Conformational Stability from Temperature-Dependent FT-IR Spectra of Liquid Rare Gas Solutions, Barriers To Internal Rotation, Vibrational Assignment, and Ab Initio Calculations for 3-Chloropropene

J. R. Durig* and D. T. Durig[†]

Department of Chemistry, University of Missouri-Kansas City, Kansas City, Missouri

B. J. van der Veken and W. A. Herrebout

Department of Chemistry, Universitair Centrum Antwerpen Groenenborgerlaan 171,
B 2020 Antwerpen, Belgium

Received: March 9, 1999; In Final Form: June 5, 1999

The infrared spectra of 3-chloropropene, (allyl chloride) $CH_2{=}CHCH_2Cl$, dissolved in liquid argon (94−124 K), liquid krypton (117−167 K), and liquid xenon (161−221 K) at concentrations of about 1×10^{-2} M are reported. In argon the solubility is too low to determine the enthalpy difference between the conformers. For liquid krypton and xenon the temperature dependence of the infrared spectra in the CH_2 deformation region has been used to obtain an enthalpy difference of 96 ± 5 cm^{-1} (1.15 ± 0.06 kJ/mol) for the krypton solution and 147 ± 20 cm^{-1} (1.76 ± 0.24 kJ/mol) for the xenon solution with the gauche conformer the more stable rotamer. The asymmetric torsional transitions have been remeasured in the far-infrared spectrum and the fundamental for the cis conformer is observed at 147.3 cm^{-1} with four successive hot bands falling to lower frequency and the fundamental for the gauche conformer is observed at 102 cm^{-1} with four accompanying hot bands. Utilizing the enthalpy and torsional data along with the gauche dihedral angle (ClCCC) of 120.0°, the potential function governing the conformational interchange has been determined. The cis to gauche, gauche to gauche, and gauche to cis barriers have been determined to be 881, 699, and 1005 cm^{-1}, respectively. The structural parameters, conformational stability, infrared intensities, Raman activities, and depolarization ratios, along with the vibrational frequencies, have been obtained from ab initio calculations at the MP2/6-31G(d) level. These data are compared to the corresponding experimental quantities, and the overall results are compared and contrasted to those for some similar molecules.

Introduction

We previously determined the conformational barriers to internal rotation of 3-fluoropropene[1−4] (allyl fluoride) and 3-chloropropene[5] (allyl chloride) from an analysis of the far-infrared and low frequency Raman spectra of the vapor. From the analysis of these data for the fluoride it was concluded, in agreement with several previously reported studies (see ref 6 and references therein), that the conformation which has the fluorine atom cis to the double bond is thermodynamically preferred over the gauche rotamer in both the gaseous and liquid phases and is the only conformation present in the spectrum of the annealed solid. We[1,2] also have carried out ab initio calculations for 3-fluoropropene employing a variety of basis sets at the restricted Hartree−Fock (RHF) and Moller−Plesset (MP) to second-order levels. These calculations showed that the longer C═C bond distance and shorter C−F distance for the gauche conformer as determined from the earlier microwave study[7] compared to the similar distances for the cis conformer were in error and resulted from one of the carbon atoms lying nearly on one of the rotational axes for the gauche conformer. Therefore, the ab initio calculations provided guidelines for estimating the differences in the structural parameters between the two conformers along with predicted frequencies and the potential energy distribution for the normal modes.

More recently, we[6] carried out a temperature dependent study of the FT-IR spectra of the liquid rare gas solutions of 3-fluoropropene in order to better determine the enthalpy difference between the conformers. We also carried out some additional ab initio calculations with larger basis sets, but the MP2/6-311++G(d,p) calculations give the gauche conformer as the more stable rotamer which is inconsistent with all of the experimental data. Therefore, experimental determinations of the conformer stability of the allyl halides are important to evaluate the ab initio results.

In our earlier conformational study[5] of 3-chloropropene, the variable temperature study of the Raman spectrum of the liquid gave the gauche conformer as the more stable rotamer with an enthalpy difference of 178 ± 11 cm^{-1} (2.13 ± 0.38 kJ/mol). This value is much lower than the ab initio values of 368 cm^{-1} (4.40 kJ/mol) and 439 cm^{-1} (5.25 kJ/mol) previously obtained from the RHF/3-21G(d) and RHF/6-31G(d) calculations, respectively. From the variable temperature study of the Raman spectrum of the gas, the cis conformer appeared more stable but by less than 70 cm^{-1} (0.84 kJ/mol). However, considerable difficulty was encountered because of sample decomposition at elevated temperatures as well as from hot bands on the skeletal bending mode utilized for the enthalpy determination,

---

* Corresponding author phone, 01 816-235-1136; fax; 01 816-235-5191; e-mail, durigj@umkc.edu.

[†] Studies carried out while on sabbatical leave from the Departments of Chemistry and Physics, The University of the South, Sewanee, Tennessee.

10.1021/jp990831v CCC: $18.00

presumably from excited states of the asymmetric torsion. The potential function obtained from the low-frequency Raman and far-infrared data also gave rather inconclusive results with an enthalpy difference of 60 ± 51 cm^{-1} (0.72 ± 0.61 kJ/mol) with the cis rotamer the more stable form. These results were in contrast to those obtained from an electron diffraction study[8] where the gauche form was found to be more stable by 76 cm^{-1} (0.91 kJ/mol) as well as from an infrared spectral study[9] of the gas. In the latter study[9] no energy difference between the conformers was reported although the gauche form was proposed to be more stable. Finally, it should be noted that molecular mechanics calculations[10] give the cis conformer as the more stable rotamer by 35 cm^{-1} (0.42 kJ/mol). Therefore, there is still a question of the conformational stability of 3-chloropropene in the vapor state. To provide more definitive conformational data, we have carried out a study of the temperature-dependent FT-IR spectra of liquid rare gas solutions. Additionally, ab initio calculations have been carried out utilizing the 6-31G(d) basis set with full electron correlation by the perturbation method to second order (MP2)[11] as well as with the larger 6-311++G(d,p) basis set.

Although there have been several vibrational assignments proposed for 3-chloropropene, there are still several normal modes which have not been confidently assigned. Therefore, we have predicted the frequencies of the fundamentals along with the intensities of the infrared and Raman bands to aid in the vibrational assignment. The results of this experimental and theoretical study are reported herein.

Experimental

The sample of 3-chloropropene was obtained from Columbia Organic Chemical Co., Columbia, SC, and the purification was accomplished by a low-temperature, low-pressure fractionation column. The purity of the sample was checked by comparing the mid-infrared spectrum of the vapor with the previously reported[5,12] spectrum.

The mid-infrared spectra of the sample dissolved in liquified noble gases as a function of temperature were recorded on a Bruker model IFS-66V FT-IR equipped with a globar source, a Ge/KBr beam splitter, and an MCT detector. High purity noble gases (Matheson, 99.99%) were used typically in ca. 500−3000-fold excess. The temperature studies, ranging from 94 to 221 K with an accuracy of ±0.3 K, were performed in a specially designed cryostat cell which consisted of a 4 cm path length copper cell with wedged silicon windows sealed to the cell with indium gaskets and attached to a pressure manifold to allow for the filling and evacuation of the cell. The temperature was monitored with two Pt thermoresistors, and the cell was cooled with boiling liquid nitrogen. Once the cell was cooled to the desired temperature, a small amount of sample was condensed into the cell. The cell was then pressurized with noble gases, which immediately start to condense, allowing the compound to dissolve. For each temperature investigated, 200 interferograms were collected at 0.5 cm^{-1} resolution, averaged, and transformed with a Happ−Genzel function. The matrix isolation experiments were performed using a Leybold ROK 10−300 cryostat with closed-cycle refrigeration.

The far-infrared spectrum of the gas was recorded on a Nicolet model 200 SVX Fourier transform interferometer equipped with a vacuum bench, a Hg arc lamp source, and a liquid helium cooled Ge bolometer containing a wedged sapphire filter and a polyethylene window. A 6.25 μ Mylar beam splitter was employed, and the sample was contained in a 1 m multipass cell. The effective resolution was 0.08 cm^{-1}, and 512 interferograms were taken for both the sample and the empty cell. The interferograms were averaged and transformed by using a boxcar truncation function.

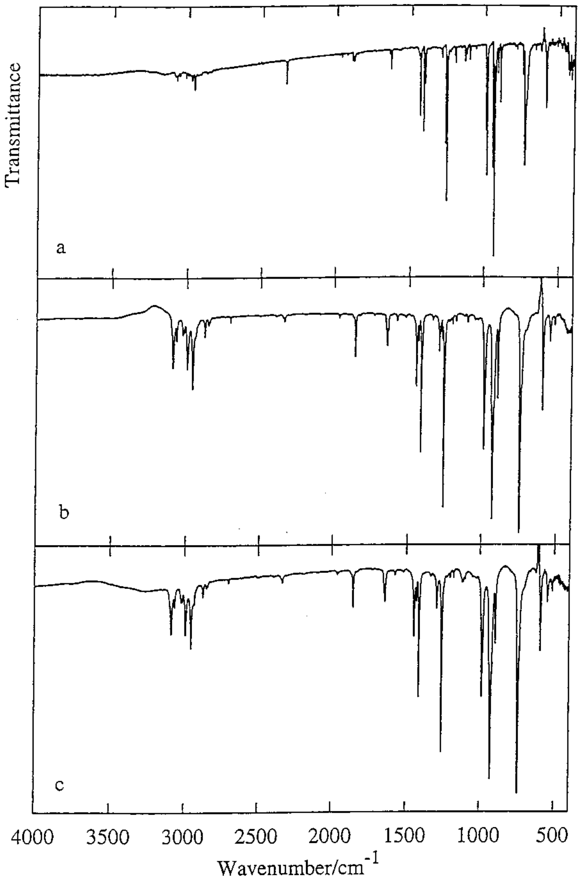

Figure 1. Mid-infrared spectra of 3-chloropropene dissolved in (a) liquified argon at 123 K; (b) liquified krypton at 166 K; and (c) liquified xenon at 216 K.

Results

Liquified Noble Gas Solutions. The mid-infrared spectra of allyl chloride dissolved in three liquified noble gas solutions were examined. Survey infrared spectra of these solutions are given in Figure 1, and the observed frequencies, together with the proposed assignments, are presented in Table 1. Only at the highest temperatures available in liquified argon could dilute solutions be prepared that were free from bands due to undissolved allyl chloride (small crystals floating in the liquid argon or absorbed on cell windows). This indicates poor solubility of the compound in this solvent, and prevented the enthalpy difference from being measured in liquified argon. Solubility problems did not occur in krypton or xenon, and mid-infrared spectra were recorded of a solution of allyl chloride in liquified krypton, at 10 different temperatures varying from 120.2 to 165.9 K, and of a solution in liquified xenon, at 6 different temperatures varying from 173.1 to 216.4 K. Details of some regions in which conformational doublets are present are given in Figures 2 and 3. As can be seen in these figures, most conformational doublets show a substantial degree of overlap, and are also overlapped by other bands in the spectrum. A number of such doublets were resolved by least-squares fitting, using Gauss/Lorentz sum bands. Detailed analysis of the results showed that reliable intensities for the components of the conformational doublets, for both solvents, were obtained only in the region between 1475 and 1375 cm^{-1}, shown in the

TABLE 1: Observed[a] Infrared Frequencies of 3-Chloropropene in the Gas, Amorphous, and Crystalline Solid Phases, and in Solution of Rare Gases

gas	rel. int.	amorp.	rel. int.	crystal	rel. int.	argon	rel. int.	krypton	rel. int.	xenon	rel. int.	ν_id	approximate description[b]
3111 Q	m			3096	vw			3104	w,sh	3100	w,sh	$\nu_1{}'$	$=CH_2$ antisymmetric stretch
				3091	w								
3009 Q	s	3086	m	3082	m	3098	m,sh	3095	m	3092	m,sh	ν_1	$=CH_2$ antisymmetric stretch
						3096	m	3092	m	3089	m		
				3066	w								
3078	w	3063	m	3062	w	3074	w	3071	w	3068	w		
3034	w	3021	m	3021	m	3031	w	3028	w	3025	w	ν_2	$=CH$ stretch
3026	w												
						3022	vw	3019	vw	3016	w	$\nu_2{}'$	$=CH$ stretch
3003	s	3006	w	3007	w	3000	m	2997	m	2994	m	ν_3	$=CH$ symmetric stretch
				2986	w								
2982	m	2984	m	2980	m	2994	w,sh	2991	w,sh	2988	w,sh	ν_4	CH antisymmetric stretch
2966	s	2959	m	2961	m	2962	m	2959	m	2954	m	ν_5	CH symmetric stretch
				1895	m								
1863	m	1884	m	1885	m	1861	m	1860	m	1857	m		combination
1657	m	1648	w			1655	w	1653	w	1650	w	$\nu_6{}'$	$C{=}C$ stretch
1647	m	1640	m	1640	m	1649	w	1647	w	1645	w	ν_6	$C{=}C$ stretch
				1638	w	1642	w	1641	w	1639	w		
		1589	w	1588	vw	1583	vw	1581	vw	1579	vw		
1452	m	1443	s	1453	m	1449	m	1448	m	1446	m	ν_7	CH_2 deformation
				1441	s								
		1426	vw			1433	w	1432	w	1430	w	$\nu_7{}'$	CH_2 deformation
				1417	s								
1418	s	1409	s	1412	s	1415	s	1413	s	1412	s	ν_8	$=CH_2$ deformation
				1407	s								
						1409	w	1407	w	1406	w	$\nu_8{}'$	$=CH_2$ deformation
						1341	v,vw	1338	vw	1336	vw	$\nu_9{}'$	$=CH$ bend
1294	w	1290	w	1293	m	1294	m			1290	m	ν_9	$=CH$ bend
						1289	w,sh			1285	w	$\nu_{10}{}'$	CH_2 wag
				1265	s								
1260	vs	1258	s	1260	m								
				1255	s	1259	vs			1256	vs	ν_{10}	CH_2 wag
		1235	w,sh	1235	w								
				1227	w								
1206	w	1203	w	1205	m	1204	vw	1202	vw	1200	vw	ν_{11}	CH_2 twist
				1199	m								
1180	vw	1178	vvw			1178	vw	1178	vw	1175	vw	$\nu_{11}{}'$	CH_2 twist
				1105	m								
		1100	w	1101	w	1101	vw					ν_{12}	$=CH_2$ wag
						1053	vw	1052	vw	1051	vw	$\nu_{12}{}'$	$=CH_2$ wag
989	s	993	s	993	s	988	s	987	s	985	s	ν_{13}	$=CH$ bend
				986	s								
983	s					982	m,sh	980	m	978	m	$\nu_{13}{}'$	$=CH$ bend
941	s	936	bd,vs	947	s	940	m	938	m	936	s	ν_{14}	$C-C$ stretch
				942	s								
								934	m				
930	vs			936	vs	930	vs	929	vs	927	vs	ν_{15}	$=CH_2$ wag
				931	s								
				929	m								
920	s	919	m,sh			920	m	918	m	916	m	$\nu_{14}{}'$	$C-C$ stretch
898	m	895	m	899	s	897	m	896	m	895	m	ν_{16}	CH_2 rock
751	vs	731	vs	731	vs	747	vs	746	vs	744	vs	ν_{17}	$C-Cl$ stretch
				719	vs								
748	s					745	m,sh	744	m	742	m,sh	ν_{17}	$C-{}^{37}Cl$ stretch
						735	w	734	w	732	w	$\nu_{17}{}'$	$C-Cl$ stretch
690	vw												
				598	m								
597	s	594	s	590	s	596	m	594	m	592	m	ν_{18}	$=CH_2$ twist
				588	s								
546	m	560	w			548	w	547	w	547	w	$\nu_{18}{}'$	$=CH_2$ twist
517	w	512	w			516	w	516	w	516	w	$\nu_{19}{}'$	$C{=}C-C$ bend
411	w	406	m	411	m							ν_{19}	$C{=}C-C$ bend
310	w	325	vw	325	vw								$2\nu_{21}{}'$
				306	w								
285	m	296	m	297	m							ν_{20}	$C-C-Cl$ bend
				290	m								
∼250	vw	∼250	vw									$\nu_{20}{}'$	$C-C-Cl$ bend
147.3	w											$\nu_{21}{}'$	torsion
102	vw	133	w	137	vw							ν_{21}	torsion
				133	vw								
				113	w								lattice modes
				86	w								

[a] Abbreviations used: s, strong; m, moderate; w, weak; v, very; bd, broad; sh, shoulder. [b] Normal modes are numbered according to the gauche conformer, and the cis fundamentals are indicated by a prime.

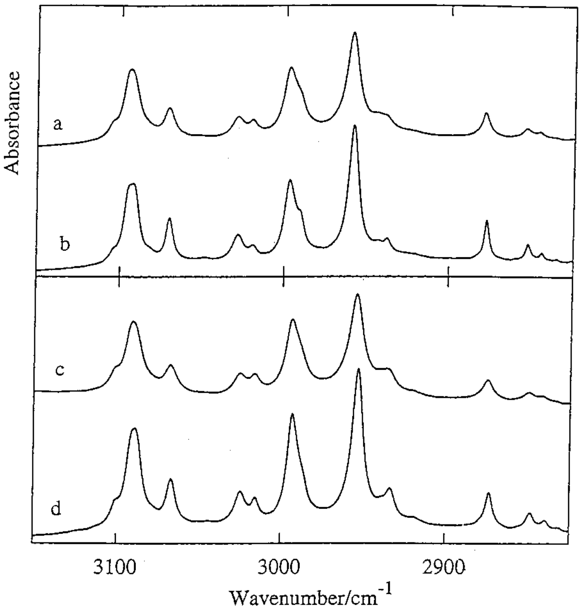

Figure 2. The C−H stretching region of 3-chloropropene dissolved in liquified krypton (top, a and b) and liquified xenon (bottom, c and d). The spectra in krypton were recorded at (a) 165.9 K and (b) 120.2 K, and the spectra in xenon were recorded at (c) 216.4 K and (d) 173.1 K.

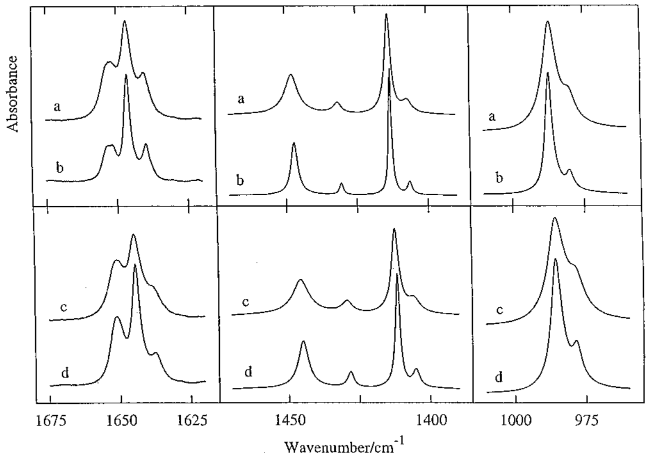

Figure 3. Details of the mid-infrared spectra of 3-chloropropene dissolved in liquified krypton (top, a and b) and liquified xenon (bottom, c and d). The spectra in krypton were recorded at (a) 165.9 K and (b) 120.2 K, and the spectra in xenon were recorded at (c) 216.4 K and (d) 173.1 K.

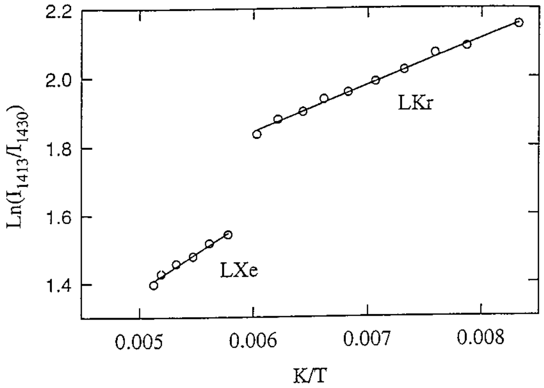

Figure 4. van't Hoff plots for the conformational equilibrium in 3-chloropropene dissolved in liquified krypton and xenon.

middle panel of Figure 3. As can be seen in Table 1, the bands at 1448 and 1413 cm^{-1} are assigned to the gauche conformer, whereas the bands at 1432 and 1407 cm^{-1} are due to the cis conformer. However, evidence to be presented below suggests that under the band at 1448 cm^{-1} a combination band due to the cis conformer is also present, so that the intensity of this band is not a reliable measure of the concentration of the gauche conformer. Also, it is believed that at the higher temperatures in each solvent the parameters, and therefore the intensity calculated, for the 1407 cm^{-1} band are less reliable. In view of the relative weakness of this band, the uncertainty of its parameters has little influence on the intensity calculated for the more intense band at 1413 cm^{-1}. Therefore, for the measurement of the ΔH, for both solvents, only the intensities of the bands at 1432 cm^{-1} (cis) and 1413 cm^{-1} (gauche) were used. The van't Hoff plots resulting from this analysis are shown in Figure 4. From these plots, the enthalpy difference between the more stable gauche and the less stable cis conformer was calculated to be 96 ± 5 cm^{-1} (1.15 ± 0.06 kJ/mol) for the solution in krypton and 147 ± 20 cm^{-1} (1.76 ± 0.24 kJ/mol) for the solution in xenon.

The ab initio calculations suggest that the conformers have different dipole moments, and it is tempting to ascribe the difference in ΔH between krypton and xenon solutions to differences in solvent stabilization of the gauche and cis conformers,[6] as predicted from reaction field theory.[13] However, it must be realized that the solutions in krypton and xenon have been investigated in different temperature intervals, and that ΔH is a temperature-dependent quantity. The change in the experimental ΔH value is relatively small, and the difference for the greater part presumably reflects the temperature dependence of ΔH only. Therefore, no attempts were made to apply reaction field theory to extrapolate a vapor phase value for ΔH by the method previously described.[13]

Matrix-Isolation: Photorotamerization. The mid-infrared spectra of solid argon matrixes containing allyl chloride were also investigated. With these experiments, the photorotamerization of cis and gauche allyl chloride was investigated. To this end, 1:500 allyl chloride/argon mixtures were deposited at 8 K, and the evolution of the spectra were followed, at regular intervals, for 48 h. For some experiments, the matrix was illuminated for the full period with unfiltered radiation of the globar source of the spectrometer, whereas for some other experiments the radiation was filtered through a quartz plate. Finally, some experiments were performed in which the matrix was subjected to the radiation only during recording of the spectra.

For experiments in which the matrix was continuously irradiated either with unfiltered or with filtered radiation, a gradual decrease of the bands due to the cis conformer was observed, while at the same time the bands due to the gauche conformer slightly increased in intensity. No such changes were observed for matrixes that were not irradiated. These observations suggest that the intensity changes in irradiated matrixes must be due to photorotamerization,[14−16] in which the cis conformer is partly transformed into the gauche conformer. The results obtained here for allyl chloride agree well with those obtained for allylamine,[17] for which a similar interconversion of the (cis, trans) to the (gauche, trans) conformer was observed.

The changes observed are illustrated in Figure 5, for two different regions of the spectra. In each case, the top spectrum was recorded from the freshly deposited matrix, whereas the middle spectrum was obtained after 48 h. The lower trace is obtained by subtracting the first spectrum from the second one where the negative dips show decreases in intensity and positive peaks signal increased intensity. It can be seen that the bands

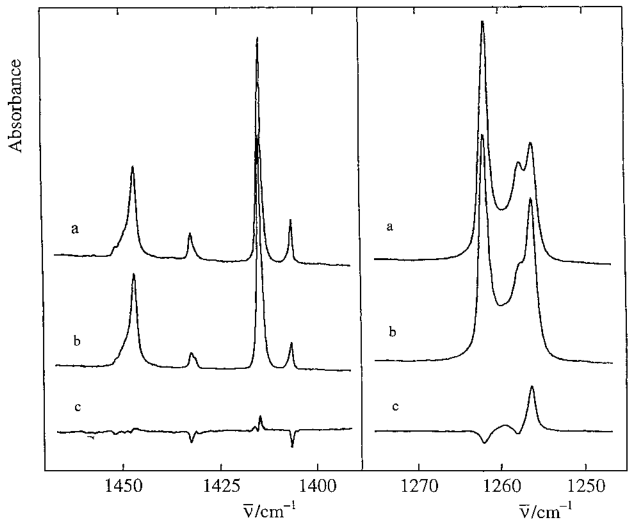

Figure 5. Photorotamerization experiments on 3-chloropropene deposited in an argon matrix. In both panels the (a) top spectrum was recorded from the freshly deposited matrix, and (b) the middle spectrum was recorded after 48 h of irradiation of the matrix with the globar source. The (c) lower trace is the result of subtracting spectrum a from spectrum b.

TABLE 2: Photorotamerization Results for 3-Chloropropene

iradiation time/h	I_{1432}/I_{1414}	I_{1406}/I_{1414}
0	0.123	0.202
4	0.108	0.170
8	0.086	0.138
12	0.077	0.130
16	0.077	0.127
24	0.076	0.126
48	0.075	0.127

at 1432 and 1407 cm^{-1}, assigned to the cis conformer, decrease in intensity, whereas the band at 1415 cm^{-1}, due to the gauche conformer, slightly increases. Similarly, in the region between 1270 and 1250 cm^{-1}, two cis bands are seen to decrease, whereas the third one, due to the gauche conformer, increases. However, a problem arises with the band at 1447 cm^{-1} where this band is assigned to a fundamental of the gauche conformer and should slightly increase, similarly to the other gauche bands in the spectrum, but no intensity change is observed experimentally. This can be explained only by assuming the expected intensity increase is offset by an intensity decrease, caused by the presence of a band due to the cis conformer. As no fundamental cis vibration is left to be assigned in this region, this band of the cis rotamer can be only a combination band. Inspection of the data in Table 1 shows that several combinations are possible, but with the information available, no definite assignment appears possible.

In Table 2 the ratios of the intensity I_c for a cis band to the intensity I_g for a gauche band, as obtained in a typical experiment, are collected for the 1432/1414 cm^{-1} and the 1408/1414 cm^{-1} doublets. The data clearly suggest that after about 12 h of irradiation, a photostationary state is reached, in which the rate of conversion from cis to gauche forms equals the rate of the inverse interconversion. By realizing that every molecule of the cis conformer that rotamerizes results in a gauche molecule, the intensity changes can be related to the ratio of the extinction coefficients ϵ_c/ϵ_g of the bands studied

$$\frac{\epsilon_c}{\epsilon_g} = \frac{I'_c - I_c}{I_g - I'_g} \tag{1}$$

where the unprimed intensities refer to the initial spectrum, and the primed intensities refer to the spectrum after a certain irradiation time. From this expression, the ratio ϵ_c/ϵ_g was calculated to be 0.600 for the 1432/1414 cm^{-1} doublet and 0.902 for the 1408/1414 cm^{-1} doublet. Using these data the ratio of the concentrations can be calculated:

$$\frac{[c]}{[g]} = \frac{I_c}{I_g}\frac{\epsilon_c}{\epsilon_g} \tag{2}$$

For the 1432/1414 cm^{-1} doublet, this ratio is calculated to be 0.204, while for the 1406/1414 cm^{-1} doublet a value of 0.224 is obtained.

The photostationary state is characterized by the equation

$$\Phi_g\,[g] = \Phi_c\,[c] \tag{3}$$

in which Φ_g and Φ_c are the quantum efficiencies for rotamerization of the gauche and cis conformers, respectively. Utilizing eq 2, this relation can be rearranged into:

$$\frac{\theta_c}{\theta_g} = \frac{I_g}{I_c}\frac{\epsilon_c}{\epsilon_g} \tag{4}$$

Using I_c and I_g from the spectrum recorded after 48 h of irradiation, and using the ratio of extinction coefficients obtained above, the ratio Φ_c/Φ_g of quantum efficiencies was calculated to be 8.0 for the 1432/1414 cm^{-1} doublet and 7.0 for the 1406/1414 cm^{-1} doublet. Thus, for the same number of absorbed photons, the cis to gauche rotamerization will occur 7−8 times more than the gauche to cis interconversion. This difference may be interpreted as a result of the higher stability of the gauche conformer, making it more difficult for this conformer to cross the internal rotation barrier.

For *n*-butane[14] and for propyl halides[15] it was observed that photorotamerization is primarily due to photons absorbed by the C−H stretches. The quartz filter used in some of our experiments filters out the radiation corresponding to frequencies of all fundamentals except the C−H stretches. The ratios of the quantum efficiencies found in these experiments are very similar to those obtained from unfiltered experiments. This result also shows that for allyl chloride the photorotamerization is due to absorption of radiation by the C−H stretches.

Ab Initio Calculations. The LCAO−MO−SCF restricted Hartree−Fock calculations were performed with the *Gaussian-94* program[18] using Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all of the geometric parameters using the gradient method of Pulay.[19] The energy difference between the gauche and cis conformers is 439, 333, and 457 cm^{-1} from the RHF/6-31G(d), MP2/6-31G(d), and MP2/6-311++G(d,p) calculations, respectively. The calculated structural parameters, rotational constants, and dipole moments were determined for both conformers from the ab initio calculations and are listed in Table 3. We have also listed in Table 3, under the heading “adjusted parameters,” the results of integrating the rotational constants from microwave data with the ab initio structural parameters to obtain r_o structural parameters. These results are analyzed further in the discussion. The optimized geometry for the gauche conformer from the MP2/6-31G(d) calculation was used to estimate an asymmetric torsional potential surface by allowing the torsional dihedral angle to vary in 30° increments with optimization at each point.

The internal coordinates are shown in Figure 6. The symmetry coordinates, which were developed from the internal coordinates,

TABLE 3: Structural Parameters[a] of 3-Chloropropene

		RHF/6-31G(d)		MP2/6-31G(d)		MP2/6-311++G(d,p)		adjusted parameters[e]	
	r_a[b]	gauche	cis	gauche	cis	gauche	cis	gauche	cis
C_1-C_2	1.344 ± 0.005	1.318	1.316	1.337	1.334	1.340	1.337	1.335	1.333
C_2-C_3	1.506 ± 0.006	1.496	1.502	1.490	1.498	1.491	1.499	1.491	1.499
C_3-Cl	1.802 ± 0.004	1.804	1.791	1.796	1.782	1.793	1.778	1.798	1.785
C_1-H_1	1.088 ± 0.010	1.076	1.074	1.086	1.083	1.084	1.084	1.086	1.083
C_1-H_2	1.088 ± 0.010	1.075	1.075	1.084	1.084	1.086	1.084	1.084	1.084
C_2-H_3	1.088 ± 0.010	1.077	1.079	1.088	1.090	1.088	1.090	1.088	1.090
C_3-H_4	1.088 ± 0.010	1.080	1.081	1.092	1.093	1.090	1.092	1.092	1.093
C_3-H_5	1.088 ± 0.010	1.078	1.081	1.091	1.093	1.091	1.092	1.091	1.093
$\angle C_1C_2C_3$	122.7 ± 1.1	123.6	128.1	123.0	127.1	123.0	127.0	123.3	127.3
$\angle C_2C_3Cl$	110.3 ± 0.6	111.3	114.9	111.2	114.5	110.7	114.6	111.2	114.0
$\angle C_2C_1H_1$	122.2[c]	122.0	122.5	121.6	121.9	121.3	121.6	121.5	121.8
$\angle C_2C_1H_2$	121.6[c]	121.4	120.5	121.5	120.6	121.2	120.3	120.4	120.5
$\angle H_1C_1H_2$		116.6	117.0	116.9	117.4	117.5	118.0	117.1	117.1
$\angle C_1C_2H_3$	120.4[c]	120.4	119.5	120.5	119.7	120.5	119.5	120.4	119.6
$\angle C_2C_3H_4$	112.5[c]	111.8	110.4	111.7	110.3	111.0	109.9	111.8	110.4
$\angle C_2C_3H_5$	112.5[c]	111.8	110.4	111.2	110.3	111.4	109.9	111.3	110.4
$\angle H_4C_3H_5$		109.3	108.1	109.0	107.7	109.5	108.1	108.9	107.6
$\angle H_4C_3Cl$	108.0 ± 2.2	105.5	106.3	106.2	106.9	107.6	107.1	106.4	107.1
$\angle H_5C_3Cl$	108.0 ± 2.2	106.7	106.3	107.4	106.9	106.4	107.1	107.0	107.1
dihedral angle	122.7 ± 4.6	119.6	0.0	119.2	0.0	117.25	0.0	120.0	0.0
A	21669 13581[d]	21953	13921	21681	13641	21130	13643	21671	13577
B	2801 3817	2790	3731	2797	3801	2829	3805	2800	3816
C	2714 3035	2705	2996	2716	3029	2743	3032	2715	3035
$-(E+575)$		0.91770	0.969804	1.507301	1.505782	1.7087253	1.7066451		
ΔE (cm^{-1})			439		333		457		

[a] Bond lengths in Å, bond angles in degrees, rotational constants in MHz and energies in Hartrees. [b] Reference 8 from electron diffraction data. [c] Estimated from ab initio results not from electron diffraction data. [d] Cis conformer in second column, data from ref 7. [e] Obtained from combining ab initio calculations with microwave rotational constants to obtain an r_o structure. For further explanation see discussion.

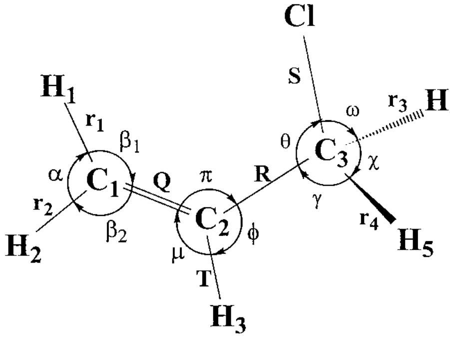

Figure 6. Internal coordinates of 3-chloropropene.

are listed in Table 1S. The force field in Cartesian coordinates was obtained from the MP2/6-31G(d) calculations from the *Gaussian-94* program.[18] The following procedure was used to transform the ab initio results in Cartesian coordinates into the form required for the iterative normal coordinate programs. The Cartesian coordinates obtained for the optimized structure were input into the G-matrix program written by Schachtschneider[20] together with the complete set of 41 internal coordinates to calculate the B matrix. The B matrix was then used to convert ab initio force fields in Cartesian coordinates to the desired internal coordinates using a program developed in our laboratory. The resulting force field can be obtained from the authors. Initially, all scaling factors were kept fixed at a value of 1.0 to produce the pure ab initio calculated vibrational frequencies. Subsequently, scaling factors of 0.90 for the stretching modes, 0.95 for bending modes, and 1.0 for the torsional modes were input into a program to obtain the fixed scaled force fields, vibrational frequencies, and potential energy distributions (PED). The resulting frequencies, infrared intensities, Raman scattering activities, depolarized ratios, observed frequencies, and PEDs are listed in Table 4.

Vibrational Assignment. The vibrational assignment for the gauche conformer is relatively straightforward since it is the conformer remaining in the solid. Therefore, the bands chosen as the fundamental modes in the earlier studies[5,9,12,21] were essentially the same although there were different descriptions of the molecular motions ascribed to a particular band. However, the assignment for the fundamentals for the cis conformer differs since in many of the earlier studies it was assumed that many of the fundamentals were coincidental for the two conformers.

The infrared spectrum of the sample dissolved in the liquid rare gases makes it possible to assign most of the fundamentals for the cis conformer. The assignments of the observed bands are listed in Table 1. In the carbon−hydrogen stretching region, only the ν_1 and ν_3 fundamentals are clearly distinguished for the cis rotamer from the corresponding modes for the gauche conformer. However, in the Raman spectrum, the ν_5 mode for the cis conformer is also observed. The ν_{16} fundamentals cannot be distinguished for the two conformers so they are assumed to be coincidental at 898 cm^{-1}, but all of the other fundamentals have different frequencies for the cis rotamer from the corresponding modes for the gauche rotamer. These are all observed in the infrared spectrum except for ν_{12} which is observed in the Raman spectrum.

Excluding the carbon−hydrogen stretching vibrations, the ab initio predicted frequencies for the fundamentals from the MP2/6-31G(d) calculation with a single scaling factor of 0.9 agree better than within 8 cm^{-1} of the observed values. The carbon−hydrogen stretches should be better predicted with a scaling factor of 0.88. Also, it should be noted that the predicted intensities (Table 4) for the infrared bands agree very well with the observed intensities of the fundamentals in the rare gas solutions. The PEDs for the gauche conformer are remarkably pure for a molecule without symmetry. The $=CH_2$ is the only mode with significant contributions from more than three symmetry coordinates. There is even less mixing of the modes for the cis conformer (Table 4).

Asymmetric Potential Function. The potential function for conformer interconversion has been redetermined utilizing the

TABLE 4: Comparison of Observed and Calculated Frequencies (cm^{-1}) for 3-Chloropropene

		gauche							cis						
vib. no.	fundamental[a]	ab initio[b]	fixed scaled[c]	IR int.$_d$	Raman act.[e]	dp ratio	obs.	PED[f]	ab initio[b]	fixed scaled[c]	IR int.[d]	Raman act.[e]	dp ratio	obs.[b]	PED[f]
ν_1	=CH$_2$ antisymmetric stretch	3312	3142	9.18	71.21	0.60	3099	$97S_1$	3328	3158	4.92	47.41	0.72	3111	$100S_1$
ν_2	=CH stretch	3237	3071	5.05	61.46	0.21	3034	$86S_2$	3235	3069	3.15	137.67	0.13	3019*	$92S_2$
ν_3	=CH$_2$ symmetric stretch	3217	3052	7.27	114.44	0.55	3003	$59S_3$,$40S_4$	3207	3043	7.75	75.67	0.40	(3034)	$92S_3$
ν_4	CH$_2$ antisymmetric stretch	3214	3049	0.44	49.91	0.10	2982	$51S_4$,$35S_3$,$12S_2$	3192	3028	5.27	89.45	0.75	(2968)	$100S_4$
ν_5	CH$_2$ symmetric stretch	3149	2987	14.78	94.75	0.12	2966	$100S_5$	3136	2975	4.35	124.45	0.14	2954	$100S_5$
ν_6	C=C stretch	1734	1645	0.69	46.49	0.20	1647	$67S_6$,$16S_8$	1743	1654	5.45	23.97	0.17	1657	$68S_6$,$14S_8$
ν_7	CH$_2$deformation	1545	1466	4.32	8.12	0.68	1452	$91S_7$	1537	1458	5.51	19.12	0.68	1432*	$100S_7$
ν_8	=CH$_2$ deformation	1497	1420	7.95	22.37	0.49	1418	$71S_8$,$10S_{10}$	1490	1413	5.42	10.72	0.52	1407*	$81S_8$
ν_9	=CH bend	1365	1295	20.64	12.41	0.43	1294	$63S_9$,$18S_{10}$,$10S_6$	1387	1316	24.25	4.81	0.63	1341*	$86S_9$
ν_{10}	CH$_2$ wag	1344	1275	15.69	17.57	0.49	1260	$46S_{10}$,$34S_9$	1350	1280	0.18	18.58	0.41	1289*	$61S_{10}$,$14S_{12}$,$13S_6$
ν_{11}	CH$_2$ twist	1273	1208	0.95	19.64	0.66	1206	$67S_{11}$,$12S_{12}$,$11S_{14}$	1249	1185	3.10	8.83	0.75	1180	$98S_{11}$
ν_{12}	=CH$_2$ wag	1164	1105	1.17	3.87	0.66	1101	$17S_{12}$,$26S_{11}$,$22S_{14}$,$14S_{16}$,$11S_{10}$	1107	1050	2.50	1.23	0.43	1052*	$47S_{12}$,$16S_{10}$,$14S_{14}$
ν_{13}	=CH bend	1036	983	19.58	2.71	0.73	989	$100S_{13}$	1031	978	22.11	2.22	0.75	983	$100S_{13}$
ν_{14}	C−C stretch	983	933	6.34	1.57	0.75	941	$48S_{14}$,$26S_{12}$,$10S_{16}$	989	917	0.35	1.51	0.75	920	$57S_{14}$,$25S_{12}$
ν_{15}	=CH$_2$ rock	951	902	37.46	2.02	0.55	930	$100S_{15}$	966	894	8.08	2.89	0.75	(898)	$100S_{15}$
ν_{16}	CH$_2$ rock	939	891	7.22	1.70	0.68	898	$61S_{16}$,$24S_{12}$	942	939	36.19	7.45	0.58	965	$80S_{16}$,$19S_{18}$
ν_{17}	C−Cl stretch	798	757	46.98	31.94	0.44	751	$59S_{17}$,$21S_{18}$,$14S_{20}$	774	734	19.37	16.06	0.21	735*	$64S_{17}$,$15S_{20}$
ν_{18}	=CH$_2$ twist	623	591	5.27	12.17	0.29	597	$62S_{18}$,$29S_{17}$	563	533	11.87	11.73	0.75	546	$83S_{18}$,$19S_{16}$
ν_{19}	C=CC bend	414	394	0.57	5.13	0.26	411	$74S_{19}$	533	505	2.18	5.38	0.57	517	$45S_{19}$,$26S_{17}$,$19S_{20}$
ν_{20}	C−C−Cl bend	295	281	4.63	6.98	0.69	285	$74S_{20}$,$11S_{18}$	253	240	0.67	2.63	0.60	250	$62S_{20}$,$35S_{19}$
ν_{21}	antisymmetric torsion	105	105	0.43	8.65	0.75	102	$96S_{21}$	138	138	1.84	4.37	0.75	147	$100S_{21}$

[a] For the cis conformer vibration numbers 3, 11, 13, 15, 16, 18, and 21 are A″ modes. [b] Frequencies from ab initio MP2/6-31G* calculations. [c] Frequencies from ab initio MP2/6-31G* calculations with a scaling factor of 0.9 for stretches and bends, 1.0 for torsion. [d] Infrared intensities in km/mol from MP2/6-31G* calculations. [e] Raman scattering activities in Å^4 u^{-1} depolarization values from RHF/6-31G* calculations. [f] From scaled results. [g] Observed frequencies are from the gas, values in parentheses are coincident with gauche assignments, and values with an asterisk are from rare gas matrixes.

TABLE 5: Far-Infrared Torsional Transitions (cm^{-1}) and Assignments for Gaseous 3-Chloropropene

transition	obsd[a]	calcd	obsd − calcd
gauche			
$1\mp \leftarrow 0\pm$	101.97	101.96	0.01
$2\mp \leftarrow 1\pm$	100.12	100.22	−0.10
$3\mp \leftarrow 2\pm$	98.11	97.81	0.30
$4\mp \leftarrow 3\pm$	95.81	94.63	1.18
$5\mp \leftarrow 4\pm$		90.22	
cis			
$1 \leftarrow 0$	147.28	147.28	0.00
$2 \leftarrow 1$	140.90	140.90	0.00
$3 \leftarrow 2$	135.42	135.44	−0.02
$4 \leftarrow 3$	128.50	128.64	−0.14

[a] Reference 5.

ΔH obtained from the xenon solution, the dihedral angle (120.0°) of the gauche rotamer, and the asymmetric torsional transitions of the cis and gauche conformers obtained with a resolution of 0.06 cm^{-1} and published earlier[5] (Table 5). The torsional dihedral angular dependence of the internal rotation constant, $F(\phi)$, can be represented as a Fourier series

$$F(\phi) = F_0 + \sum_{k=1}^{8} F_k \cos k\phi$$

The relaxation of the structural parameters, B(ϕ), during the internal rotation can be incorporated into the above equation by assuming that they are small periodic functions of the torsional angle of the general type

$$B(\phi) = a + b \cos \phi + c \sin \phi$$

The structural parameters (Table 3) obtained from the optimized geometries for both the cis and gauche conformers, utilizing the adjusted structural parameters, were used to obtain the kinetic constants.

The torsional potential is also represented as a Fourier cosine series in the internal angle (ϕ)

$$\mathrm{V}(\phi) = \sum_{i=1}^{6} (V/2)(1 - \cos i\phi)$$

The kinetic terms, the asymmetric torsional frequencies for both conformers, the experimental enthalpy, and the gauche dihedral angle were used to fit the potential function utilizing a computer program developed in our laboratory.[22] As an iterative process, this calculation was continued until the differences between the observed and calculated frequencies, as well as the dispersions in the potential constants, were minimized. From the calculated potential function, the gauche to cis and gauche to gauche barriers are determined to be 1005 and 699 cm^{-1}, respectively, with an energy difference between the two conformers of 147 cm^{-1}. These results are listed in Table 6 along with the results previously reported.[5] Although the potential coefficients have significantly different values from those obtained earlier, the gauche to cis and gauche to gauche barriers have very similar values. The spacings for the hot band torsional transitions for the gauche and cis conformers essentially determine the potential barriers for the conformational interchange. The large differences in the values for the V_1 and V_2 terms between this study and the results reported[5] earlier are due to the fact that in the earlier study the cis conformer was proposed to be the more stable rotamer at ambient temperature. Additionally, the dihedral angle, 120.0°, of the gauche conformer is somewhat smaller than the value of 122.5° obtained from the previously determined[5]

TABLE 6: Potential Coefficients (cm^{-1}) and Barriers (cm^{-1}) to Conformational Interchange for 3-Chloropropene

parameter	previous values[a]	this study[b]	MP2/6-31G(d)
V_1	-47 ± 1	-275 ± 1	-236
V_2	145 ± 17	40 ± 2	-217
V_3	862 ± 8	859 ± 1	823
V_4	14 ± 6	78 ± 1	-11
V_5		-9 ± 1	19
V_6	-50 ± 4	-42 ± 1	-55
gauche to cis barrier	969	1005	944
gauche to gauche barrier	739	699	939
cis to gauche barrier	888	881	609
enthalpy difference	-81 ± 44	147	333
dihedral angle	122.5	120.0	119.2

[a] Reference 5. [b] Values are determined from the assignment of the observed torsional transitions given in Table 5 and $F_0 = 2.270275$, $F_1 = 0.647136$, $F_2 = 0.273674$, $F_3 = 0.057205$, $F_4 = 0.019136$, $F_5 = 0.004369$, $F_6 = 0.001417$, $F_7 = 0.000348$, and $F_8 = 0.000105$ cm^{-1}. Uncertainties are from a statistical analysis, and the actual values may be somewhat higher.

potential function. The V_1 and V_2 terms are strongly correlated, and the use of the gauche dihedral angle for the potential function determination reduces the correlation between these two terms. The uncertainties listed in Table 7 are from a statistical analysis, and the actual deviations may be somewhat higher.

Discussion

The determination of the enthalpy difference for the conformers of 3-chloropropene from the rare gas solutions clearly shows that the gauche conformer is the more stable rotamer and it is expected to be the more stable rotamer in the gas phase.[13,23-26] The small interaction of the rare gas atoms with the 3-chloropropene molecule is not expected to significantly affect the ΔH value. The value previously reported,[5] with the cis conformer more stable from the Raman spectrum of the gas, suffered from problems of sample decomposition and Q-branch broadening from excited states of the asymmetric torsional mode. The currently determined value is in reasonable agreement with the predicted energy difference obtained from the MP2/6-31G(d) calculations. Additional support is found from the relative intensities of many of the infrared bands for the cis conformer relative to those obtained for the corresponding gauche bands with corrections predicted from the ab initio MP2/6-31G(d) calculations.

From the MP2/6-31G(d) calculation the energy difference was more than two times the value of the enthalpy difference obtained from the rare gas solutions. Because of this large difference, we carried out an additional calculation with a larger basis set, MP2/6-311++G(d,p), but the energy difference became even larger rather than closer to the experimental value. Thus, it appears that a very high level of calculation would be needed to obtain the experimental value for the energy difference between the two conformers. A similar problem was found for the allyl fluoride molecule where the MP2/6-311++G(d,p) calculation predicted the more stable conformer, the gauche form, whereas the experimental results[1-4,6] clearly showed the cis form to be the more stable rotamer. It appears that with these basis sets, at the MP2 level there is a bias toward the gauche conformer for these types of molecules.

The ab initio predicted structural parameters are quite similar for the two conformers. The only major bond distances that are different are the CCl and CC distances where they are predicted to be longer for the cis conformer. Also there are only small differences in the angles with the major one the CCCl angle, which opens significantly for the cis conformer compared to the corresponding angle in the gauche. This opening is undoubtedly due to steric hindrance in the cis form.

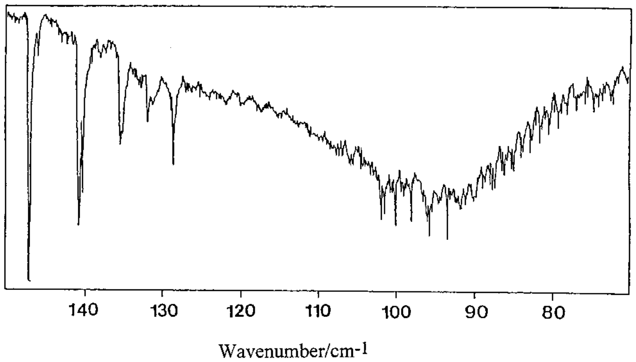

Figure 7. The far-infrared spectra of gaseous 3-chloropropene in the region of the asymmetric torsion.

We used the ΔH value of 147 cm^{-1} obtained from the xenon solution to fit the asymmetric potential function for several reasons. We tried values of 60, 96, 125, and 147 cm^{-1}, and only with a value of 147 cm^{-1} could we obtain a reasonable fit for the transitions in the cis well. This value also gave the smallest uncertainties in the determined potential constants and, although much smaller than the values obtained from the ab initio calculations (439, 333, and 457 cm^{-1}), the value of 147 cm^{-1} is closer to these values than 96 cm^{-1} obtained from the krypton solution.

When we originally[5] assigned the far-infrared transitions, we used a value of 93.53 cm^{-1} for the $5\mp \leftarrow 4\pm$ transition in the gauche potential well. We had trouble fitting this value in our potential function and our present potential function calculation indicates that the $5\mp \leftarrow 4\pm$ transition should be found closer to 90.5 cm^{-1}. Actually, our calculation indicates that the two gauche transitions have become split, with calculated values of 90.22 and 90.50 cm^{-1}. Reinspection of the spectra indeed shows that there is a band near this position (Figure 7). We feel that the band at 93.53 cm^{-1} might represent the asymmetric torsion in an excited state of the C−C−Cl bend. Indeed, a similar extraneous band is found at 131.86 cm^{-1}, mixed in with the series of transitions of the cis conformer.

In the earlier microwave investigation, only the rotational constants for the ^{35}Cl and ^{37}Cl isotopomers of the gauche conformer were obtained. Similarly, only the rotational constants for the ^{35}Cl isotopomer were obtained for the cis conformer, although A−C and B−C were obtained for the ^{37}Cl isotopomer. From these limited rotational constants, it was not possible to obtain a complete structural determination. However, we have developed a computer program which utilizes the rotational constants obtained from microwave data along with the ab initio predictions to obtain r_o structural parameters. With this A&M program,[6] (ab initio and microwave information) it is possible to obtain all of the parameters since it is an iterative method and distances which are predicted to be essentially the same from the ab initio calculations are input as a single parameter. A simplex method is used for optimization rather than the matrix least-squares method usually used. The combination of the ab initio prediction of the structural parameters and the fit of the rotational constants provides all of the structural parameters for both conformers. These values are listed in Table 3 and it is believed that the distances should be predicted within ±0.005 Å and the angles within one-half degree. The average fit of the rotational constants is better than 1 MHz for all B and C rotational constants and better than 3 MHz for the A constants, i.e., better than 0.02%. The fit of the rotational constants for the gauche conformer is better than those for the cis, probably because more information is available from the six rotational constants.

It is interesting to compare the heavy atom structural parameters with those obtained for the corresponding allyl fluoride. The C=C distance is not significantly affected by the substitution of a different halogen atom on the methyl group. However, the CC single bond distance is shorter in the fluoride, as expected, from the larger electronegativity of the fluorine atom. Other small changes in the parameters can be rationalized on the basis of the larger size of the halogen atom in the chloride molecule. It is also of interest to compare the adjusted r_o parameters to those obtained from the previously published electron diffraction results. In the electron diffraction investigation the heavy atom parameters were assumed to be the same for the two conformers, but undoubtedly the C−Cl distance as well as the C_2-C_3 distance are significantly different for the two conformers. It would be of interest to reanalyze the electron diffraction data utilizing the experimental ΔH value between the conformers and the predicted difference of the heavy atom distances and CCCl angles for the two conformers.

Acknowledgment. W.A.H. thanks the National Fund for Scientific Research (NFWO, Belgium) for successive appointments as Research Assistant and Postdoctoral Fellow. The NFWO is also thanked for financial help toward the spectroscopic equipment used in this study. Acknowledgment is given to NATO for a grant, which made this cooperative research project possible.

Supporting Information Available: Symmetry coordinates, developed from the internal coordinates, for the gauche conformer from the MP2/6-31G(d) calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Durig, D. T.; Little, T. S.; Costner, T. G.; Durig, J. R. *J. Mol. Struct.* **1992**, *266*, 277.

(2) Durig, J. R.; Geyer, T. J.; Little, T. S.; Durig, D. T. *J. Mol. Struct.* **1988**, *172*, 165.

(3) Durig, J. R.; Zhen, M.; Heusel, H. L.; Joseph, P. J.; Groner, P.; Little, T. S. *J. Phys. Chem.* **1985**, *89*, 2877.

(4) Durig, J. R.; Zhen, M.; Little, T. S. *J. Chem. Phys.* **1984**, *81*, 4259.

(5) Durig, J. R.; Durig, D. T.; Jalilian, M. R.; Zhen, M.; Little, T. S. *J. Mol. Struct.* **1989**, *194*, 259.

(6) van der Veken, B. J.; Herrebout, W. A.; Durig, D. T.; Zhao, W.; Durig, J. R. *J. Phys. Chem.* **1999**, *103*, 1976.

(7) Hirota, E. *J. Chem. Phys.* **1965**, *42*, 2071.

(8) Schei, S. H.; Shen, Q. *J. Mol. Struct.* **1985**, *128*, 161.

(9) Barnes, A.; Holroyd, S.; George, W.; Goodfield, J.; Maddams, W. *Spectrochim. Acta* **1982**, *38A*, 1245.

(10) Stolevik, R.; Thingstad, O. *J. Mol. Struct. (THEOCHEM)* **1984**, *106*, 333.

(11) Moller C.; Plesset, H. S. *Phys. Rev.* **1934**, *46*, 618.

(12) McLachlan, R. D.; Nyquist, R. A. *Spectrochim. Acta* **1968**, *24A*, 103.

(13) Herrebout, W. A.; van der Veken, B. J. *J. Phys. Chem.* **1996**, *100*, 9671.

(14) Rasanen, M.; Bondybey, V. E. *Chem. Phys. Lett.* **1984**, *111*, 515.

(15) Rasanen, M.; Bondybey, V. E. *J. Chem. Phys.* **1985**, *82*, 4718.

(16) Rasanen, M.; Bondybey, V. E. *J. Phys. Chem.* **1986**, *90*, 5038.

(17) Barnes, A. J. *J. Mol. Struct.* **1988**, *177*, 209, and references therein.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94 (Revision B. 3)*, Gaussian Inc.: Pittsburgh, PA, 1995.

(19) Pulay, P. *Mol. Phys.* **1969**, *17*, 197.

(20) Schachtschneider, J. H. In *Vibrational Analysis of Polyatomic Molecules*, Parts V and VI; Technical Report Nos. 231 and 57; Shell Development Co.: Houston, TX, 1964 and 1965.

(21) Silvi, B.; Sourisseau, C. *Spectrochim. Acta* **1975**, *31A*, 565.

(22) Groner, P.; Johnson, R. D.; Durig, J. R. *J. Mol. Struct.* **1986**, *142*, 363.

(23) Bulanin, M. O. *J. Mol. Struct.* **1973**, *19*, 59.

(24) van der Veken, B. J.; De Munck, F. R. *J. Chem. Phys.* **1992**, *9*, 3060.

(25) Bulanin, M. O. *J. Mol. Struct.* **1995**, *347*, 73.

(26) Herrebout, W. A.; van der Veken, B. J.; Wang, A.; Durig, J. R. *J. Phys. Chem.* **1995**, *99*, 578.