673.57309	-0.0003	0.02500	0.00000
258	6	3	4	5	5	2	3	4	14673.94399	14673.94529	-0.0013	0.02500	0.00000
259	6	3	3	7	5	2	4	6	14711.5068	14711.50999	-0.00319	0.02500	0.00000
260	6	3	3	6	5	2	4	5	14711.72245	14711.72504	-0.00259	0.02500	0.00000
261	6	3	3	8	5	2	4	7	14712.09915	14712.09937	-0.00022	0.02500	0.00000
262	6	3	3	5	5	2	4	4	14712.33664	14712.33667	-0.00003	0.02500	0.00000
263	5	4	2	6	4	3	1	5	14897.67151	14897.6709	0.00061	0.02500	0.00000
264	5	4	1	5	4	3	2	4	14898.00267	14898.00278	-0.00011	0.02500	0.00000
265	5	4	2	7	4	3	1	6	14898.53235	14898.52904	0.00331	0.02500	0.00000
266	5	4	1	7	4	3	2	6	14898.67315	14898.67282	0.00033	0.02500	0.00000
267	5	4	1	4	4	3	2	3	14898.80285	14898.80839	-0.00554	0.02500	0.00000
268	7	2	5	6	6	1	6	5	15004.88553	15004.88123	0.0043	0.02500	0.00000
269	7	2	5	9	6	1	6	8	15005.34397	15005.34479	-0.00082	0.02500	0.00000
270	7	2	5	7	6	1	6	6	15007.52672	15007.53128	-0.00456	0.02500	0.00000
271	7	2	5	8	6	1	6	7	15008.12572	15008.12428	0.00144	0.02500	0.00000
272	9	6	4	9	8	6	3	8	15029.8769	15029.86928	0.00762	0.02500	0.00000
273	9	6	3	10	8	6	2	9	15030.05948	15030.05578	0.0037	0.02500	0.00000
274	9	5	5	8	8	5	4	7	15030.75744	15030.74841	0.00903	0.02500	0.00000
275	9	3	7	11	8	3	6	10	15037.59625	15037.59224	0.00401	0.02500	0.00000
276	9	3	6	11	8	3	5	10	15046.4224	15046.42862	-0.00622	0.02500	0.00000
277	9	3	6	8	8	3	5	7	15046.54282	15046.53873	0.00409	0.02500	0.00000

									Exp Freq	Calc. Freq	Diff	Exp Err	Est Err Avg
278	9	3	6	9	8	3	5	8	15046.75004	15046.74867	0.00137	0.02500	0.00000
279	9	3	6	10	8	3	5	9	15046.84638	15046.84256	0.00382	0.02500	0.00000
280	9	1	8	10	8	1	7	9	15152.95864	15152.97218	-0.01354	0.02500	0.00000
281	9	1	8	11	8	1	7	10	15153.07521	15153.07079	0.00442	0.02500	0.00000
282	9	1	8	8	8	1	7	7	15153.1677	15153.17305	-0.00535	0.02500	0.00000
283	9	1	9	10	8	0	8	9	15277.01288	15277.01259	0.00029	0.02500	0.00000
284	9	1	9	9	8	0	8	8	15277.25309	15277.2514	0.00169	0.02500	0.00000
285	9	1	9	11	8	0	8	10	15278.26234	15278.25981	0.00253	0.02500	0.00000
286	9	1	9	8	8	0	8	7	15278.49433	15278.49259	0.00174	0.02500	0.00000
287	13	3	10	14	12	4	9	13	15344.63547	15344.6407	-0.00523	0.02500	0.00000
288	13	3	10	13	12	4	9	12	15344.54456	15344.54608	-0.00152	0.02500	0.00000
289	8	2	7	9	7	1	6	8	15652.11136	15652.11131	0.00005	0.02500	0.00000
290	8	2	7	8	7	1	6	7	15652.68814	15652.68603	0.00211	0.02500	0.00000
291	8	2	7	10	7	1	6	9	15654.52157	15654.52127	0.0003	0.02500	0.00000
292	8	2	7	7	7	1	6	6	15655.04235	15655.04294	-0.00059	0.02500	0.00000
293	10	3	8	9	9	4	5	8	10171.8791	10171.87781	0.00129	0.02500	0.00000
294	10	3	8	12	9	4	5	11	10171.99068	10171.99327	-0.00259	0.02500	0.00000
295	10	3	7	9	9	4	6	8	10204.97094	10204.9715	-0.00056	0.02500	0.00000
296	10	3	7	10	9	4	6	9	10206.19619	10206.1934	0.00279	0.02500	0.00000
297	10	3	7	11	9	4	6	10	10206.34732	10206.35138	-0.00406	0.02500	0.00000
298	6	1	6	7	5	0	5	7	10591.6463	10591.64588	0.00042	0.02500	0.00000
299	5	2	4	6	4	1	3	6	10974.25938	10974.25632	0.00306	0.02500	0.00000
300	7	0	7	6	6	1	6	6	11016.26374	11016.27107	-0.00733	0.02500	0.00000
301	9	1	9	9	8	2	6	8	11134.92277	11134.91959	0.00318	0.02500	0.00000
302	9	1	9	11	8	2	6	10	11137.50019	11137.50054	-0.00035	0.02500	0.00000
303	9	1	9	8	8	2	6	7	11138.05614	11138.0501	0.00604	0.02500	0.00000
304	4	3	2	4	3	2	1	4	11353.6532	11353.66254	-0.00934	0.02500	0.00000
305	4	3	2	3	3	2	1	3	11354.94094	11354.94744	-0.0065	0.02500	0.00000
306	5	2	3	5	4	1	4	5	11374.3585	11374.35805	0.00045	0.02500	0.00000
307	5	2	3	6	4	1	4	6	11375.67814	11375.67988	-0.00174	0.02500	0.00000
308	7	2	6	8	6	2	5	7	11677.30588	11677.30173	0.00415	0.02500	0.00000

									Exp Freq	Calc. Freq	Diff	Exp Err	Est Err Avg
309	7	2	5	9	6	2	4	8	11734.06092	11734.0622	-0.00128	0.02500	0.00000
310	7	1	6	6	6	1	5	5	11798.19578	11798.20012	-0.00434	0.02500	0.00000
311	10	2	9	12	9	3	6	11	11877.61139	11877.61146	-0.00007	0.02500	0.00000
312	11	3	8	10	10	4	7	9	11905.07674	11905.06625	0.01049	0.02500	0.00000
313	11	3	8	13	10	4	7	12	11905.17547	11905.17976	-0.00429	0.02500	0.00000
314	11	3	8	11	10	4	7	10	11906.18872	11906.18051	0.00821	0.02500	0.00000
315	11	3	8	12	10	4	7	11	11906.30689	11906.30954	-0.00265	0.02500	0.00000
316	11	7	4	12	11	6	5	12	12157.77479	12157.78128	-0.00649	0.02500	0.00000
317	11	7	4	10	11	6	5	10	12158.91335	12158.91555	-0.0022	0.02500	0.00000
318	9	7	2	9	9	6	3	9	12160.92688	12160.9434	-0.01652	0.02500	0.00000
319	7	7	0	6	7	6	1	6	12164.68145	12164.67785	0.0036	0.02500	0.00000
320	10	1	10	11	9	2	7	10	12490.67077	12490.66844	0.00233	0.02500	0.00000
321	10	1	10	10	9	2	7	9	12491.25465	12491.26555	-0.0109	0.02500	0.00000
322	10	1	10	12	9	2	7	11	12494.20292	12494.21693	-0.01401	0.02500	0.00000
323	10	1	10	9	9	2	7	8	12494.77763	12494.76639	0.01124	0.02500	0.00000
324	4	4	1	5	3	3	0	5	13224.368	13224.36511	0.00289	0.02500	0.00000
325	8	7	1	7	7	7	0	6	13356.91617	13356.92038	-0.00421	0.02500	0.00000
326	8	4	4	7	7	4	3	6	13362.01875	13362.01156	0.00719	0.02500	0.00000

Parameters in fit:

LINES REQUESTED= 326 NUMBER OF PARAMETERS= 15 NUMBER OF ITERATIONS=250

MARQUARDT PARAMETER =0.0000E+000 max (OBS-CALC)/ERROR =1.0000E+014

PARAMETERS - A.PRIORI ERROR

1	1	10000	1.7705472636528E+003	6.169257E+002	A
2	2	20000	8.5296219785522E+002	5.124986E+002	B
3	3	30000	8.1640821742901E+002	6.463028E+002	C
4	4	200	-7.7427422188724E-005	9.096706E+002	-DelJ
5	5	1100	7.3545708183340E-005	3.715938E+002	-DelJK
6	6	2000	-1.8165306747550E-004	3.661180E+002	-DelK

7	7	40100	-1.4210211237507E-005	4.634254E+002	-delJ
8	8	41000	-7.5310507643555E-004	1.372189E+002	-delk
9	9	110010000	1.3201041593102E+001	1.472683E+002	Xaa
10	9	-110020000	-1.3201041593102E+001	-1.000000	Xbb
11	10	110030000	1.8078030393458E+000	1.206347E+002	Xcc
12	10	-110020000	-1.8078030393458E+000	-1.000000	Xbb
13	11	110610000	-3.3626097388060E+001	2.508211E+002	Xab
14	12	110410000	-3.3672130801421E+001	4.074927E+002	Xac
15	13	110210000	-4.4011809682324E+001	5.540859E+002	Xbc

15 parameters read, 13 independent parameters

Table 4.6: Transition frequencies and assignments for the observed Cl-37 isotope in chloropentafluoroacetone.

									Exp Freq	Calc. Freq	Diff	Exp Err	Est Err Avg
1	3	3	1	3	2	2	0	2	9590.47247	9590.47370	-0.00123	0.02500	0.00000
2	3	3	1	5	2	2	0	4	9591.37793	9591.37626	0.00167	0.02500	0.00000
3	3	3	0	5	2	2	1	4	9592.45743	9592.45548	0.00195	0.02500	0.00000
4	4	2	2	6	3	1	3	5	9503.15615	9503.15762	-0.00147	0.02500	0.00000
5	4	2	2	5	3	1	3	4	9505.32405	9505.32160	0.00245	0.02500	0.00000
6	3	3	1	4	2	2	0	3	9590.69767	9590.69580	0.00187	0.02500	0.00000
7	3	3	1	4	2	2	0	4	9588.47982	9588.48705	-0.00723	0.02500	0.00000
8	3	3	0	4	2	2	1	4	9589.57186	9589.56652	0.00534	0.02500	0.00000
9	4	2	2	4	3	1	3	3	9504.36658	9504.36705	-0.00047	0.02500	0.00000
10	4	2	2	3	3	1	3	2	9502.53383	9502.53743	-0.00360	0.02500	0.00000
11	3	3	1	2	2	2	0	1	9591.06179	9591.06178	0.00001	0.02500	0.00000
12	3	3	0	3	2	2	1	2	9591.57484	9591.57409	0.00075	0.02500	0.00000
13	3	3	0	3	2	2	1	3	9593.23990	9593.23668	0.00322	0.02500	0.00000
14	3	3	1	2	2	2	0	2	9593.41753	9593.41845	-0.00092	0.02500	0.00000
15	3	3	0	2	2	2	1	2	9594.50876	9594.51532	-0.00656	0.02500	0.00000
16	3	3	0	4	2	2	1	3	9591.89380	9591.89264	0.00116	0.02500	0.00000
17	3	3	0	2	2	2	1	1	9592.09289	9592.11413	-0.02124	0.02500	0.00000

									Exp Freq	Calc. Freq	Diff	Exp Err	Est Err Avg
18	4	2	3	5	3	1	2	4	9264.51691	9264.51991	-0.00300	0.02500	0.00000
19	4	2	3	4	3	1	2	3	9266.26613	9266.26953	-0.00340	0.02500	0.00000
20	4	2	3	6	3	1	2	5	9267.86782	9267.87052	-0.00270	0.02500	0.00000
21	4	2	3	3	3	1	2	2	9269.31953	9269.31699	0.00254	0.02500	0.00000
22	7	1	6	8	6	2	5	7	9226.95549	9226.95435	0.00114	0.02500	0.00000
23	7	1	6	9	6	2	5	8	9224.18278	9224.17996	0.00282	0.02500	0.00000
24	7	1	6	6	6	2	5	5	9223.68674	9223.69008	-0.00334	0.02500	0.00000
25	6	0	6	5	5	1	5	4	9156.24665	9156.24795	-0.00130	0.02500	0.00000
26	6	0	6	8	5	1	5	7	9156.69155	9156.69251	-0.00096	0.02500	0.00000
27	6	0	6	6	5	1	5	5	9158.07756	9158.07975	-0.00219	0.02500	0.00000
28	6	0	6	7	5	1	5	6	9158.56092	9158.56162	-0.00070	0.02500	0.00000
29	5	1	5	6	4	0	4	5	8894.76871	8894.77145	-0.00274	0.02500	0.00000
30	5	1	5	5	4	0	4	4	8895.58596	8895.58945	-0.00349	0.02500	0.00000
31	5	1	5	7	4	0	4	6	8897.14736	8897.14837	-0.00101	0.02500	0.00000
32	5	1	5	4	4	0	4	3	8897.92627	8897.92385	0.00242	0.02500	0.00000
33	6	0	6	7	5	0	5	6	9842.13775	9842.13516	0.00259	0.02500	0.00000
34	6	0	6	6	5	0	5	5	9842.27459	9842.27474	-0.00015	0.02500	0.00000
35	6	0	6	8	5	0	5	7	9842.40628	9842.40597	0.00031	0.02500	0.00000
36	6	0	6	5	5	0	5	4	9842.54576	9842.54468	0.00108	0.02500	0.00000
37	6	2	5	8	5	2	4	7	9874.46334	9874.46554	-0.00220	0.02500	0.00000
38	6	2	5	7	5	2	4	6	9874.69051	9874.68461	0.00590	0.02500	0.00000
39	6	5	2	7	5	5	1	6	9883.28943	9883.29071	-0.00128	0.02500	0.00000
40	6	3	4	5	5	3	3	4	9884.52380	9884.52390	-0.00010	0.02500	0.00000
41	6	3	4	8	5	3	3	7	9884.66590	9884.66511	0.00079	0.02500	0.00000
42	6	3	4	6	5	3	3	5	9885.16338	9885.16880	-0.00542	0.02500	0.00000
43	6	3	4	7	5	3	3	6	9885.30405	9885.30115	0.00290	0.02500	0.00000
44	6	3	3	5	5	3	2	4	9885.63918	9885.64056	-0.00138	0.02500	0.00000
45	6	3	3	8	5	3	2	7	9885.78148	9885.78470	-0.00322	0.02500	0.00000
46	6	3	3	6	5	3	2	5	9886.30046	9886.30216	-0.00170	0.02500	0.00000
47	6	3	3	7	5	3	2	6	9886.44366	9886.43848	0.00518	0.02500	0.00000
48	6	2	4	7	5	2	3	6	9911.96009	9911.96910	-0.00901	0.02500	0.00000

									Exp Freq	Calc. Freq	Diff	Exp Err	Est Err Avg
49	6	2	4	8	5	2	3	7	9911.48038	9911.48189	-0.00151	0.02500	0.00000
50	6	1	5	5	5	1	4	4	9980.64633	9980.64101	0.00532	0.02500	0.00000
51	5	2	3	7	4	2	2	6	8251.72522	8251.72862	-0.00340	0.02500	0.00000
52	5	2	4	7	4	2	3	6	8230.30491	8230.30562	-0.00071	0.02500	0.00000
53	5	0	5	6	4	0	4	5	8211.20026	8211.19791	0.00235	0.02500	0.00000
54	5	1	5	7	4	1	4	6	8136.39181	8136.37887	0.01294	0.02500	0.00000
55	6	1	6	7	5	0	5	6	10444.54148	10444.54058	0.00090	0.02500	0.00000
56	6	1	6	6	5	0	5	5	10445.13180	10445.13324	-0.00144	0.02500	0.00000
57	6	1	6	8	5	0	5	7	10446.67756	10446.67493	0.00263	0.02500	0.00000
58	6	1	6	5	5	0	5	4	10447.23806	10447.23824	-0.00018	0.02500	0.00000
59	5	2	4	6	4	1	3	5	10837.65404	10837.65901	-0.00497	0.02500	0.00000
60	5	2	4	5	4	1	3	4	10838.86455	10838.86769	-0.00314	0.02500	0.00000
61	5	2	4	7	4	1	3	6	10840.70703	10840.70825	-0.00122	0.02500	0.00000
62	5	2	4	4	4	1	3	3	10841.78023	10841.78016	0.00007	0.02500	0.00000
63	7	0	7	6	6	1	6	5	10863.39260	10863.39287	-0.00027	0.02500	0.00000
64	7	0	7	9	6	1	6	8	10863.71127	10863.71340	-0.00213	0.02500	0.00000
65	7	0	7	7	6	1	6	6	10864.93529	10864.93360	0.00169	0.02500	0.00000
66	7	0	7	8	6	1	6	7	10865.27887	10865.28028	-0.00141	0.02500	0.00000
67	8	1	7	7	7	2	6	6	11001.53488	11001.53362	0.00126	0.02500	0.00000
68	8	1	7	10	7	2	6	9	11001.96054	11001.95901	0.00153	0.02500	0.00000
69	8	1	7	8	7	2	6	7	11004.09288	11004.09101	0.00187	0.02500	0.00000
70	8	1	7	9	7	2	6	8	11004.51160	11004.50608	0.00552	0.02500	0.00000
71	4	3	2	5	3	2	1	4	11234.73335	11234.73332	0.00003	0.02500	0.00000
72	4	3	2	4	3	2	1	3	11235.11559	11235.11563	-0.00004	0.02500	0.00000
73	4	3	2	6	3	2	1	5	11235.73413	11235.73397	0.00016	0.02500	0.00000
74	4	3	2	3	3	2	1	2	11236.09126	11236.09184	-0.00058	0.02500	0.00000
75	4	3	1	5	3	2	2	4	11240.50684	11240.50580	0.00104	0.02500	0.00000
76	4	3	1	4	3	2	2	3	11240.74798	11240.75129	-0.00331	0.02500	0.00000
77	4	3	1	6	3	2	2	5	11241.24276	11241.24153	0.00123	0.02500	0.00000
78	4	3	1	3	3	2	2	2	11241.51458	11241.51105	0.00353	0.02500	0.00000
79	5	2	3	4	4	1	4	3	11243.61881	11243.61606	0.00275	0.02500	0.00000

									Exp Freq	Calc. Freq	Diff	Exp Err	Est Err Avg
80	5	2	3	7	4	1	4	6	11244.27860	11244.27839	0.00021	0.02500	0.00000
81	5	2	3	5	4	1	4	4	11246.04234	11246.03781	0.00453	0.02500	0.00000
82	5	2	3	6	4	1	4	5	11246.87349	11246.87063	0.00286	0.02500	0.00000
83	7	1	7	9	6	1	6	8	11384.23645	11384.22989	0.00656	0.02500	0.00000
84	7	0	7	8	6	0	6	7	11467.68280	11467.68570	-0.00290	0.02500	0.00000
85	7	0	7	7	6	0	6	6	11467.80700	11467.79209	0.01491	0.02500	0.00000
86	7	0	7	9	6	0	6	8	11467.97941	11467.98237	-0.00296	0.02500	0.00000
87	7	0	7	6	6	0	6	5	11468.08996	11468.08643	0.00353	0.02500	0.00000
88	7	2	6	9	6	2	5	8	11517.49254	11517.50122	-0.00868	0.02500	0.00000
89	7	2	5	9	6	2	4	8	11575.47814	11575.47260	0.00554	0.02500	0.00000
90	7	2	5	8	6	2	4	7	11575.88214	11575.89196	-0.00982	0.02500	0.00000
91	7	1	7	8	6	0	6	7	11986.60686	11986.60958	-0.00272	0.02500	0.00000
92	7	1	7	7	6	0	6	6	11987.04380	11987.04809	-0.00429	0.02500	0.00000
93	7	1	7	9	6	0	6	8	11988.49472	11988.49885	-0.00413	0.02500	0.00000
94	7	1	7	6	6	0	6	5	11988.91821	11988.91834	-0.00013	0.02500	0.00000
95	6	2	5	7	5	1	4	6	12392.53776	12392.53377	0.00399	0.02500	0.00000
96	6	2	5	6	5	1	4	5	12393.44691	12393.45104	-0.00413	0.02500	0.00000
97	6	2	5	8	5	1	4	7	12395.39948	12395.40315	-0.00367	0.02500	0.00000
98	6	2	5	5	5	1	4	4	12396.21725	12396.21777	-0.00052	0.02500	0.00000
99	8	0	8	7	7	1	7	6	12567.44121	12567.43254	0.00867	0.02500	0.00000
100	8	0	8	10	7	1	7	9	12567.66311	12567.66713	-0.00402	0.02500	0.00000
101	8	0	8	8	7	1	7	7	12568.69848	12568.70182	-0.00334	0.02500	0.00000
102	8	0	8	9	7	1	7	8	12568.94607	12568.95127	-0.00520	0.02500	0.00000
103	5	3	3	6	4	2	2	5	12874.83964	12874.83886	0.00078	0.02500	0.00000
104	5	3	3	5	4	2	2	4	12875.22862	12875.22875	-0.00013	0.02500	0.00000
105	5	3	3	7	4	2	2	6	12875.86077	12875.85883	0.00194	0.02500	0.00000
106	5	3	3	4	4	2	2	3	12876.21266	12876.21574	-0.00308	0.02500	0.00000
107	5	3	2	6	4	2	3	5	12892.00245	12892.00184	0.00061	0.02500	0.00000
108	5	3	2	5	4	2	3	4	12892.21994	12892.21158	0.00836	0.02500	0.00000
109	5	3	2	7	4	2	3	6	12892.55897	12892.55391	0.00506	0.02500	0.00000
110	5	3	2	4	4	2	3	3	12892.77127	12892.77770	-0.00643	0.02500	0.00000

									Exp Freq	Calc. Freq	Diff	Exp Err	Est Err Avg
111	8	1	8	9	7	1	7	8	13006.07710	13006.05439	0.02271	0.02500	0.00000
112	6	2	4	5	5	1	5	4	13018.68716	13018.68981	-0.00265	0.02500	0.00000
113	6	2	4	8	5	1	5	7	13019.38186	13019.38141	0.00045	0.02500	0.00000
114	6	2	4	6	5	1	5	5	13021.60295	13021.60492	-0.00197	0.02500	0.00000
115	6	2	4	7	5	1	5	6	13022.36026	13022.36651	-0.00625	0.02500	0.00000
116	8	0	8	10	7	0	7	9	13088.16745	13088.18361	-0.01616	0.02500	0.00000
117	4	4	0	4	3	3	1	3	13098.52079	13098.52228	-0.00149	0.02500	0.00000
118	4	4	0	5	3	3	1	4	13098.72553	13098.73273	-0.00720	0.02500	0.00000
119	4	4	0	3	3	3	1	2	13098.87077	13098.87518	-0.00441	0.02500	0.00000
120	4	4	0	6	3	3	1	5	13099.08964	13099.09636	-0.00672	0.02500	0.00000
121	8	1	7	9	7	1	6	8	13295.17758	13295.18322	-0.00564	0.02500	0.00000
122	8	1	8	9	7	0	7	8	13524.98116	13524.97827	0.00289	0.02500	0.00000
123	8	1	8	8	7	0	7	7	13525.30582	13525.30399	0.00183	0.02500	0.00000
124	8	1	8	10	7	0	7	9	13526.61917	13526.61778	0.00139	0.02500	0.00000
125	8	1	8	7	7	0	7	6	13526.93385	13526.93190	0.00195	0.02500	0.00000
126	7	2	6	8	6	1	5	7	13929.73405	13929.73483	-0.00078	0.02500	0.00000
127	7	2	6	7	6	1	5	6	13930.45922	13930.44342	0.01580	0.02500	0.00000
128	7	2	6	9	6	1	5	8	13932.45506	13932.44468	0.01038	0.02500	0.00000
129	7	2	6	6	6	1	5	5	13933.13158	13933.12883	0.00275	0.02500	0.00000
130	9	0	9	11	8	1	8	10	14265.08406	14265.08451	-0.00045	0.02500	0.00000
131	9	0	9	9	8	1	8	8	14265.91609	14265.93091	-0.01482	0.02500	0.00000
132	6	3	4	7	5	2	3	6	14507.73331	14507.74666	-0.01335	0.02500	0.00000
133	6	3	4	6	5	2	3	5	14508.10451	14508.09679	0.00772	0.02500	0.00000
134	6	3	4	8	5	2	3	7	14508.79982	14508.79532	0.00450	0.02500	0.00000
135	6	3	4	5	5	2	3	4	14509.12629	14509.11728	0.00901	0.02500	0.00000
136	6	3	3	7	5	2	4	6	14547.70102	14547.70251	-0.00149	0.02500	0.00000
137	6	3	3	6	5	2	4	5	14547.83992	14547.83514	0.00478	0.02500	0.00000
138	6	3	3	8	5	2	4	7	14548.03492	14548.03299	0.00193	0.02500	0.00000
139	6	3	3	5	5	2	4	4	14548.18552	14548.17804	0.00748	0.02500	0.00000
140	9	1	9	10	8	1	8	9	14626.49172	14626.47918	0.01254	0.02500	0.00000
141	9	0	9	10	8	0	8	9	14703.23457	14703.21217	0.02240	0.02500	0.00000

										Exp Freq	Calc. Freq	Diff	Exp Err	Est Err Avg
142	9	0	9	11	8	0	8	10		14703.52915	14703.51868	0.01047	0.02500	0.00000
143	5	4	2	6	4	3	1	5		14745.26259	14745.25353	0.00906	0.02500	0.00000
144	5	4	1	6	4	3	2	5		14745.40017	14745.40239	-0.00222	0.02500	0.00000
145	5	4	1	5	4	3	2	4		14745.53877	14745.53798	0.00079	0.02500	0.00000
146	5	4	2	7	4	3	1	6		14745.87860	14745.87199	0.00661	0.02500	0.00000
147	9	2	7	11	8	2	6	10		14914.86249	14914.86028	0.00221	0.02500	0.00000
148	9	2	7	9	8	2	6	8		14915.17942	14915.18374	-0.00432	0.02500	0.00000
149	9	1	8	10	8	1	7	9		14948.25800	14948.25657	0.00143	0.02500	0.00000
150	9	1	8	8	8	1	7	7		14948.48216	14948.47807	0.00409	0.02500	0.00000
151	9	1	9	10	8	0	8	9		15063.57989	15063.58230	-0.00241	0.02500	0.00000
152	9	1	9	9	8	0	8	8		15063.82078	15063.82394	-0.00316	0.02500	0.00000
153	9	1	9	11	8	0	8	10		15064.97082	15064.97453	-0.00371	0.02500	0.00000
154	9	1	9	8	8	0	8	7		15065.20361	15065.20698	-0.00337	0.02500	0.00000
155	8	2	7	7	7	1	6	6		15453.12477	15453.13046	-0.00569	0.02500	0.00000
156	8	2	7	10	7	1	6	9		15452.56532	15452.57555	-0.01023	0.02500	0.00000
157	10	0	10	9	9	1	9	8		15953.32810	15953.32611	0.00199	0.02500	0.00000
158	10	0	10	12	9	1	9	11		15953.44065	15953.44623	-0.00558	0.02500	0.00000
159	10	0	10	10	9	1	9	9		15954.11353	15954.11433	-0.00080	0.02500	0.00000
160	10	0	10	11	9	1	9	10		15954.23792	15954.24245	-0.00453	0.02500	0.00000
161	9	2	7	9	8	3	6	8		10421.36196	10421.37810	-0.01614	0.02500	0.00000
162	9	2	7	10	8	3	6	9		10421.66497	10421.66167	0.00330	0.02500	0.00000
163	5	2	4	6	4	1	3	6		10842.07845	10842.07484	0.00361	0.02500	0.00000
164	9	1	9	10	8	2	6	9		10935.59679	10935.60034	-0.00355	0.02500	0.00000
165	7	5	3	9	6	5	2	8		11529.49294	11529.49357	-0.00063	0.02500	0.00000
166	7	5	3	8	6	5	2	7		11530.56856	11530.57080	-0.00224	0.02500	0.00000
167	9	1	8	10	8	2	7	9		12793.47403	12793.47292	0.00111	0.02500	0.00000
168	9	1	8	11	8	2	7	10		12791.09901	12791.08609	0.01292	0.02500	0.00000
169	8	3	6	10	7	3	5	9		13183.07583	13183.09265	-0.01682	0.02500	0.00000
170	8	3	6	9	7	3	5	8		13183.36477	13183.37243	-0.00766	0.02500	0.00000

PARAMETERS IN FIT:

LINES REQUESTED= 170 NUMBER OF PARAMETERS= 15 NUMBER OF ITERATIONS=250

MARQUARDT PARAMETER =0.0000E+000 max (OBS-CALC)/ERROR =1.0000E+014

PARAMETERS - A.PRIORI ERROR

1	1	10000	1.7536359414626E+003	6.169257E+002	A
2	2	20000	8.4169045447521E+002	5.124986E+002	B
3	3	30000	8.0489878436588E+002	6.463028E+002	C
4	4	200	-7.8716597507553E-005	9.096706E+000	-DelJ
5	5	1100	8.6004905508723E-005	3.715938E+000	-DelJK
6	6	2000	-2.4736474932593E-004	3.661180E+000	-DelK
7	7	40100	-1.8366991578245E-005	4.634254E+000	-delJ
8	8	41000	-7.3011005423095E-004	1.372189E+000	-delk
9	9	110010000	9.4125242243841E+000	1.472683E+002	Xaa
10	9	-110020000	-9.4125242243841E+000	-1.000000	Xbb
11	10	110030000	5.0166302775004E+000	1.206347E+002	Xcc
12	10	-110020000	-5.0166302775004E+000	-1.000000	Xbb
13	11	110610000	-3.3959532228676E+001	2.508211E+002	Xab
14	12	110410000	-1.6453597732017E+001	4.074927E+002	Xac
15	13	110210000	-3.3043941823800E+001	5.540859E+002	Xbc

15 parameters read, 13 independent parameters

NEW PARAMETER (EST. ERROR) -- CHANGE THIS ITERATION

1	10000	A	1753.63594(178)	0.00000
2	20000	B	841.69045(120)	0.00000
3	30000	C	804.89878(107)	-0.00000
4	200	-DelJ	-0.0787(58)E-03	-0.0000E-03
5	1100	-DelJK	0.086(33)E-03	-0.000E-03
6	2000	-DelK	-0.247(94)E-03	-0.000E-03
7	40100	-delJ	-0.01837(293)E-03	-0.00000E-03
8	41000	-delk	-0.73(39)E-03	-0.00E-03
9	110010000	Xaa	9.413(37)	0.000
10	110030000	Xcc	5.017(32)	0.000
11	110610000	Xab	-34.0(97)	-0.0
12	110410000	Xac	-16.4(208)	0.0
13	110210000	Xbc	-33.04(109)	-0.00

MICROWAVE AVG = -0.000073 MHz, IR AVG = 0.00000

MICROWAVE RMS = 0.006016 MHz, IR RMS = 0.00000

END OF ITERATION 1 OLD, NEW RMS ERROR= 0.24065 0.24065

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