

Microwave and Infrared Spectra, Adjusted r_0 Structural Parameters, Conformational Stabilities, Vibrational Assignments, and Theoretical Calculations of Cyclobutylcarboxylic Acid Chloride

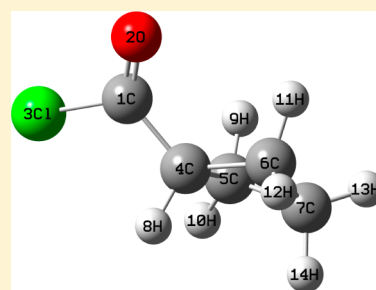
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S Supporting Information

ABSTRACT: The FT-microwave spectrum of cyclobutylcarboxylic acid chloride, $c\text{-C}_4\text{H}_7\text{C(O)Cl}$, has been recorded and 153 transitions for the ^{35}Cl and ^{37}Cl isotopologues have been assigned for the gauche-equatorial (g-Eq) conformation. The ground state rotational constants were determined for ^{35}Cl [^{37}Cl]: $A = 4349.8429(25)$ [4322.0555(56)] MHz, $B = 1414.8032(25)$ [1384.5058(25)] MHz, and $C = 1148.2411(25)$ [1126.3546(25)] MHz. From these rotational constants and ab initio predicted parameters, adjusted r_0 parameters are reported with distances (Å) $r_{\text{C}_\alpha\text{-C}} = 1.491(4)$, $r_{\text{C=O}} = 1.193(3)$, $r_{\text{C}_\alpha\text{-C}_\beta} = 1.553(4)$, $r_{\text{C}_\alpha\text{-C}_{\beta'}} = 1.540(4)$, $r_{\text{C}_\gamma\text{-C}_\beta} = 1.547(4)$, $r_{\text{C}_\gamma\text{-C}_{\beta'}} = 1.546(4)$, $r_{\text{C-Cl}} = 1.801(3)$ and angles (deg) $\tau_{\text{C}_\gamma\text{C}_\beta\text{C}_{\beta'}\text{C}_\alpha} = 30.9(5)$. Variable temperature (-70 to -100 °C) infrared spectra (4000 to 400 cm^{-1}) were recorded in liquid xenon and the g-Eq conformer was determined the most stable form, with enthalpy differences of 91 ± 9 cm^{-1} (1.09 ± 0.11 kJ/mol) for the gauche-axial (g-Ax) form and 173 ± 17 cm^{-1} (2.07 ± 0.20 kJ/mol) for the trans-equatorial (t-Eq) conformer. The relative amounts at ambient temperature are 54% g-Eq, $35 \pm 1\%$ g-Ax, and $12 \pm 1\%$ t-Eq forms. Vibrational assignments have been provided for the three conformers and theoretical calculations were carried out. The results are discussed and compared to corresponding properties of related molecules.



1. INTRODUCTION

Our interest in the conformational stabilities and structural parameters of small ring compounds, particularly monosubstituted four- and five-membered-ring molecules, has led us to reinvestigate some of these molecules where there is considerable controversy of the most stable conformers. One such molecule is the monosubstituted four-membered-ring cyclobutylcarboxylic acid chloride where there have been four different conformers/structure studies reported.¹ These four possible conformers are the gauche-equatorial (g-Eq), gauche-axial (g-Ax), trans-equatorial (t-Eq), and trans-axial (t-Ax) where the three stable conformers (g-Eq, g-Ax, and t-Eq) are shown in Figure 1.

The earlier structural determination of this molecule in the vapor state was obtained by the electron diffraction technique by Adam and Bartell¹ in 1971. These scientists were interested in the structure and conformations of the series R-COX and concluded that the cyclobutyl derivative exists almost entirely as the gauche conformations. From this study it was concluded that there was coupling between the ring bending and torsional displacements based on the electron diffraction intensities. From these couplings it was observed that the gauche conformation aligned toward the cis side favored the equatorial puckered ring and those on the trans side favored the axial puckered ring. Bond lengths and bond angles were determined and it was concluded that they were “normal” which indicates

that they were similar to those obtained in “unstrained” alkyl carboxaldehydes,^{5–7} which is rather surprising since cyclobutyl compounds are moderately strained.

Following this initial structural investigation¹ there were three^{2–4} additional structural investigations with two of them vibrational studies^{2,3} and the other a microwave and vibrational study.⁴ In the first vibrational study² the spectra were recorded of the condensed phases (liquid and solid) and it was concluded that there was a single conformer present in both phases and it was the same form.

A subsequent vibration investigation³ was reported that included the infrared spectrum of the gas as well as the spectra of the liquid and solid and the Raman spectrum of the liquid. From this study there was clear evidence from the temperature dependence of the spectrum of the liquid that multiple conformers exist in the fluid state. For example, some bands increased where others decreased as the temperature was decreased and one band disappeared in the spectrum of the crystal. From these studies it was assumed that the proposed three conformers from the electron diffraction investigation were probably nearly equal concentrations.

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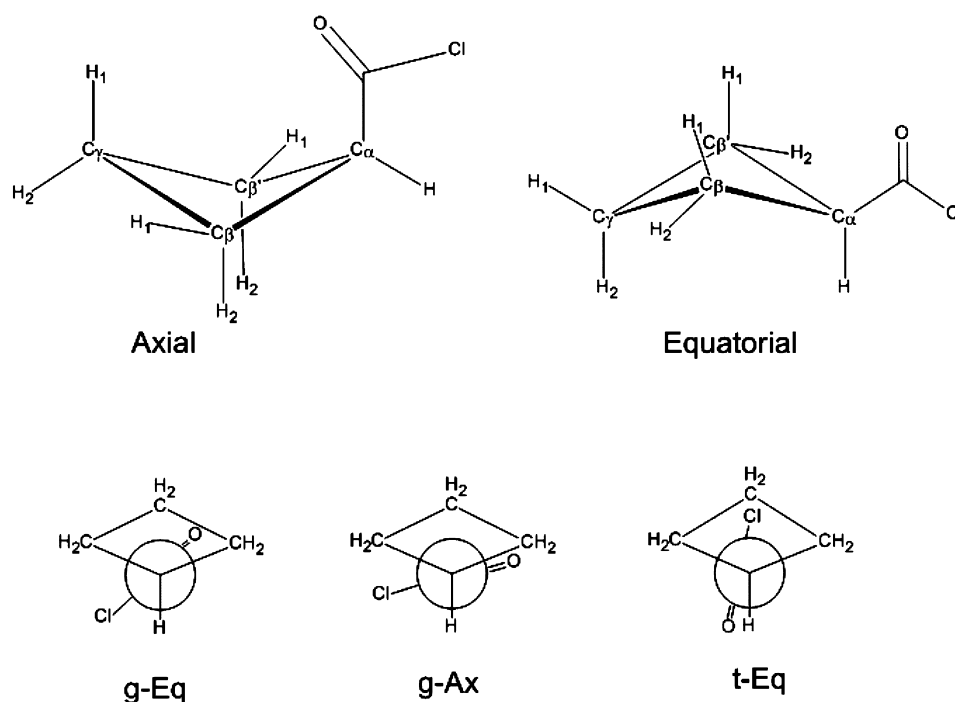


Figure 1. Labeled conformers of cyclobutylcarboxylic acid chloride with atomic numbering.

From a later microwave and vibrational investigation⁴ only the microwave spectrum of the ^{35}Cl isotope of the g-Eq form was assigned and there was no microwave data for the ^{37}Cl species or other conformers. From this microwave data a partial structure was reported for the g-Eq conformer. Also, in this study⁴ an investigation of the Raman spectrum of the liquid was reported and the energy difference between the preferred g-Eq form and high-energy (assumed to be t-Eq) conformer was determined to be $1.4 \text{ kcal mol}^{-1}$ (490 cm^{-1}). Therefore from the four reported studies to date, there are at least two and possibly three conformers present in the fluid phases but there is still a question which conformer is the most stable form and what are the energy differences, as well as, to assign the microwave spectral transitions of the ^{37}Cl isotopologue for the g-Eq form and determine a complete set of structural parameters from the microwave data. Thus, a microwave and vibration investigation has been initiated to answer these questions.

To aid in identifying the fundamental vibrations for the additional conformers and to assign fundamentals for the less stable conformers for use in determining the enthalpy differences *ab initio* calculations have been utilized. The harmonic force fields, infrared intensities, Raman activities, depolarization ratios, and vibrational frequencies were obtained from MP2/6-31G(d) *ab initio* calculations with full electron correlation. Additionally both MP2(full) *ab initio* and Density Functional Theory (DFT) calculations by the B3LYP method have been carried out with a variety of basis sets up to aug-cc-pVTZ as well as with diffuse functions to predict the conformational stabilities. The results of these spectroscopic, structural, and theoretical studies of cyclobutylcarboxylic acid chloride are reported herein.

2. EXPERIMENTAL AND THEORETICAL METHODS

The sample of cyclobutylcarboxylic acid chloride was purchased from Sigma-Aldrich Chemical Co., with stated purity of 98%.

The sample was further purified by low-temperature, low-pressure fractionation column and the purity of the sample was verified by comparing the infrared spectrum with that previously reported.⁴

Microwave spectra were recorded by using a “mini-cavity” Fourier-transform microwave spectrometer^{8,9} at Kent State University. The Fabry–Perot resonant cavity is established by two 7.5-in.-diameter diamond-tip finished aluminum mirrors with a 30.5-cm spherical radius. The Fabry–Perot cavity resides inside a vacuum chamber formed by a 6-way cross and a 15-in. long, 8-in. diameter extension tube. The two cavity mirrors are nominally separated by 30 cm.

The sample was entrained in a 70:30 Ne–He carrier gas mixture at 2 atm and expanded into the cavity to attain 4K by using a reservoir nozzle⁹ made from a modified Series-9 General Valve. The reservoir nozzle is mounted in a recessed region of the mirror flange, external to the vacuum chamber, and the expansion passes through a 0.182-in.-diameter hole into the resonant cavity. The center of the expansion is offset from the center of the mirror by 1 in.

The sample was irradiated by microwave radiation generated by an Agilent Technologies E8247C PSG CW synthesizer; details of the irradiation and heterodyne detection circuitry can be found in ref 10. The vacuum system can accommodate pulse repetition rates of up to 15 s^{-1} while maintaining a pressure below 10^{-4} Torr, and the instrument can scan 450 MHz in 6 h while averaging 100 shots per scan segment. The frequencies for the measured transitions in the region of 10 500 to 22 000 MHz are listed in Tables 1 and 2 along with their assignments.

The infrared spectrum of the gas (Figure 2A) was obtained from 4000 to 220 cm^{-1} on a Perkin-Elmer model 2000 Fourier transform spectrometer equipped with a Ge/CsI beamsplitter and a DTGS detector. Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen. The spectrum of the gas was obtained with a theoretical

Table 1. Microwave Spectrum for the g-Eq Form of $c\text{-C}_4\text{H}_7\text{C}(\text{O})^{35}\text{Cl}^a$

transition	2F'	2F''	obsd (MHz)	Δ (kHz)	transition	2F'	2F''	obsd (MHz)	Δ (kHz)
$5_{05} \leftarrow 4_{04}$	11	9	12488.0928	0.0	$5_{23} \leftarrow 4_{22}$	11	11	13102.2947	-9.0
	7	5	12488.4513	0.0		11	9	13102.8295	0.0
	13	11	12488.8314	0.0		9	7	13102.9112	1.0
$4_{23} \leftarrow 4_{04}$	7	5	12510.4984	-1.0		13	11	13103.2076	0.0
	5	5	12512.2725	-3.0	$6_{06} \leftarrow 5_{15}$	7	5	13103.2512	1.0
	11	11	12513.7552	2.0		7	7	13103.7903	-3.0
	9	7	12515.6503	2.0		9	7	13298.0792	-2.0
$5_{24} \leftarrow 5_{05}$	7	7	12801.0148	0.0		15	13	13298.7292	1.0
	13	13	12801.9124	1.0	$5_{14} \leftarrow 4_{13}$	11	9	13299.1049	-2.0
	9	9	12804.5374	0.0		13	11	13299.7042	-1.0
	11	11	12805.6276	-3.0		11	9	13397.6336	-1.0
$5_{42} \leftarrow 4_{41}$	11	9	12851.4369	1.0		9	7	13397.7486	2.0
	9	7	12852.8816	-1.0	$8_{35} \leftarrow 8_{26}$	13	11	13398.1012	0.0
	13	11	12854.9682	0.0		7	5	13398.1832	1.0
	7	5	12856.3981	1.0		17	17	13543.8893	-1.0
$5_{41} \leftarrow 4_{40}$	11	9	12851.6285	1.0		15	15	13544.1742	-1.0
	9	7	12853.0725	-1.0	$6_{33} \leftarrow 6_{24}$	19	19	13545.0002	-1.0
	13	11	12855.1571	-1.0		13	13	13545.0375	0.0
	7	5	12856.5838	-3.0		13	13	14581.4210	-4.0
$5_{33} \leftarrow 4_{32}$	11	9	12866.4754	1.0		11	11	14581.4906	-3.0
	9	7	12867.4525	-2.0	$6_{06} \leftarrow 5_{05}$	9	9	14581.5304	-1.0
	11	11	12868.2870	0.0		15	15	14581.5809	2.0
	13	11	12868.6320	2.0		11	9	14837.8797	1.0
	7	5	12869.0708	1.0	$4_{31} \leftarrow 4_{22}$	13	11	14838.0792	1.0
$5_{32} \leftarrow 4_{31}$	11	9	12881.2035	3.0		5	5	15145.9291	3.0
	9	7	12881.7769	5.0		11	11	15146.7867	0.0
	13	11	12883.0272	4.0		7	7	15148.3560	2.0
$9_{36} \leftarrow 9_{27}$	7	5	12883.7434	-2.0	$10_{29} \leftarrow 10_{110}$	9	9	15149.1610	1.0
	19	19	12938.1931	2.0		23	23	16847.3301	0.0
	17	17	12938.3418	1.0		19	19	16850.9893	0.0
	21	21	12939.1964	1.0		21	21	16851.6156	0.0
	15	15	12939.3744	-2.0	$7_{07} \leftarrow 6_{06}$	13	11	17144.2289	1.0
$7_{26} \leftarrow 7_{17}$	11	11	13089.0202	-1.0		15	13	17144.3366	2.0
	13	13	13093.7375	2.0		11	9	17144.8521	-2.0
	15	15	13094.7280	0.0					

^aObserved frequencies of hyperfine components of rotational transitions (MHz) and deviations of calculated values (kHz).

resolution of 0.5 cm^{-1} for the gas with 128 interferograms added and truncated.

The mid-infrared spectra (4000 to 400 cm^{-1}) of the sample dissolved in liquid xenon (Figure 2B) were recorded on a Bruker model IFS-66 Fourier transform spectrometer equipped with a globar source, a Ge/KBr beamsplitter, and a DTGS detector. In all cases, 100 interferograms were collected at 1.0 cm^{-1} resolution, averaged, and transformed with a boxcar truncation function. For these studies, a specially designed cryostat cell was used. It consists of a copper cell with a path length of 4 cm with wedged silicon windows sealed to the cell with indium gaskets. The copper cell was enclosed in an evacuated chamber fitted with KBr windows. The temperature was maintained with boiling liquid nitrogen and monitored by two Pt thermo resistors. After being cooled to the designated temperature, a small amount of the sample was condensed into the cell and the system was then pressurized with the noble gas,

which condensed in the cell, allowing the compound to dissolve. All of the observed bands in the infrared spectra of the gas along with their proposed assignments of the g-Eq, g-Ax, and t-Eq conformers are listed in Tables 3, 4 and 5, respectively.

The LCAO-MO-SCF restricted Hartree-Fock calculations were performed with the Gaussian-03 program¹¹ with Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters by using the gradient method of Pulay.¹² Several basis sets as well as the corresponding ones with diffuse functions were employed with the Møller-Plesset perturbation method¹³ to second order (MP2(full)) as well as with the density functional theory by the B3LYP method. The predicted conformational energy differences are listed in Table 6.

Table 2. Microwave Spectrum for the g-Eq Form of c-C₄H₇C(O)³⁷Cl^a

transition	2F'	2F''	obsd (MHz)	Δ (kHz)	transition	2F'	2F''	obsd (MHz)	Δ (kHz)
5 ₁₅ ← 4 ₁₄	9	7	11843.7145	0.0	7 ₂₆ ← 7 ₁₇	11	11	12959.0087	−1.0
	7	5	11844.1191	−2.0		17	17	12959.7415	2.0
	11	9	11844.1191	6.0		13	13	12962.6624	0.0
	13	11	11844.3502	0.0		15	15	12963.4274	−1.0
	9	9	11845.9516	−1.0	6 ₀₆ ← 5 ₁₅	9	7	12981.6414	−1.0
	7	7	11850.3009	0.0		15	13	12982.1523	1.0
4 ₁₄ ← 3 ₀₃	9	9	11854.2267	−3.0		11	9	12982.4399	−1.0
	9	7	11858.5569	0.0	5 ₁₄ ← 4 ₁₃	13	11	12982.9145	0.0
	7	5	11858.7653	−2.0		11	9	13121.1218	−2.0
	11	9	11860.5299	−1.0		9	7	13121.2000	6.0
	5	3	11860.6000	5.0		13	11	13121.4873	1.0
5 ₀₅ ← 4 ₀₄	9	7	12246.1823	0.0		7	5	13121.5366	0.0
	11	9	12246.3667	1.0	6 ₀₆ ← 5 ₀₅	11	9	14554.8534	−2.0
	7	5	12246.6679	−1.0		13	11	14554.9830	3.0
	13	11	12246.8701	2.0		9	7	14555.3695	−2.0
	9	9	12247.8543	−2.0		15	13	14555.4882	2.0
	7	7	12251.4504	−2.0	6 ₅₂ ← 5 ₅₁	13	11	15104.3045	7.0
5 ₂₄ ← 4 ₂₃	11	9	12517.5782	−1.0		11	9	15105.1831	3.0
	9	7	12517.7214	1.0		15	13	15106.9214	2.0
	13	11	12518.4264	−1.0		9	7	15107.7958	0.0
	7	5	12518.5449	2.0	6 ₅₁ ← 5 ₅₀	13	11	15104.3045	1.0
	7	7	12520.1200	−2.0		11	9	15105.1831	−4.0
5 ₄₂ ← 4 ₄₁	11	9	12588.5521	1.0		15	13	15106.9214	−4.0
	9	7	12589.7455	−2.0		9	7	15107.7958	−6.0
	13	11	12591.4810	−1.0	6 ₄₃ ← 5 ₄₂	13	11	15119.1757	0.0
	7	5	12592.6693	0.0		11	9	15119.6815	0.0
5 ₄₁ ← 4 ₄₀	11	9	12588.7204	1.0		15	13	15120.8317	1.0
	9	7	12589.9163	0.0		9	7	15121.3266	2.0
	13	11	12591.6493	0.0	6 ₄₂ ← 5 ₄₁	13	11	15119.9299	−2.0
	7	5	12592.8426	6.0		11	9	15120.4393	2.0
5 ₃₃ ← 4 ₃₂	11	9	12602.7191	−1.0		15	13	15121.5822	−1.0
	9	7	12603.3464	1.0		9	7	15122.0754	−1.0
	13	11	12604.3872	1.0	6 ₃₄ ← 5 ₃₃	13	11	15137.0321	−2.0
	7	5	12604.8893	−1.0		11	9	15137.1476	0.0
5 ₃₂ ← 4 ₃₁	11	9	12616.1242	−1.0		15	13	15137.8741	0.0
	9	7	12616.5958	−2.0		9	7	15138.1516	−3.0
	13	11	12617.6440	−2.0	6 ₃₃ ← 5 ₃₂	13	11	15172.4394	1.0
	7	5	12618.2493	0.0		11	9	15172.6830	−2.0
5 ₂₃ ← 4 ₂₂	11	11	12824.7289	−7.0		15	13	15173.3002	1.0
	11	9	12825.2798	−2.0		9	7	15173.4499	3.0
	9	7	12825.3557	6.0					
	13	11	12825.6322	−1.0					
	7	5	12825.6801	0.0					
	7	7	12826.2405	2.0					

^aObserved frequencies of hyperfine components of rotational transitions (MHz) and deviations of calculated values (kHz).

To obtain a complete description of the molecular motions involved in the fundamental modes of cyclobutylcarboxylic acid chloride, a normal coordinate analysis has been carried out. The force field in Cartesian coordinates was obtained with the Gaussian 03 program¹¹ at the MP2(full) level with the 6-31G(d) basis set. The internal coordinates used to calculate the **G** and **B** matrices are given in Table 7 with the atomic

numbering shown in Figure 1. By using the **B** matrix,¹⁴ the force field in Cartesian coordinates was converted to a force field in internal coordinates. Subsequently, a scaling factor of 0.88 for the CH stretches, β-CH₂ and γ-CH₂ deformations and 0.90 for all other modes excluding the heavy atom bending modes were used, along with the geometric average of the scaling factors for the interaction force constants, to obtain the

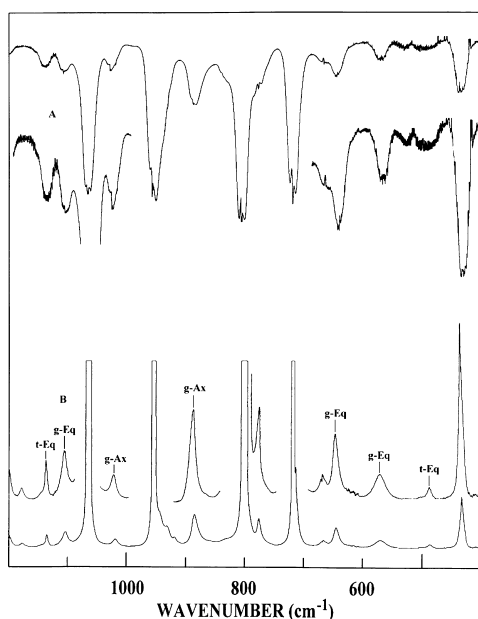


Figure 2. Midinfrared spectra of cyclobutylcarboxylic acid chloride (A) spectrum of gas; (B) spectrum of xenon solution at $-80\text{ }^{\circ}\text{C}$ with bands used in the enthalpy determination assigned on spectra.

fixed scaled force field and resultant wavenumbers. A set of symmetry coordinates was used for the g-Eq and g-Ax forms (Table S1) and another set for the symmetric t-Eq conformer (Table S2) to determine the corresponding potential energy distributions (P.E.D.s).

The vibrational spectra were predicted from the MP2(full)/6-31G(d) calculations. The predicted scaled wavenumbers were used together with a Lorentzian function to obtain the simulated spectra. Infrared intensities were obtained based on the dipole moment derivatives with respect to Cartesian coordinates. The derivatives were transformed with respect to normal coordinates by $(\partial\mu_u/\partial Q_i) = \sum_j (\partial\mu_u/\partial X_j) L_{ij}$, where Q_i is the i th normal coordinate, X_j is the j th Cartesian displacement coordinate, and L_{ij} is the transformation matrix between the Cartesian displacement coordinates and the normal coordinates. The infrared intensities were then calculated by $(N\pi)/(3c^2)[(\partial\mu_x/\partial Q_i)^2 + (\partial\mu_y/\partial Q_i)^2 + (\partial\mu_z/\partial Q_i)^2]$. The resulting simulated spectra are shown in Figure 3 and are compared to the infrared spectra of the xenon solutions at three different temperatures where the simulated spectrum of the mixture of conformers should be comparable to the experimental infrared spectra. It is interesting to note that whereas the band positions are reasonably predicted the band intensities are relatively poorly predicted.

3. MICROWAVE RESULTS

The Cl atom in cyclobutylcarboxylic acid chloride contains a nucleus with a spin quantum number $I = 3/2$ and, therefore, a nuclear quadrupole moment that interacts with the electric field gradient created by the electrons of the rotating molecule. The quadrupole moments of ^{35}Cl and ^{37}Cl are not equal. The angular momentum J of the rotating molecule couples with the angular momentum I of the nuclear spin to create an overall angular momentum F whose quantum number F can assume any of the values $F = J + I, J + I - 1, \dots, |J - I|$. Only F is an exact quantum number whereas J is only an approximate value. Therefore, a rotational level with quantum number J in the

absence of quadrupole coupling splits into sublevels that can be labeled by the exact quantum number F when a nuclear quadrupole is present. Each rotational level with $J > 1$ splits into 4 components (1 and 3 components for $J = 0$ and 1, respectively). The selection rules for rotational transitions are $\Delta F = 0, \pm 1$ and the strongest components are those given by $\Delta F = \Delta J$.

The frequencies of the components of the split rotational transitions were used in a least-squares fit to determine rotational, centrifugal distortional, and quadrupole coupling constants. For that purpose, a computer program developed for molecules with one or two quadrupole nuclei in a plane of symmetry^{15,16} was used. Of course, g-Eq cyclobutylcarboxylic acid chloride does not have a molecular symmetry plane. Because ab initio calculations performed by using the MP2(full) method with the 6-311+G(d,p) basis set predicted the full nuclear quadrupole coupling tensor with rather small values for the off-diagonal elements χ_{ac} and χ_{bc} (a few MHz) but a significant χ_{ab} (tens of MHz), fitting the spectrum with this program seemed worth a trial. The rotational and centrifugal distortion constants reported earlier⁴ from conventional microwave spectroscopy for the Cl isotopologue together with quadrupole coupling constants from ab initio calculations were used to predict the spectrum for initial assignments. The final results of the least-squares fits (Table 8) justified the use of this program. The Fit 1 for the ^{35}Cl isotopologue of 69 components of 18 rotational transitions ended with a standard deviation of 2.2 kHz and for the Fit 2 included transitions from ref 4 and transition from this study where the hyperfine components could not be resolved. For the fit of the ^{37}Cl substituted species, 84 components of 19 transitions led to a standard deviation of 2.6 kHz. The frequencies of the assigned components of the observed transitions with their residuals in the least-squares fit are listed in Tables 1 and 2 and are excellent with errors equal to or less than 4 kHz for ^{35}Cl and 7 kHz for the ^{37}Cl . With accurately determined rotational constants the adjusted r_0 structure may also be determined. It should, however, be noted that the fit of these rotational constants is probably better than the experimental data can achieve where the digital precision for the instrument used is 2.5 kHz. Therefore, the rotational constants are reported for the ^{35}Cl [^{37}Cl] isotope (MHz): $A = 4349.8429(25)$ [$4322.0555(56)$], $B = 1414.8032(25)$ [$1384.5058(25)$], and $C = 1148.2411(25)$ [$1126.3546(25)$].

4. VIBRATIONAL ASSIGNMENT

An earlier vibrational assignment⁴ for cyclobutylcarboxylic acid chloride was made by utilizing the Raman spectra of liquid and solid and the infrared spectra of the gas and solid for a complete assignment of the g-Eq conformer fundamentals and to assign two fundamentals for the high-energy conformer which could not be determined but it was assumed to be t-Eq. By the utilization of MP2(full)/6-31G(d) fundamental wavenumber predictions along with ab initio predicted intensities, and infrared data from xenon solutions it has been possible to assign nearly all of the fundamentals for the g-Eq conformer in the current study. Additionally, a nearly complete assignment of the fundamentals of the g-Ax form was made and a significant number of fundamentals for the t-Eq conformer were assigned. These assignments are important for obtaining the enthalpy differences since the fundamentals which are used in the variable temperature study need to be identified correctly for a single conformer. Therefore, an attempt was made to assign the

Table 3. Observed^a and Predicted Fundamental^b Frequencies for the g-Eq Conformer of Cyclobutylcarboxylic Acid chloride

	fundamental	ab initio	fixed scaled ^c	IR int.	Raman act.	dp ratio	IR				Raman liquid ^d	P.E.D. ^f	band contour		
							gas	Xe soln	gas ^d	solid ^d			A	B	C
ν_1	β -CH ₂ antisymmetric stretch	3213	3014	25.2	45.8	0.66	3003	3000	3004	3002	3004	73S ₁ ,25S ₂	6	16	84
ν_2	β -CH ₂ antisymmetric stretch	3207	3008	13.2	62.4	0.75	2996	2994	2995	2995		97S ₂	6	75	19
ν_3	γ -CH ₂ antisymmetric stretch	3194	2996	7.7	78.1	0.48	2986	2984		2980	2984	73S ₃ ,23S ₁	70		30
ν_4	α -CH stretch	3147	2952	2.1	30.7	0.69	2961	2959	2964	2952	2956	88S ₄ ,11S ₅	45	16	39
ν_5	β -CH ₂ symmetric stretch	3141	2946	12.9	122.0	0.09	2945	2944				48S ₃ ,42S ₇	23	65	12
ν_6	β -CH ₂ symmetric stretch	3134	2940	25.6	98.8	0.14	2943	2943				93S ₆	76	24	
ν_7	β -CH ₂ symmetric stretch	3133	2939	14.4	54.1	0.24	2926	2926	2887	2866	2879	51S ₇ ,38S ₅	27	31	42
ν_8	C=O stretch	1853	1760	205.2	14.2	0.53	1807	1807	1808	1792	1805	92S ₈	3	93	4
ν_9	γ -CH ₂ deformation	1575	1483	2.0	5.3	0.73	1470	1469		1467	1466	62S ₉ ,34S ₁₀	23	36	41
ν_{10}	γ -CH ₂ deformation	1550	1459	5.2	17.8	0.74	1453	1453	1451	1446	1452	64S ₁₀ ,34S ₉	8	42	50
ν_{11}	β -CH ₂ deformation	1542	1452	2.3	5.6	0.74	1442	1442	1451 ^e	1446 ^e		98S ₁₁	29	42	29
ν_{12}	α -CH in plane bend	1404	1337	17.9	8.9	0.56	1324	1322	1328	1319	1328	56S ₁₂ ,11S ₂₀ ,10S ₁₄	94	5	1
ν_{13}	γ -CH ₂ wag	1320	1254	5.0	5.5	0.73	1247	1246	1252	1246	1250	63S ₁₃ ,10S ₁₆ ,10S ₂₁	6	82	12
ν_{14}	β -CH ₂ wag	1315	1251	11.4	0.6	0.60	1245	1244	1252 ^e	1242 ^e	1250	72S ₁₄ ,10S ₂₅	78	19	3
ν_{15}	β -CH ₂ wag	1294	1229	0.9	4.3	0.73	1232	1232		1228 ^e	1232 ^e	43S ₁₅ ,22S ₁₈ ,14S ₁₇ ,10S ₂₃	13	87	
ν_{16}	α -CH out of plane bend	1282	1217	1.4	6.6	0.75	1213	1213	1209	1215	1217	37S ₁₆ ,14S ₁₇ ,14S ₁₃ ,10S ₁₈ ,10S ₁₅	25	75	
ν_{17}	β -CH ₂ twist	1268	1205	4.8	5.9	0.72	1204	1201		1198	1208	43S ₁₇ ,18S ₁₆ ,12S ₂₈ ,10S ₂₃	87	4	9
ν_{18}	γ -CH ₂ twist	1239	1179	3.4	8.7	0.75	1177	1176		1176	1190	31S ₁₈ ,39S ₁₅ ,10S ₂₃ ,10S ₂₃	53	45	2
ν_{19}	β -CH ₂ rock	1170	1120	23.9	4.2	0.06	1110	1108	1110	1104	1109	37S ₁₉ ,14S ₂₂ ,11S ₂₈ ,11S ₃₅	98	2	
ν_{20}	C-C stretch	1127	1075	62.6	4.4	0.35	1069	1067	1071	1070	1071	25S ₂₀ ,21S ₁₂ ,11S ₂₂	78	22	
ν_{21}	ring deformation	1078	1032	3.8	5.2	0.33	1027	1026	1030	1017	1025	22S ₂₁ ,21S ₂₄ ,17S ₂₃ ,14S ₂₂ ,10S ₂₀	96	2	2
ν_{22}	ring breathing	1013	970	52.9	9.7	0.07	960	958	955	954	962	45S ₂₂ ,18S ₂₅ ,11S ₂₀	90	10	
ν_{23}	β -CH ₂ twist	994	946	0.9	2.5	0.72	946	946				37S ₂₃ ,23S ₁₆ ,16S ₁₈ ,10S ₂₄ ,10S ₂₁	1	68	31
ν_{24}	ring deformation	975	932	1.7	10.1	0.75	933	933		923	930 ^e	51S ₂₄ ,29S ₁₁ ,10S ₁₃	83	17	
ν_{25}	ring deformation	942	911	7.7	2.1	0.47	889	887	888	888	891	33S ₂₅ ,24S ₃₀ ,13S ₂₈ ,11S ₁₉ ,10S ₁₄	46	51	3
ν_{26}	COCl scissors	847	823	152.8	2.4	0.30	809	807	810	799	804	19S ₂₆ ,14S ₃₀ ,13S ₂₅ ,12S ₂₈	83	17	
ν_{27}	β -CH ₂ rock	818	779	7.3	0.9	0.72	778	776	775	779	784	68S ₂₇ ,11S ₁₈	90		10
ν_{28}	γ -CH ₂ rock	750	728	36.5	4.6	0.26	721	720	721	722	721	30S ₂₈ ,13S ₂₉ ,12S ₃₃ ,10S ₁₇ ,10S ₃₂	86	14	
ν_{29}	COCl wag	661	651	8.2	2.4	0.10	645	645	646	640	651	48S ₂₉ ,11S ₃₀ ,11S ₁₉	69	2	29
ν_{30}	ring deformation	591	578	6.9	3.7	0.14	569	569	570	566	572	31S ₃₀ ,16S ₃₂ ,13S ₁₉ ,11S ₂₀	43	52	5
ν_{31}	C-Cl stretch	446	432	24.0	12.0	0.41	433	431	437	433	434	61S ₃₁ ,35S ₂₆	41	56	3
ν_{32}	COCl rock	345	339	19.1	5.8	0.36	340		338	338	343	11S ₃₂ ,22S ₂₆ ,19S ₃₁ ,19S ₃₄ ,11S ₂₀	78	22	
ν_{33}	ring-COCl bend	304	298	2.6	0.5	0.72			278	282	290	26S ₃₃ ,35S ₃₅ ,13S ₃₂ ,12S ₂₉	82		18
ν_{34}	ring-COCl bend	163	163	1.1	0.6	0.74			168	176	181	55S ₃₄ ,33S ₃₂	21	45	34
ν_{35}	ring puckering	145	144	1.7	0.4	0.42				153		48S ₃₅ ,40S ₃₃	39	61	
ν_{36}	COCl asymmetric torsion	47	47	0.0	1.0	0.73			83			100S ₃₆	3	60	37

^aObserved spectra: gas, Xe, and solid are IR while liquid is Raman. ^bMP2(full)/6-31G(d) ab initio calculations, scaled frequencies, infrared intensities (km/mol), Raman activities ($\text{\AA}^4/\text{u}$), depolarization ratios (dp), and potential energy distributions (P.E.D.s). ^cScaled frequencies with scaling factors of 0.88 for the CH stretches, β -CH₂, and γ -CH₂ deformations and 0.90 for all other modes except the heavy atom bending modes. ^dReference 4. ^eOur assignment. ^fSymmetry coordinates with P.E.D. contribution less than 10% are omitted.

Table 4. Observed^a and Predicted Fundamental^b Frequencies for the g-Ax Conformer of Cyclobutylcarboxylic Acid Chloride

	fundamental	ab initio	fixed scaled ^c	IR int.	Raman act.	dp ratio	IR gas	IR Xe soln.	P.E.D. ^e	band contour		
										A	B	C
ν_1	β -CH ₂ antisymmetric stretch	3214	3015	23.6	49.7	0.71	3012	3012	48S ₁ ,42S ₃ ,10S ₂	47	43	10
ν_2	β -CH ₂ antisymmetric stretch	3205	3007	8.9	62.8	0.66	3008	3007	76S ₂ ,21S ₃	74	6	20
ν_3	γ -CH ₂ antisymmetric stretch	3195	2997	4.8	62.4	0.72	3002	2999	35S ₃ ,49S ₁ ,13S ₂	18	2	80
ν_4	α -CH stretch	3165	2969	4.6	79.4	0.16	2963	2963	96S ₄	38	5	57
ν_6	γ -CH ₂ symmetric stretch	3142	2947	21.4	112.8	0.08	2945	2944	96S ₆	61		39
ν_5	β -CH ₂ symmetric stretch	3138	2944	14.7	84.8	0.23	2944	2943	58S ₅ ,35S ₇	23	6	71
ν_7	β -CH ₂ symmetric stretch	3134	2940	18.8	41.9	0.23	2943	2943	63S ₇ ,34S ₆	5	86	9
ν_8	C=O stretch	1847	1754	189.8	10.1	0.49	1760	1759	91S ₈	15	82	3
ν_{10}	γ -CH ₂ deformation	1572	1480	2.8	7.6	0.72	1468	1468	53S ₁₀ ,44S ₉	39	33	28
ν_9	β -CH ₂ deformation	1550	1459	3.7	15.7	0.75	1458	1457	47S ₁₀ ,44S ₁₀	3	54	43
ν_{11}	β -CH ₂ deformation	1535	1445	5.2	7.2	0.75	1446	1443	90S ₁₁ ,10S ₉	21	43	36
ν_{12}	α -CH in plane bend	1402	1334	24.9	3.8	0.61	1339	1337	54S ₁₂ ,15S ₁₇ ,11S ₂₂	94		6
ν_{14}	β -CH ₂ wag	1331	1266	2.8	0.4	0.29	1260	1259	60S ₁₄ ,17S ₁₃ ,10S ₂₅		1	99
ν_{13}	γ -CH ₂ wag	1322	1257	3.3	1.2	0.63	1251	1248	49S ₁₃ ,20S ₁₄	1	99	
ν_{15}	β -CH ₂ wag	1293	1227	0.0	0.3	0.75			70S ₁₅ ,14S ₁₃ ,10S ₁₆	44	15	41
ν_{18}	γ -CH ₂ twist	1282	1219	3.6	15.3	0.75	1209	1208	39S ₁₈ ,24S ₁₆ ,14S ₁₇ ,10S ₂₁	5	89	6
ν_{17}	β -CH ₂ twist	1265	1203	3.9	9.8	0.71	1200	1199	43S ₁₇ ,17S ₂₈ ,11S ₁₂ ,10S ₁₉	41	59	
ν_{16}	α -CH out of plane bend	1207	1147	1.4	3.7	0.73	1145	1143	27S ₁₆ ,18S ₂₃ ,16S ₁₅ ,13S ₂₄ ,11S ₁₈	17	83	
ν_{19}	β -CH ₂ rock	1155	1105	5.6	3.2	0.38	1090	1089	30S ₁₉ ,17S ₁₂ ,17S ₃₃ ,10S ₂₀ ,10S ₂₈	22	61	17
ν_{23}	β -CH ₂ twist	1117	1069	52.7	6.5	0.35	1065	1063	37S ₂₃ ,10S ₂₇ ,10S ₂₂	92	8	
ν_{22}	ring breathing	1075	1022	31.0	14.0	0.08	1021	1020	51S ₂₂ ,14S ₂₃ ,10S ₂₀	100		
ν_{20}	C–C stretch	999	956	88.8	5.9	0.36	957	956	10S ₂₀ ,26S ₂₅ ,23S ₂₂	98	2	
ν_{24}	ring deformation	985	938	22.9	11.1	0.75	940	938	69S ₂₄	100		
ν_{21}	ring deformation	966	930	2.2	0.3	0.74	933 ^d	932	52S ₂₁ ,12S ₁₆ ,11S ₂₃ ,10S ₁₃ ,10S ₂₇	18	54	28
ν_{25}	ring deformation	940	907	47.9	2.3	0.53	903	902	32S ₂₅ ,16S ₂₈ ,15S ₃₀ ,10S ₁₄	87	8	5
ν_{26}	COCl scissors	896	872	47.5	1.4	0.70	875	873	10S ₂₆ ,40S ₃₀ ,17S ₁₉ ,10S ₂₅	92	7	1
ν_{27}	β -CH ₂ rock	804	767	0.9	0.3	0.08	773	773	58S ₂₇ ,17S ₂₄ ,13S ₁₈	100		
ν_{28}	γ -CH ₂ rock	746	723	58.0	3.3	0.41	721 ^d	719	31S ₂₈ ,11S ₁₇ ,11S ₃₂ ,10S ₃₃	95	5	
ν_{29}	COCl wag	669	654	18.7	4.7	0.08	662	660	35S ₂₉ ,12S ₃₄ ,11S ₂₀ ,10S ₃₂ ,10S ₂₇	71	23	6
ν_{30}	ring deformation	635	623	14.5	2.1	0.38	625	624	33S ₃₀ ,20S ₂₉ ,19S ₁₉ ,10S ₂₈	67	25	8
ν_{31}	C–Cl stretch	452	439	18.3	10.9	0.40	439	437	52S ₃₁ ,44S ₂₆	54	43	3
ν_{32}	COCl rock	354	347	20.7	5.8	0.32	345		11S ₃₂ ,25S ₃₁ ,22S ₃₄ ,14S ₂₆	86	11	3
ν_{33}	ring–COCl bend	300	297	1.2	0.8	0.50	293		26S ₃₃ ,32S ₃₅ ,23S ₃₂ ,10S ₂₉	90		10
ν_{34}	ring–COCl bend	200	200	0.7	0.7	0.65			51S ₃₄ ,26S ₃₂ ,12S ₂₉	4	34	62
ν_{35}	ring puckering	153	150	1.5	0.2	0.68			52S ₃₅ ,38S ₃₃	78		22
ν_{36}	COCl assymetric torsion	55	55	0.0	1.2	0.74			100S ₃₆		31	69

^aObserved spectra: gas and Xe are IR. ^bMP2(full)/6-31G(d) ab initio calculations, scaled frequencies, infrared intensities (km/mol), Raman activities ($\text{\AA}^4/\text{u}$), depolarization ratios (dp), and potential energy distributions (P.E.D.s). ^cScaled frequencies with scaling factors of 0.88 for the CH stretches, β -CH₂ and γ -CH₂ deformations and 0.90 for all other modes except the heavy atom bending modes. ^dThis band is also assigned as a g-Eq conformer fundamental. ^eSymmetry coordinates with P.E.D. contribution less than 10% are omitted.

fundamentals in the region from 1200 to 400 cm^{-1} for the three most stable conformers, where the overtone and combination bands are greatly reduced in this region compared to those possible in the higher wavenumber region. It is also interesting to determine what effect the acid chloride group will have on the fundamental frequencies, particularly those which involve the ring modes. The vibrations of the CH₂ groups are expected to be very similar to those found in the usual four-membered-ring molecules and a discussion of their assignments in detail is usually not necessary.

The most interesting assignments will be for the heavy atom fundamentals but these are in the region where the lower frequency CH₂ bending modes will undoubtedly interact with these heavy atom vibrations. Therefore, these modes are expected to have contributions of three or four motions. For example, in the case of the β -CH₂ twist for the g-Eq form the band at 946 cm^{-1} in the infrared spectra of the gas has

contributions from two of the heavy atom ring deformation modes.

Four-membered carbon-atom rings have well-known ring deformations usually occurring in a pattern of one near 1000 cm^{-1} and three near 900 cm^{-1} . This pattern makes the assignment of these modes relatively simple for the g-Eq conformer where they are predicted at 1032, 932, and 911 cm^{-1} and observed at 1027, 933, and 889 cm^{-1} in the infrared spectra of the gas. The ring breathing mode usually occurs in this region as well and it is predicted at 970 cm^{-1} for the g-Eq form and assigned at 960 cm^{-1} in the infrared spectra of the gas. This mode was predicted to have an “A” type band contour and the band in the spectra of the gas corresponds clearly to an “A” type band contour and it was assigned based on this prediction.

For the g-Eq conformer there are some assignments necessary for bands in the infrared spectra of the gas since from the previous study⁴ there were four fundamentals in the

Table 5. Observed^a and Predicted Fundamental^b Frequencies for the t-Eq Conformer of Cyclobutylcarboxylic Acid Chloride

		fundamental	ab initio	fixed scaled ^c	IR int.	Raman act.	dp ratio	IR gas	IR Xe soln.	P.E.D. ^e	band contour	
											A	B
A'	ν_1	β -CH ₂ antisymmetric stretch	3217	3018	22.2	33.3	0.65	3014	3014	79S ₁₁ ,19S ₂	1	99
	ν_2	γ -CH ₂ antisymmetric stretch	3195	2997	8.6	70.6	0.56	2997	2995	79S ₂ ,19S ₁	12	88
	ν_3	α CH stretch	3148	2953	3.3	54.2	0.52	2961	2960	93S ₃	39	61
	ν_4	β -CH ₂ symmetric stretch	3144	2949	1.8	198.7	0.07	2945	2944	91S ₄	2	98
	ν_5	γ -CH ₂ symmetric stretch	3135	2941	25.6	66.3	0.29	2924	2922	94S ₅	99	1
	ν_6	C=O stretch	1841	1748	229.8	21.1	0.49	1750	1750	92S ₆	98	2
	ν_7	β -CH ₂ deformation	1574	1482	1.0	4.1	0.69	1468	1465	52S ₇ ,46S ₈	10	90
	ν_8	γ -CH ₂ deformation	1550	1459	5.0	23.3	0.72	1453	1451	53S ₈ ,47S ₇	8	92
	ν_9	α CH in plane bend	1389	1320	1.0	6.6	0.64	1321	1320	66S ₉ ,14S ₁₀ ,10S ₁₅	30	70
	ν_{10}	β -CH ₂ wag	1312	1248	0.8	1.1	0.66	1248	1245	70S ₁₀ ,12S ₉	99	1
	ν_{11}	β -CH ₂ twist	1282	1220	3.3	10.7	0.75	1222	1221	73S ₁₁ ,13S ₁₆	56	44
	ν_{12}	β -CH ₂ rock	1198	1149	84.7	2.5	0.38	1140	1137	25S ₁₂ ,22S ₁₃ ,19S ₂₂ ,10S ₁₈ ,10S ₁₆	8	92
	ν_{13}	C–C stretch	1155	1101	50.1	9.4	0.08	1081	1079	24S ₁₃ ,37S ₁₄ ,13S ₁₂	42	58
	ν_{14}	ring breathing	1018	975	27.8	12.2	0.14	964	962	46S ₁₄ ,19S ₁₅ ,10S ₁₂ ,10S ₁₀	80	20
	ν_{15}	ring deformation 1	948	917	11.0	2.0	0.73	919	919	31S ₁₅ ,26S ₁₇ ,15S ₁₂ ,12S ₁₆ ,10S ₁₀	69	31
	ν_{16}	γ -CH ₂ rock	835	805	67.0	1.1	0.74	803	801	30S ₁₆ ,16S ₁₅ ,13S ₁₁ ,11S ₂₀ ,10S ₁₇	19	81
	ν_{17}	ring deformation 2	688	670	67.1	2.9	0.29	666	666	32S ₁₇ ,23S ₁₆ ,14S ₁₂ ,13S ₂₀	46	54
	ν_{18}	COCl rock	527	517	0.2	4.0	0.30	~500	500	17S ₁₈ ,34S ₂₂ ,21S ₂₀ ,10S ₁₂	35	65
	ν_{19}	C–Cl stretch	502	481	47.7	12.1	0.14	490	488	47S ₁₉ ,17S ₁₇ ,16S ₁₃ ,10S ₁₂	46	54
	ν_{20}	COCl scissors	414	403	9.8	6.0	0.70	389		29S ₂₀ ,37S ₁₉ ,10S ₁₈ ,10S ₁₃	24	76
	ν_{21}	ring puckering	264	261	0.8	1.1	0.71			39S ₂₁ ,33S ₁₈ ,11S ₂₀	2	98
	ν_{22}	ring–COCl bend	137	136	0.7	0.6	0.57			42S ₂₂ ,38S ₂₁ ,16S ₁₈	48	52
A''	ν_{23}	β' -CH ₂ antisymmetric stretch	3211	3012	12.0	56.4	0.75	3014	3014	100S ₂₃		
	ν_{24}	β -CH ₂ symmetric stretch	3142	2948	32.8	5.5	0.75	2945	2945	100S ₂₄		
	ν_{25}	β -CH ₂ deformation	1539	1449	2.3	5.1	0.75			100S ₂₅		
	ν_{26}	γ -CH ₂ wag	1324	1259	3.9	6.8	0.75			53S ₂₆ ,23S ₂₇ ,10S ₃₃ ,10S ₂₉		
	ν_{27}	α CH out of plane bend	1298	1233	0.0	2.0	0.75			34S ₂₇ ,23S ₃₀ ,21S ₂₈ ,11S ₂₆ ,10S ₂₉		
	ν_{28}	β -CH ₂ wag	1289	1224	0.0	2.9	0.75			40S ₂₈ ,21S ₂₉ ,19S ₂₆ ,14S ₂₇		
	ν_{29}	γ -CH ₂ twist	1241	1181	0.6	7.9	0.75			33S ₂₉ ,33S ₂₈ ,14S ₃₀ ,10S ₃₁		
	ν_{30}	β -CH ₂ twist	1072	1029	0.6	0.9	0.75	1031	1029	35S ₃₀ ,22S ₃₁ ,21S ₃₂ ,10S ₃₄ ,10S ₃₅		
	ν_{31}	ring deformation 2	988	944	0.8	0.7	0.75	946 ^d	946 ^d	32S ₃₁ ,22S ₃₀ ,19S ₂₇ ,16S ₂₉		
	ν_{32}	ring deformation 1	977	931	1.5	13.7	0.75	933	932	65S ₃₂ ,13S ₃₁ ,10S ₂₆		
	ν_{33}	β -CH ₂ rock	824	785	2.3	1.1	0.75	778	776 ^d	72S ₃₃ ,12S ₂₉		
	ν_{34}	COCl wag	660	654	0.7	0.1	0.75			61S ₃₄ ,14S ₃₁ ,13S ₃₅		
	ν_{35}	ring–COCl bend	217	217	2.1	0.6	0.75			64S ₃₅ ,28S ₃₄		
	ν_{36}	COCl torsion	54	54	0.6	1.0	0.75			90S ₃₆ ,10S ₃₅		

^aObserved spectra: gas and Xe are IR. ^bMP2(full)/6-31G(d) ab initio calculations, scaled frequencies, infrared intensities (km/mol), Raman activities ($\text{\AA}^4/\text{u}$), depolarization ratios (dp), and potential energy distributions (P.E.D.s). ^cScaled frequencies with scaling factors of 0.88 for the CH stretches, β -CH₂ and γ -CH₂ deformations and 0.90 for all other modes except the heavy atom bending modes. ^dThis band is also assigned as a g-Eq conformer fundamental. ^eSymmetry coordinates with P.E.D. contribution less than 10% are omitted.

fingerprint region that were not assigned in the infrared spectra of the gas. Three of these fundamentals are CH₂ bending modes and they are now assigned based on frequencies observed in the spectra of the xenon solutions and are in agreement with the CH₂ bending modes of the usual four-membered-ring molecules and the previous assignment from the infrared and/or Raman spectra of the liquid and solid. The ring deformation fundamental is predicted at 932 cm⁻¹ and is now assigned at 933 cm⁻¹ in the infrared spectra of the gas. This band has a predicted Raman activity of 10.1 and was previously assigned at 927 cm⁻¹ in the Raman spectra of the liquid. This assignment is further away than expected and the previous assignment is for a shoulder of a much stronger band, therefore, we have reassigned the band center to 930 cm⁻¹ by using the previously reported⁴ Raman spectra of the liquid.

It should be noted that most of the bands which are reassigned in the current study in the infrared spectra of the gas

are within a few wavenumber differences from the previously reported assignments except for ν_{17} , the β -CH₂ twist. This fundamental is predicted at 1205 cm⁻¹ but it was previously assigned at 1143 cm⁻¹ in the infrared spectra of gas but it is now reassigned to the band at 1204 cm⁻¹. The band at 1143 cm⁻¹ is now assigned as ν_{16}' for the g-Ax conformer based on the predicted band position and the temperature dependence in the infrared spectra of the xenon solutions.

The vibrational assignments were also made for the g-Ax conformer, which is the second most abundant conformer. It should be noted that this conformer had not been mentioned in any of the previous reported vibrational studies.^{2–4} Most of the fundamental frequencies assigned for this conformer are based on the spectra obtained from the xenon solutions. The C–C stretch from the g-Ax conformer is predicted with high intensity and assigned to the strong band at 957 cm⁻¹ from the spectra of the gas and it is mainly attributed to this heavy atom stretch.

Table 6. Calculated Energies^a in (H) and Energy Differences (cm⁻¹) for the Four Possible Conformers of Cyclobutylcarboxylic Acid Chloride

method/basis set	g-Eq	energy differences, Δ^b		
		g-Ax	t-Eq	t-Ax ^c
RHF/6-31G(d)	-0.739087	287	551	952
MP2(full)/6-31G(d)	-1.729837	125	454	954
MP2(full)/6-31+G(d)	-1.748407	293	468	918
MP2(full)/6-31G(d,p)	-1.787077	153	433	1005
MP2(full)/6-31+G(d,p)	-1.804584	302	438	947
MP2(full)/6-311G(d,p)	-2.046919	120	509	1001
MP2(full)/6-311+G(d,p)	-2.058889	216	377	869
MP2(full)/6-311G(2d,2p)	-2.151748	83	425	834
MP2(full)/6-311+G(2d,2p)	-2.160468	171	310	702
MP2(full)/6-311G(2df,2pd)	-2.282393	82	383	818
MP2(full)/6-311+G(2df,2pd)	-2.290185	168	279	693
MP2(full)/aug-cc-pVTZ	-2.293038	149	213	550
B3LYP/6-31G(d)	-3.147955	288	396	775
B3LYP/6-31+G(d)	-3.159073	335	363	
B3LYP/6-311G(d,p)	-3.249426	280	525	863
B3LYP/6-311+G(d,p)	-3.255032	345	400	
B3LYP/6-311G(2d,2p)	-3.261525	284	513	866
B3LYP/6-311+G(2d,2p)	-3.266090	334	417	
B3LYP/6-311G(2df,2pd)	-3.270451	294	522	
B3LYP/6-311+G(2df,2pd)	-3.274864	326	416	
B3LYP/aug-cc-pVTZ	-3.288942	320	410	

^aEnergy of conformer is given as $-(E + 727)$ H. ^bDifference is relative to g-Eq form and given in cm⁻¹. ^cBlank energy differences optimize to t-Eq conformer when using that method/basis set.

The COCl scissoring motion for this conformer is predicted at 872 cm⁻¹, which is 49 cm⁻¹ higher frequency with respect to the corresponding mode of g-Eq conformer with approximately one-third the intensity and is therefore assigned at 875 cm⁻¹.

There are only a few of the vibrational assignments which could be made for the t-Eq conformer. This is not unexpected since the intensity predictions are low and this conformer is present at ambient temperature as only 12(±1)% of the sample. Again from the spectra of the xenon solutions, it was possible to assign the ring breathing mode and three of the ring deformational fundamentals and these fundamentals were observed at 964, 933, 919, and 672 cm⁻¹, respectively. Once these vibrations were observed in the xenon solutions, it was possible to assign them in the infrared spectra of the gas. The mode predicted at 975 cm⁻¹ is observed at lower frequency than the corresponding modes of the two most abundant conformers and is now assigned to the band at 964 cm⁻¹. The ring deformation assignments at 933 and 919 cm⁻¹ are in good agreement with the corresponding vibrations of the other two conformers. However, the band at 666 cm⁻¹ is assigned at a higher frequency compared to the band assignments of these fundamentals of the other two conformers. The fifth ring deformation, ν_{31}'' , was not observed but it is believed to be at 946 cm⁻¹, which is the same frequency for the corresponding mode for the g-Eq conformer.

5. CONFORMATIONAL STABILITY

To determine the enthalpy differences among the three observed conformers of cyclobutylcarboxylic acid chloride, the sample was dissolved in liquefied xenon and the infrared spectra were recorded as a function of temperature from -70 to -100 °C. Relatively small interactions are expected to occur between

xenon and the sample. Therefore, only small wavenumber shifts are anticipated for the xenon interactions when passing from the gas phase to the liquefied xenon, which is confirmed with an average shift of 1 cm⁻¹ for the fundamentals for the three observed conformers indicating this should not be a major influence on the enthalpy difference between the forms. A significant advantage of this study is that the conformer bands are better resolved in comparison with those in the infrared spectrum of the vapor. From ab initio calculations, the dipole moments of the three conformers are predicted to have similar values and the molecular sizes of the three conformers are nearly the same, and thus, the ΔH value obtained from the temperature dependent infrared study is expected to be near that for the gas.^{18–22}

Once confident assignments have been made for the fundamentals of three observed conformers the task was then to find pairs of bands from which the enthalpy difference could be obtained. The bands should be sufficiently resolved for determining their intensities. The selection of the bands to use in the enthalpy determination was complicated due to the presence of three conformers with each having several broad intense bands; however, it was significantly simplified by the exceptionally good predictions of the relative band positions for the g-Eq, g-Ax, and t-Eq fundamentals in the 1200 to 400 cm⁻¹ region of the spectra (Figure 3) where there are a limited number of overtone and combination bands possible. Examples of this are the fundamentals at 1177 and 1021 cm⁻¹ for the g-Eq and g-Ax forms where the bands are predicted at 1179 and 1022 cm⁻¹, respectively. The g-Eq band at 1177 cm⁻¹ was found to not be significantly affected by the underlying t-Eq fundamental predicted at 1181 cm⁻¹ with a predicted intensity of 0.6 km/mol. The bands at 1137 and 1143 cm⁻¹ were assigned for the t-Eq and g-Ax fundamentals, respectively, where these assignments are based on their relative band positions and intensities. The g-Ax band at 1020 cm⁻¹ predicted at 1022 cm⁻¹ was found to not be significantly affected by the underlying t-Eq fundamental at 1029 cm⁻¹, which has a predicted intensity of 0.6 km/mol. Finally the band at 1108 cm⁻¹ was assigned to the g-Eq fundamental (β -CH₂ rock) predicted at 1120 cm⁻¹, which was found to not be significantly affected by the broad band of the same conformer at 1066 cm⁻¹ nor the two fundamentals located beneath the 1065 cm⁻¹ band predicted at 1105 cm⁻¹ for the g-Ax conformer and 1101 cm⁻¹ for the t-Eq form and assigned at 1089 and 1079 cm⁻¹, respectively.

The fundamentals at 569 cm⁻¹ for the g-Eq conformer and 488 cm⁻¹ for the t-Eq form are predicted to be free of any bands in near coincidence. The bands at 645, 660, and 666 cm⁻¹ were selected for the g-Eq, g-Ax, and t-Eq conformers, respectively, which can be confidently assigned based on their relative frequencies from the ab initio calculations. These four g-Eq, three g-Ax, and three t-Eq bands were used for the enthalpy determination as they were each found to not be significantly affected by any nearby predicted fundamentals. The assignment of these bands is shown in Figure 2, where the conformer assigned is labeled above the band.

The intensities of the individual bands were measured as a function of temperature and their ratios were determined. An example set of assigned fundamental bands with one from the g-eq (645 cm⁻¹), g-Ax (873 cm⁻¹), and t-eq (1137 cm⁻¹) conformers each have been provided in Figure 4. The intensities of the g-Eq and t-Eq bands in the figure have been doubled to allow for better comparison of the bands, but this

Table 7. Structural Parameters (Å and deg), Rotational Constants (MHz), and Dipole Moments (Debye) for the g-Eq Form of Cyclobutylcarboxylic Acid Chloride

structural parameters	int. coord	MP2(full)/6-311+G(d,p)	microwave ^a	ED ^c	adjusted r_0^e
$r_{C_\alpha-C}$	R_1	1.492	1.509 ^b	1.490(3) ^d	1.491(4)
$r_{C=O}$	R_2	1.193	1.191 ^b	1.195(13)	1.193(3)
$r_{C_\alpha-C_\beta}$	R_3	1.555	1.535 ^b	1.540(3) ^d	1.553(4)
$r_{C_\alpha-C_{\beta'}}$	R_4	1.542	1.535 ^b	1.540(3) ^d	1.540(4)
$r_{C_\gamma-C_\beta}$	R_5	1.548	1.55 ^b	1.540(3) ^d	1.547(4)
$r_{C_\gamma-C_{\beta'}}$	R_6	1.548	1.55 ^b	1.540(3) ^d	1.546(4)
r_{C-Cl}	R_7	1.798	1.790 ^b	1.793(6) ^d	1.801(3)
$r_{C_\alpha-H}$	r_1	1.094	1.10 ^b	1.128(14) ^d	1.094(2)
$r_{C_\beta-H_1}$	r_2	1.094	1.085 ^b	1.128(14) ^d	1.094(2)
$r_{C_{\beta'}-H_1}$	r_3	1.093	1.085 ^b	1.128(14) ^d	1.093(2)
$r_{C_\beta-H_2}$	r_4	1.091	1.085 ^b	1.128(14) ^d	1.091(2)
$r_{C_{\beta'}-H_2}$	r_5	1.091	1.085 ^b	1.128(14) ^d	1.091(2)
$r_{C_\gamma-H_1}$	r_6	1.091		1.128(14) ^d	1.091(2)
$r_{C_\gamma-H_2}$	r_7	1.093		1.128(14) ^d	1.093(2)
$\angle C_\alpha CO$	ϕ_1	128.0	123.2(29)	127.0(15)	127.8(5)
$\angle ClCC_\alpha$	ϕ_2	111.1	112.7(15)	111.0(20)	110.8(5)
$\angle ClCO$	ϕ_3	120.8		122.0	121.2(5)
$\angle C_\beta C_\alpha C$	ϕ_4	116.6		112.8	117.5(5)
$\angle C_\beta C_\alpha C$	ϕ_5	118.7		112.8	119.6(5)
$\angle C_\beta C_\alpha C_\beta$	θ_1	88.4		90.9	87.4(5)
$\angle C_\gamma C_\beta C_\alpha$	θ_2	87.1		90.9	88.0(5)
$\angle C_\gamma C_{\beta'} C_\alpha$	θ_3	87.6		90.9	88.6(5)
$\angle C_\beta C_\gamma C_\beta$	θ_4	88.4		90.9	87.5(5)
$\angle HC_\alpha C_\beta$	σ_1	109.9		116.2	107.6(5)
$\angle HC_\alpha C_{\beta'}$	σ_2	112.6		116.2	113.7(5)
$\angle HC_\alpha C$	σ_3	109.2	110.07 ^b	107.5	109.2(5)
$\angle H_1 C_\beta C_\alpha$	λ_1	110.3		116.2	110.3(5)
$\angle H_1 C_{\beta'} C_\alpha$	λ_2	110.1		116.2	110.1(5)
$\angle H_1 C_\beta C_\gamma$	λ_3	111.1		116.2	111.4(5)
$\angle H_1 C_{\beta'} C_\gamma$	λ_4	111.4		116.2	111.7(5)
$\angle H_2 C_\beta C_\alpha$	λ_5	117.5		116.2	117.3(5)
$\angle H_2 C_{\beta'} C_\alpha$	λ_6	117.7		116.2	117.9(5)
$\angle H_2 C_\beta C_\gamma$	λ_7	119.3		116.2	118.4(5)
$\angle H_2 C_{\beta'} C_\gamma$	λ_8	118.8		116.2	117.9(5)
$\angle H_1 C_\beta H_2$	λ_9	109.7		102.0	109.7(5)
$\angle H_1 C_{\beta'} H_2$	λ_{10}	109.6		102.0	109.6(5)
$\angle H_1 C_\gamma C_\beta$	π_1	117.7		116.2	118.1(5)
$\angle H_1 C_\gamma C_{\beta'}$	π_2	118.0		116.2	118.3(5)
$\angle H_2 C_\gamma C_\beta$	π_3	110.7		116.2	110.8(5)
$\angle H_2 C_\gamma C_{\beta'}$	π_4	111.1		116.2	111.1(5)
$\angle H_1 C_\gamma H_2$	π_5	109.5		102.0	109.5(5)
$\tau_{C_\gamma C_\beta C_{\beta'} C_\alpha}$	τ_1	31.3	20.0(24)	21(5)	30.9(5)
$\tau_{HC_\alpha CO}$	τ_2	127.5		123	130.0(5)
$\tau_{HC_\alpha CCl}$	τ_3	55.0	61.1(24)	57(5)	55.0(5)
$\tau_{ClC_2C_\alpha O}$	τ_4				
A (MHz)		4368.30	4349.86(17)		4350.60
B (MHz)		1411.29	1414.78(1)		1414.66
C (MHz)		1150.70	1148.24(1)		1148.28
$ \mu_a $		3.049			
$ \mu_b $		1.743			
$ \mu_c $		0.848			
$ \mu_t $		3.613			

^aProposed structural parameters, rotational constants, and dipole moments from ref 4. ^bAssumed values. ^cProposed structural parameters from the electron diffraction study.¹ ^dC–C bond length values and all C–H distances are assumed to be the same. ^eAdjusted parameters using the microwave data from Table 1 for the given ground states.

doubling in no way affects the enthalpy determination. With the measured intensity values of the conformer fundamentals the enthalpy values were obtained by application of the van't Hoff

equation $-\ln K = \Delta H/(RT) - \Delta S/R$. The enthalpy difference was determined from a plot of $-\ln K$ versus $1/T$, where $\Delta H/R$ is the slope of the line and K is substituted with the appropriate

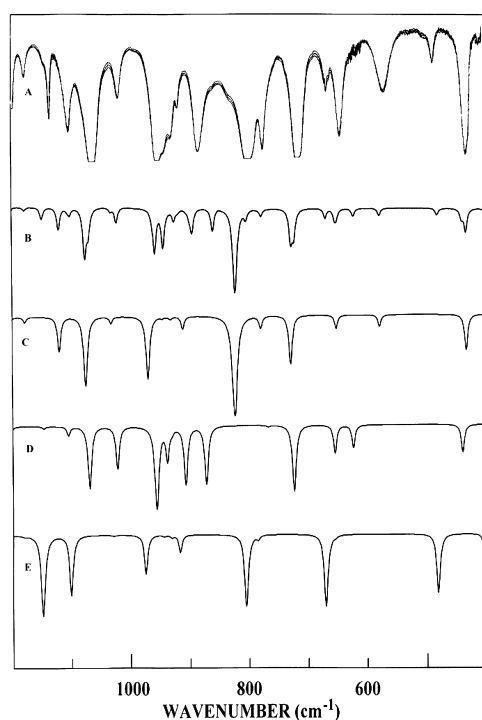


Figure 3. Experimental and predicted mid-infrared spectra of cyclobutylcarboxylic acid chloride: (A) observed spectra of xenon solutions at -80 , -90 , and -100 °C; (B) simulated spectrum of mixture of g-Eq, g-Ax ($\Delta H = 91$ cm $^{-1}$), and t-Eq ($\Delta H = 173$ cm $^{-1}$) conformers at -80 °C; (C) simulated g-Eq conformer; (D) simulated g-Ax conformer; and (E) simulated t-Eq conformer.

intensity ratios, i.e. $I_{\text{conf-1}}/I_{\text{conf-2}}$, etc. It was assumed that ΔS and α (thermal expansion constant) are not functions of temperature in the range studied.

These bands were utilized for the determination of the enthalpy difference by combining them to form 12 independent band pairs each for the g-Eq to g-Ax and for the g-Eq to t-Eq independent enthalpy values and 9 band pairs for the g-Ax to t-Eq independent enthalpy values. These values are listed for each band pair in Tables 9–11 and are within a relatively small

range. The intensity data from each band pair is combined with the other band pairs to form a single data set for each conformer pair. From this single data set for each pair of conformers the enthalpy differences and error limits were determined to be 91 ± 4 cm $^{-1}$ from the g-Eq to the g-Ax form, 173 ± 4 cm $^{-1}$ from the g-Eq to the t-Eq conformer, and 82 ± 3 cm $^{-1}$ from the g-Ax to the t-Eq conformer as listed in Tables 9–11. The error limit is derived from the statistical standard deviation of 1σ of the measured intensity data taken as a single data set, but it does not take into account small associations with the liquid xenon or the possible presence of overtones and combination bands in near coincidence of the measured fundamentals. The variations in the individual values are undoubtedly due to these types of interferences, but by taking several pairs, the effect of such interferences should cancel. However, this statistical uncertainty is probably better than can be expected from this technique and, therefore, an uncertainty of about 10% in the enthalpy difference is probably more realistic, i.e., 91 ± 9 cm $^{-1}$ from the g-Eq to the g-Ax conformer, 173 ± 17 cm $^{-1}$ from the g-Eq to the t-Eq form, and 82 ± 8 cm $^{-1}$ from the g-Ax to the t-Eq conformer. From the enthalpy differences the conformer abundance is estimated to be 54% g-Eq, 35(± 1)% g-Ax, and 12(± 1)% t-Eq at ambient temperature.

6. STRUCTURAL PARAMETERS

An electron diffraction (ED) study¹ was the first study performed on cyclobutylcarboxylic acid chloride where the structure was determined for the g-Eq conformer with a mean C–C distance of 1.540(3) Å for all the carbons in the ring and +0.05 (1.590) Å for the C–C distance outside the ring. The remaining structural parameters have very large errors which makes them somewhat meaningless for comparison with other structures. This was followed by a combined microwave and vibrational study⁴ where the ^{35}Cl isotopologue of the g-Eq conformer was observed and rotational constants were determined. In this microwave study the diagnostic least-squares adjusted structural parameters were determined by utilizing a combination of assumed parameters and parameters taken from the structure reported in the ED study.¹ The resulting extremely large uncertainties in the heavy atom angles

Table 8. Rotational Constants (MHz), Quadratic Centrifugal Distortion Constants (kHz), and Quadrupole Coupling Constants (MHz) for the ^{35}Cl and ^{37}Cl Isotopomers of the g-Eq Conformer of Cyclobutylcarboxylic Acid Chloride

	$c\text{-C}_4\text{H}_7\text{C}(\text{O})^{35}\text{Cl}$				$c\text{-C}_4\text{H}_7\text{C}(\text{O})^{37}\text{Cl}$	
	MP2(full)/6-311+G(d,p)	ref 4	Fit 1	Fit 2	MP2(full)/6-311+G(d,p)	fit
A	4368.2065	4349.86(17)	4349.84294(48)	4349.8383(103)	4339.5884	4322.0555(56)
B	1411.2866	1414.78(1)	1414.80319(36)	1414.8038(18)	1381.0680	1384.50581(105)
C	1150.6863	1148.24(1)	1148.24114(18)	1148.2389(15)	1128.6613	1126.35465(101)
Δ_J	0.2999	0.25(2)	0.2786(40)	0.2811(85)	0.2925	0.2730(46)
Δ_{JK}	−1.1256	−2.44(49)	−0.9523(32)	−0.988(83)	−1.167	−1.001(21)
Δ_K	5.047		4.741(37)	4.52(97)	5.2	5.8(1)
δ_J	0.11171	0.088(16)	0.09685(96)	0.1034(32)	0.1092	0.0994(77)
δ_K	1.642		1.401(55)	1.61(26)	1.59	1.44(19)
χ_{aa}	−16.9372		−18.2005(43)	−18.17(13)	−14.0482	−15.0614(42)
χ_{ab}	−44.63		−46.21(11)	−46.3(32)	−35.08	−36.01(18)
χ_{bb}	−6.2552		−5.9667(49)	−5.88(14)	−4.2349	−3.9980(59)
χ_{cc}	23.1924		24.1672(56)	24.06(16)	18.2831	19.0594(52)
n		17	69	95		84
s		64	2.2	64		2.6
rsm (FT)		8		8		
rsm (MW)		114		114		

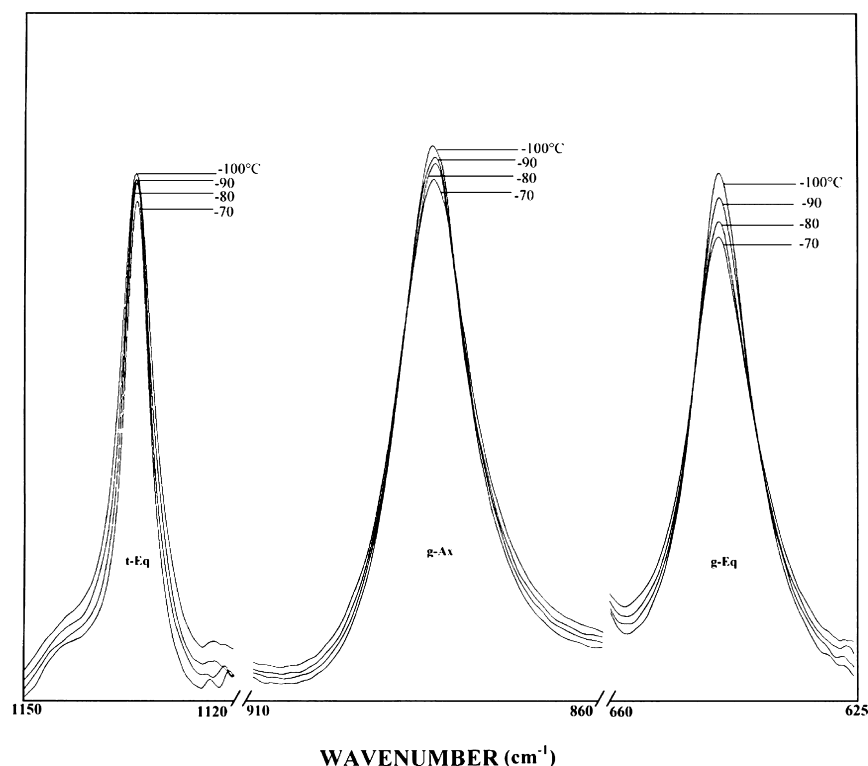


Figure 4. Temperature-dependent (−70 to −100 °C) mid-infrared spectrum of cyclobutylcarboxylic acid chloride dissolved in liquid xenon.

Table 9. Temperature and Intensity Ratios of the g-Eq and g-Ax Bands of Cyclobutylcarboxylic Acid Chloride

	T (°C)	$1/T$ ($\times 10^{-3}$ K $^{-1}$)	I_{569}/I_{660}	I_{569}/I_{1020}	I_{569}/I_{1143}	I_{645}/I_{660}	I_{645}/I_{1020}	I_{645}/I_{1143}
liquid xenon	−70	4.922	1.250	0.816	1.860	1.406	0.918	2.093
	−75	5.047	1.302	0.848	1.909	1.426	0.929	2.091
	−80	5.177	1.323	0.847	1.955	1.462	0.936	2.159
	−85	5.315	1.328	0.845	1.933	1.496	0.951	2.178
	−90	5.460	1.379	0.875	1.978	1.530	0.971	2.196
	−95	5.613	1.414	0.895	2.000	1.564	0.990	2.213
	−100	5.775	1.433	0.906	2.043	1.597	1.009	2.277
ΔH^a			107 ± 9	80 ± 11	67 ± 9	107 ± 3	78 ± 4	67 ± 7
	T (°C)	$1/T$ ($\times 10^{-3}$ K $^{-1}$)	I_{1108}/I_{660}	I_{1108}/I_{1020}	I_{1108}/I_{1143}	I_{1176}/I_{660}	I_{1176}/I_{1020}	I_{1176}/I_{1143}
liquid xenon	−70	4.922	1.328	0.867	1.977	1.359	0.888	2.023
	−75	5.047	1.380	0.899	2.023	1.395	0.909	2.045
	−80	5.177	1.385	0.887	2.045	1.431	0.916	2.114
	−85	5.315	1.420	0.903	2.067	1.511	0.961	2.200
	−90	5.460	1.455	0.923	2.087	1.530	0.971	2.196
	−95	5.613	1.459	0.924	2.064	1.519	0.962	2.149
	−100	5.775	1.567	0.991	2.234	1.597	1.009	2.277
ΔH^a			115 ± 14	89 ± 17	75 ± 18	125 ± 16	97 ± 13	85 ± 19

^aAverage value $\Delta H = 91 \pm 4$ cm $^{-1}$ (1.09 ± 0.05 kJ mol $^{-1}$) with the g-Eq conformer the more stable form and the statistical uncertainty (1σ) obtained by utilizing all of the data as a single set.

determined are most likely a result of these assumed parameters and the parameters taken from the ED study. Therefore, we have determined the rotational constants for two isotopic species for the g-Eq conformer giving six constants available for the structural determination.

We have found that good structural parameters for hydrocarbons and many substituted ones can be determined by adjusting the structural parameters obtained from the ab initio MP2(full)/6-311+G(d,p) calculations to fit the rotational constants obtained from microwave experimental data by using

a computer program “A&M” (Ab initio and Microwave) developed²³ in our laboratory.

We²⁴ have shown that ab initio MP2(full)/6-311+G(d,p) calculations predict the carbon–hydrogen r_0 structural parameters for more than fifty hydrocarbons to at least 0.002 Å compared to the experimentally determined²⁵ values from isolated CH stretching frequencies which agree with previously determined values from earlier microwave studies. Therefore, all of the carbon–hydrogen parameters can be taken from the MP2(full)/6-311+G(d,p) predicted values for the g-Eq conformer of cyclobutylcarboxylic acid chloride. To further reduce

Table 10. Temperature and Intensity Ratios of the g-Eq and t-Eq Bands of Cyclobutylcarboxylic Acid Chloride

	T (°C)	$1/T$ ($\times 10^{-3}$ K $^{-1}$)	I_{569}/I_{488}	I_{569}/I_{666}	I_{569}/I_{1137}	I_{645}/I_{488}	I_{645}/I_{666}	I_{645}/I_{1137}
liquid xenon	−70	4.922	0.842	0.833	0.792	0.947	0.938	0.891
	−75	5.047	0.884	0.878	0.840	0.968	0.961	0.920
	−80	5.177	0.915	0.901	0.860	1.011	0.995	0.950
	−85	5.315	0.926	0.915	0.870	1.043	1.030	0.980
	−90	5.460	0.989	0.959	0.919	1.098	1.065	1.020
	−95	5.613	1.022	0.994	0.949	1.130	1.099	1.051
	−100	5.775	1.043	1.018	0.980	1.163	1.134	1.092
ΔH^a			176 ± 12	159 ± 10	166 ± 11	176 ± 8	158 ± 4	166 ± 3
	T (°C)	$1/T$ ($\times 10^{-3}$ K $^{-1}$)	I_{1108}/I_{488}	I_{1108}/I_{666}	I_{1108}/I_{1137}	I_{1176}/I_{488}	I_{1176}/I_{666}	I_{1176}/I_{1137}
liquid xenon	−70	4.922	0.895	0.885	0.842	0.916	0.906	0.861
	−75	5.047	0.937	0.930	0.890	0.947	0.940	0.900
	−80	5.177	0.957	0.943	0.900	0.989	0.974	0.930
	−85	5.315	0.989	0.977	0.930	1.053	1.040	0.990
	−90	5.460	1.043	1.012	0.970	1.098	1.065	1.020
	−95	5.613	1.054	1.025	0.980	1.098	1.068	1.020
	−100	5.775	1.141	1.113	1.071	1.163	1.134	1.092
ΔH^a			184 ± 12	167 ± 14	174 ± 16	194 ± 16	177 ± 16	184 ± 16

^aAverage value $\Delta H = 173 \pm 4$ cm $^{-1}$ (2.07 ± 0.04 kJ mol $^{-1}$) with the g-Eq conformer the more stable form and the statistical uncertainty (1 σ) obtained by utilizing all of the data as a single set.

the number of independent variables, the structural parameters are separated into sets according to their types where bond distances in the same set keep their relative ratio, and bond angles and torsional angles in the same set keep their difference in degrees. This assumption is based on the fact that errors from ab initio calculations are systematic. Therefore, it should be possible to obtain “adjusted r_0 ” structural parameters for the eleven parameters of the seven heavy atoms by adjusting the C–C distances as a single set and adjusting the \angle CCC angles as another set leaving seven sets of parameters to adjust. This structure, however, must be evaluated by using parameters from similar molecules to help account for the relatively low number of rotational constants available and, thus, the $-\text{C}(\text{O})\text{Cl}$ parameters have a limited range that they change from the ab initio predicted values as has been reported in the literature. This is particularly true for the C=O bond distance which changes very little from its molecular environment.

The resulting adjusted r_0 parameters are listed in Table 7, where it is believed that the Cl–C and O=C distances should be accurate to ± 0.003 Å, the C–C distances accurate to ± 0.004 Å, the C–H distances accurate to ± 0.002 Å, and the uncertainties of the angles should be within $\pm 0.5^\circ$. The fit of the six determined rotational constants (Table 12) by the adjusted r_0 structural parameters is good with variations of the differences with values being less than 0.9 MHz. Therefore, it is believed that the suggested uncertainties are realistic values and the determined structural parameters are probably as accurate as can be obtained for the molecule in the gas phase by either electron diffraction or microwave substitution methods. However, with more rotational constants from further isotopic substitutions the accuracy of the adjusted r_0 parameter values could be improved.

7. DISCUSSION

The vibrational assignments reported herein are based on a significant amount of information with the infrared spectrum of the xenon solutions, band contours in the infrared spectra of the gas, and predictions of the fundamental frequencies from the scaled ab initio MP2(full)/6-31G(d) calculations as well as the predicted intensities. For the g-Eq conformer the ab initio

predicted frequencies differ by an average of 8 cm $^{-1}$, which represents 0.6% error. The percent error for the predictions for the g-Ax conformer is 4 cm $^{-1}$ or 0.3% error. Thus the relatively small basis set of 6-31G(d) by the MP2(full) calculations with two scaling factors provides excellent predicted frequencies for aiding the vibrational assignments.

There are three repeated t-Eq frequencies which were assigned based on the most stable g-Eq conformer. These fundamentals are the C–C stretch, which is now assigned at 1110 cm $^{-1}$ in the infrared spectra of the gas, and the ring deformation, which is assigned at 946 cm $^{-1}$. The third fundamental is the β -CH $_2$ rock, which is assigned to the band at 776 cm $^{-1}$ in the infrared spectra of the xenon solutions. The t-Eq $-\text{COCl}$ wag motion is an interesting fundamental where this motion is predicted at 654 cm $^{-1}$ with a low infrared intensity of 0.7 km/mol and was not observed in the infrared spectra of the gas unlike the other two forms where this motion was observed at 645 and 662 cm $^{-1}$ for the g-Eq and g-Ax conformers, respectively. This is due to the low intensity of this fundamental as compared to the g-Eq fundamental with an intensity of 8.2 km/mol. These are several examples where the fundamentals of the g-Eq and g-Ax form have significantly different intensities than the same mode from the t-Eq conformer.

In general for the g-Eq conformer the mixing was extensive for the fundamentals starting at 1232 cm $^{-1}$ and lower frequencies. Most of the fundamentals have extensive contributions from three or four symmetry coordinates and several of the descriptions are more for bookkeeping than an accurate description of the molecular motions. The g-Ax conformer is similar, with extensive mixing starting from the vibration at 1209 cm $^{-1}$ and below. Similarly, several of the approximate descriptions for the fundamentals of the g-Ax form are again more for bookkeeping than providing descriptions of the molecular motions. Of significant note is the ν_{20}' fundamental where it has been assigned as S_{20} (C–C stretch) despite only being 10% contribution and it has been described as such as any other placement results in several bookkeeping descriptions. However, for the t-Eq conformer, the descriptions are much more realistic than the other two conformers except

Table 11. Temperature and Intensity Ratios of the g-Ax and t-Eq Bands of Cyclobutylcarboxylic Acid Chloride

T (°C)	1/T (×10 ⁻³ K ⁻¹)	I ₆₆₀ /I ₄₈₈	I ₆₆₀ /I ₆₆₆	I ₆₆₀ /I ₁₁₃₇	I ₁₀₂₀ /I ₄₈₈	I ₁₀₂₀ /I ₆₆₆	I ₁₀₂₀ /I ₁₁₃₇	I ₁₁₄₃ /I ₄₈₈	I ₁₁₄₃ /I ₆₆₆	I ₁₁₄₃ /I ₁₁₃₇
liquid xenon										
-70	4.922	0.674	0.667	0.634	1.032	1.021	0.970	0.453	0.448	0.426
-75	5.047	0.679	0.674	0.645	1.042	1.034	0.990	0.463	0.460	0.440
-80	5.177	0.691	0.681	0.650	1.080	1.063	1.015	0.468	0.461	0.440
-85	5.315	0.697	0.688	0.655	1.096	1.082	1.030	0.479	0.473	0.450
-90	5.460	0.717	0.696	0.667	1.130	1.096	1.051	0.500	0.485	0.465
-95	5.613	0.723	0.703	0.672	1.141	1.110	1.061	0.511	0.497	0.475
-100	5.775	0.728	0.710	0.684	1.152	1.124	1.082	0.511	0.498	0.480
ΔH ^a		69 ± 5	51 ± 1	59 ± 3	97 ± 9	80 ± 6	87 ± 6	109 ± 10	91 ± 8	99 ± 8

^aAverage value ΔH = 82 ± 3 cm⁻¹ (0.98 ± 0.04 kJ mol⁻¹) with the g-Ax conformer the more stable form and the statistical uncertainty (1σ) obtained by utilizing all of the data as a single set.

Table 12. Comparison of Rotational Constants (MHz) Obtained from Modified Ab Initio MP2(full)/6-311+G(d,p) Structural Parameters and the Experimental Values from the Microwave Spectra of g-Eq Conformer of Cyclobutylcarboxylic Acid Chloride

isotopomers	rotational constant	Fit 1 from Table 8	adjusted r ₀	Δ
c-C ₄ H ₇ C(O) ³⁵ Cl	A	4349.8429(25)	4350.60	0.76
	B	1414.8032(25)	1414.66	0.14
	C	1148.2411(25)	1148.28	0.04
c-C ₄ H ₇ C(O) ³⁷ Cl	A	4322.0555(56)	4321.22	0.84
	B	1384.5058(25)	1384.54	0.04
	C	1126.3546(25)	1126.43	0.08

for the ν₁₈'' fundamental described as the COCl rock which have only 17% S₁₈(COCl rock) with contributions of 34% S₂₂, 21% S₂₀, and 10% S₁₂ modes. The A'' modes are reasonably well described with no specific arbitrary descriptions necessary. This reduction of the mixing is largely due to the symmetry constraints due to the change from C₁ to C_v symmetry going from gauche to trans. Therefore, the approximate descriptions for the normal modes provide reasonable information on the molecular motions of vibrations with several modes described more for bookkeeping purposes than as a complete description. It should be noted that this large change in mixing due to the symmetry constraints may be at least partially responsible for the significant differences in the fundamental intensities noted above.

Because the measured information was just barely sufficient to determine all quadratic centrifugal distortion constants, another fit was made for the ³⁵Cl isotopologue that included 13 frequencies involving higher rotational constants from the earlier microwave investigation.¹⁷ Each of these represented a blend of unresolved hyperfine components; each blend's frequency was assigned to the two innermost components of the predicted hyperfine quartet. (Four transitions from the previous study¹⁷ were omitted because their hyperfine pattern consisted of a widely spaced pair of narrow doublets.) Of course this fit (Fit 2 in Table 8) had a much larger standard deviation of 64 kHz, but the root-mean-square of the residuals for the FT data was only 8.0 kHz whereas the rms of the low-resolution measurements was 114 kHz. The difference of any constant between Fit 1 and Fit 2 was smaller than the combined error limits except for ΔJ where the difference was only slightly larger.

The derived centrifugal distortion constants generally agree between the isotopic species and the ab initio predictions (Table 8). The same can be said for the quadrupole coupling constants, taking into account that the theoretical ratio χ(³⁵Cl)/χ(³⁷Cl) for any coupling constant χ should be 1.269²⁶ provided there is no rotation of the principal inertial axes between the isotopologues.

The natural population analysis (NPA) was carried out for the g-Eq, g-Ax, and t-Eq conformers of cyclobutylcarboxylic acid chloride and for cyclobutane with the MP2(full) method at the 6-311+G(d,p) basis set. The C atoms for cyclobutane all carry a -0.34 charge. However the -C(O)Cl substitution of cyclobutane gives a charge distribution for the g-Eq form of C_α = -0.32, C_β = -0.31, C_{β'} = -0.32, C_γ = -0.33, Cl = -0.12, O = -0.59, and C = 0.69. The difference in NPA predicted for the other two stable conformers is less than 0.01 from those listed for the g-Eq form. The majority of the ring has similar charges

as those of cyclobutane indicating that $-\text{C}(\text{O})\text{Cl}$ has relatively little influence on the electron charge density in the ring.

Due to the relatively low number of rotational constants available for the g-Eq form of cyclobutylcarboxylic acid chloride the structural parameters must be evaluated for their accuracy and the number of parameters to change must be decreased. As stated in the structural parameters section the C–C distances were taken as a single set and the $-\text{C}(\text{O})\text{Cl}$ parameters were constrained within the limits determined from similar molecules. As can be seen in Table 13 the ab initio MP2(full)

Table 13. Structural Parameters^a of a Few Acetyl Chloride Molecules of the Form R-C(O)Cl (Å and deg)

structural parameters	R = CH ₃ ^b	R = CH ₂ CH ₃ ^c (cis)	R = CH(CH ₃) ₂ ^d (cis)
rC=O	1.192 [1.189(3)]	1.192 [1.192(3)]	1.193 [1.186(3)]
rC–Cl	1.795 [1.794(3)]	1.795 [1.796(4)]	1.798 [1.804(4)]
rC–C _α	1.500 [1.499(3)]	1.505 [1.506(3)]	1.510 [1.511(3)]
rC _α –C _β		1.522 [1.523(3)]	1.525 [1.534(3)]
rC _α –C _{β'}			1.535 [1.540(3)]
∠OCCl	120.6 [120.4(5)]	120.6 [120.7(6)]	120.3 [119.1(6)]
∠OCC	127.6 [127.2(5)]	127.4 [127.2(7)]	127.2 [127.3(7)]
∠ClCC	111.9 [112.4(5)]	111.9 [112.1(5)]	112.4 [113.6(5)]
∠CC _α C _β		112.3 [112.4(8)]	110.1 [109.7(8)]
∠CC _α C _{β'}			108.9 [109.9(8)]
∠C _β C _α C _{β'}			111.7 [113.8(27)]

^aMP2(full)/6-311+G(d,p) [experimental]. ^bAdjusted r_0 parameters determined from rotational constants taken from ref 26. ^cReference 27; adjusted r_0 parameters. ^dReference 28; adjusted r_0 parameters.

calculation at the 6-311+G(d,p) basis set does an excellent job predicting the bond distances and angles for this moiety. The predicted structural parameter values for the methyl²⁷ and ethyl compounds²⁸ for the distances are usually within 0.001 Å and within 0.5° for the angles of the r_0 structural parameter values. The isopropyl molecule²⁹ shows larger differences between the predicted structural parameter values and the values from the r_0 structural parameters. The structure was determined for the g-Eq form of cyclobutylcarboxylic acid chloride and the parameters were allowed to change in fitting of the rotational constants. As can be seen from Table 7 the differences between the MP2(full)/6-311+G(d,p) and the adjusted r_0 structural parameter values for the $-\text{C}(\text{O})\text{Cl}$ bond distances and angles are less than the proposed experimental errors and are very close to the values for similar bond distances and angles in Table 13.

The ring parameters are much more variable where the ring distances and angles for four-membered rings are often relatively sensitive to substitution as shown in Table 14. As the charges in the ring are fairly consistent with those for the cyclobutane molecule the ring structural parameters should be comparable between the two. It can be seen that the C_γ–C_β bond distances are ~0.008 Å shorter for the $-\text{C}(\text{O})\text{Cl}$ molecule as opposed to unsubstituted cyclobutane. These are probably not due to the electronic effects in the rings as these effects are predicted to be relatively small but rather due to the steric effects of the larger $-\text{C}(\text{O})\text{Cl}$ molecule's ring puckering angle. The C_α–C_β bond distances in the $-\text{C}(\text{O})\text{Cl}$ molecule are different from each other due to the oxygen group overlapping one of the C–C bonds, this bond distance is drastically reduced due to the steric effects of this overlap. The other C_α–C_β bond distance is much longer and is within the experimental error to the value from the cyclobutane r_0 structure. The ring structure of cyclobutylcarboxylic acid chloride is similar to that of cyclobutane as expected but with some logical departures brought on by the substitution of a –H with a $-\text{C}(\text{O})\text{Cl}$ group.

In this current study, the adjusted r_0 structural parameters have been determined for the g-Eq conformer; these should be comparable to the previously reported ED study.¹ In the ED study the structural parameters were obtained for the g-Eq form from a least-squares analysis of the anharmonic radial distribution function³⁵ in the interval $r \approx 0.0$ to 1.95 Å. All of the parameters have very large errors except the mean ring C–C, out of ring C–C, and the C–Cl distances which equal 1.540(3), 1.590(3), and 1.793(6) Å, respectively. These values are in excellent agreement with the adjusted r_0 structural parameters obtained in this study. The remaining parameters with large uncertainties are not meaningful though due to these large uncertainties, for the most part they agree within the stated errors with the adjusted r_0 structural parameters.

A decade later, a microwave and vibrational study followed⁴ where one isotopomer of the g-Eq conformer was observed and the rotational constants were determined. The structural parameters were determined by fixing all but five parameters where these assumptions were in part informed by using the ED study structural parameters. The five parameters were then determined with a diagnostic least-squares adjustment as described by Curl.³⁵ The structural parameters obtained have very large errors, which is partially due to the assumed parameters being off from the actual structure but also due to fitting three rotational constants with five parameters. The error is so large on these parameters that the ones that are far off from the adjusted r_0 structural parameters are probably not meaningful.

One of the major goals of this current study was the determination of the enthalpy difference between the con-

Table 14. Structural Parameters^a of a Few Four-Membered-Ring Molecules of the Form c-C₄H₇X (Å and deg)

structural parameters	X = F ^c			X = SiH ₃ ^f			
	X = H ^b	X = OH ^c (t-Eq)	X = Br ^d (Eq)	Eq	Ax	Eq	Ax
rC _α –C _β	1.5478 [1.5555(2)]	1.542 [1.547(3)]	1.535 [1.541(3)]	1.530 [1.543(3)]	1.534 [1.546(3)]	1.559 [1.562(3)]	1.559 [1.561(3)]
rC _β –C _γ	1.5478 [1.5555(2)]	1.548 [1.556(3)]	1.551 [1.552(3)]	1.551 [1.554(3)]	1.552 [1.554(3)]	1.546 [1.551(3)]	1.547 [1.553(3)]
puckering angle	32.34 [28.58(9)]	28.5 [31.3(10)]	34.4 [29.8(5)]	34.0 [37.4(5)]	29.2 [20.7(5)]	31.6 [29.0(5)]	29.0 [23.5(5)]

^aMP2(full)/6-311+G(d,p) [experimental]. ^bReference 29; r_0 parameters. ^cReference 30; adjusted r_0 parameters. ^dReference 31; adjusted r_0 parameters. ^eReference 31; adjusted r_0 parameters. ^fReference 32; adjusted r_0 parameters.

formers of the cyclobutylcarboxylic acid chloride where there had been different results reported. Fabregue² reported that the cyclobutylcarboxylic acid chloride exists in both the solid and liquid phases as the same nonsymmetrical isomer in which the COCl group is in the equatorial position with respect to the ring. From the ED study¹ it was indicated that the molecule exists as a conformational equilibrium mixture of gauche-like axial and gauche-like equatorial conformers. A decade later, the vibrational spectra was reinvestigated³ and it was found that the sample exists in a conformational equilibrium in the liquid and vapor phases. A few years later, the variable temperature Raman spectra of the liquid were studied⁴ from which the enthalpy difference between the g-Eq and high-energy (assumed t-Eq) conformations was determined to be 1.4 kcal mol⁻¹ (490 cm⁻¹). The enthalpy value obtained in this study from the Raman spectra of the liquid would give a population of 4% t-Eq at room temperature. This population is extremely small though with the assignment they propose it is not beyond reason. When compared to the vibrational assignment as determined in the current study it can be seen that this enthalpy value is far too large. In comparison the enthalpy determination between the g-Eq and t-Eq conformers is determined to be 173 ± 17 cm⁻¹ in the current study where it was determined from 12 band pairs. This is nearly one-third of the value determined in the liquid state. However, enthalpy values determined from spectra of the liquid state are normally significantly higher than those determined for samples in the vapor state or in xenon solutions, and therefore, the difference in the determined enthalpy values may be largely due to the difference from the samples from which they were obtained.

The experimental values determined from the variable temperature infrared spectra of the xenon solutions should be near those of the gas which should be similar to those of the isolated molecule. Therefore it can be useful to compare the ab initio and DFT energy differences shown in Table 6 with the experimental enthalpy differences. The order of stability is well predicted by the ab initio and DFT calculations where the correct order of stability is predicted by both the MP2 and B3LYP methods for all basis sets. The energy differences determined by the calculations approximately doubles for the g-Eq to g-Ax difference with addition of diffuse functions for the MP2 method, where the largest basis set without diffuse functions is very close to the experimental value. The B3LYP method for the same energy difference predicts the energy difference significantly higher and over three times the experimental value. The g-Eq to t-Eq energy difference is predicted significantly too large for all basis sets and both calculation methods. This is an interesting phenomenon where the addition of more functions into the ab initio basis sets actually causes poorer results. However, as is previously stated the order of stability is predicted correctly for all the calculations attempted.

There are few molecular geometries of the carboxylic acid chloride derivatives determined in the literature, which lead to a scarcity of molecular structural parameters and conformational determinations with which the current molecule could be compared. This would be an interesting topic to research and the five-membered ring and open chain derivatives would be of particular interest.

8. CONCLUSIONS

The microwave spectra for the two isotopologues of g-Eq have been assigned and the rotational constants have been reported.

From these rotational constants a complete structure has been determined which is made possible due to the reduction in the number of independent parameters as the C–H distances can be taken from the MP2(full)/6-311+G(d,p) structural parameters for substituted hydrocarbons.

The ring parameters appear to be largely determined due to steric effects rather than electrostatic effects. This is supported by the NPA predictions where the ring for cyclobutylcarboxylic acid chloride is nearly the same as cyclobutane in contrast to the significant difference in the ring puckering angle and C_α–C_β bond distances.

The observed fundamentals for the g-Eq, g-Ax, and t-Eq conformers have been assigned based upon the variable temperature infrared spectra of the xenon solutions. From the band intensities of several of these assigned fundamentals the enthalpy differences have been determined. The relative amounts at ambient temperature are 54% g-Eq, 35(±1)% g-Ax, and 12(±1)% t-Eq forms. This relatively small difference in the amount of each conformer is in direct contrast to the results from previous studies^{2–4} where the g-Ax and t-Eq conformers went largely unassigned and were assumed to be either high energy or transition states.

■ ASSOCIATED CONTENT

■ Supporting Information

. Symmetry coordinates for cyclobutylcarboxylic acid chloride g-Eq (Table S1) and cyclobutylcarboxylic acid chloride t-Eq (Table S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

[§]Taken in part from the thesis of Joshua J. Klaassen, which will be submitted in partial fulfillment of the Ph.D. degrees.

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[‡]Taken in part from the thesis of Bhushan S. Deodhar, which will be submitted in partial fulfillment of the Ph.D. degrees.

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