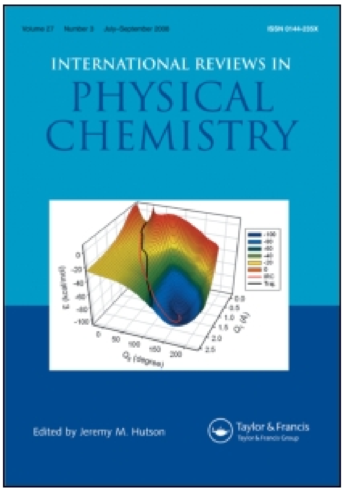

International Reviews in Physical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

Conformational stability of the haloacetyl halides

J. R. Durig[a]; Ai Ying Wang[a]; T. S. Little[a]
[a] Department of Chemistry, University of South Carolina, Columbia, South Carolina, USA

To cite this Article Durig, J. R. , Wang, Ai Ying and Little, T. S.(1990) 'Conformational stability of the haloacetyl halides', International Reviews in Physical Chemistry, 9: 4, 349 — 379
To link to this Article: DOI: 10.1080/01442359009353251
URL: http://dx.doi.org/10.1080/01442359009353251

INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1990, VOL. 9, NO. 4, 349–379

Conformational stability of the haloacetyl halides

by J. R. DURIG, AI YING WANG and T. S. LITTLE
Department of Chemistry, University of South Carolina,
Columbia, South Carolina 29208, U.S.A.

The far-infrared spectra of a series of haloacetyl halides, $CH_2XC(O)X$, in the vapour phase have been recorded at a resolution of 0·10 cm^{-1} in the 350–35 cm^{-1} region. The fundamental asymmetric torsional frequencies of the more stable *trans* (two halogen atoms oriented *trans* to one another) and high-energy conformers have been observed. From these data the asymmetric torsional potential functions governing internal rotation about the C–C bond have been determined. Only fluoroacetyl fluoride and fluoroacetyl chloride have the *cis* conformation for the high-energy form whereas all the other haloacetyl halides have the *gauche* conformation for the high-energy form. For those molecules in this series which have the *gauche* form as the high-energy rotamer the importance of using the value for the torsional dihedral angle in the determination of the potential function governing internal rotation is reviewed. It is shown how complete equilibrium geometries, which have been determined by *ab initio* Hartree–Fock gradient calculations, can be used in conjunction with microwave and/or electron diffraction studies to obtain more reliable experimental structural parameters for these molecules. Finally, the reliability of the *ab initio* techniques used at predicting trends in the optimized geometries and potential functions governing internal rotation are assessed.

1. Introduction

The *a priori* determination of molecular structures and parameters determining thermodynamic properties of molecules has encompassed the research activities of theoreticians for many years. It has been among the major goals of theoretical research to establish the limits of reliability of theoretical predictions for a variety of molecular properties. In order to reach this goal the theoretical approach has often been to choose a 'parent' molecule and then to carry out calculations for a variety of substituted derivatives of the parent. The resultant effects of the substituents on the calculated properties are subsequently monitored. The experimentalist has used a similar approach but most systematic studies of substituent effects on conformational stability have been carried out in solution where the determined stabilities often reflect predominating intermolecular interactions as opposed to intramolecular structural stabilities.

The complexities associated with the determination of molecular structural stabilities from analysis of data obtained for the vapour phase have resulted in the publication of relatively few systematic studies of substituent effects on conformer stability. Therefore it is often required of the experimentalist that data obtained from a variety of methods, over numerous years, be compared in order to derive trends in conformational behaviour. Similarly, the theoretician is often forced to compare calculated results with those obtained from experiment many years prior. This presence of either an incomplete or incorrect experimental data base, when compared with theoretical results obtained today, may lead to erroneous conclusions with regard to the reliability and accuracy of the theoretical method.

All physical and chemical properties of a substance ultimately are derived from its molecular structures. One specific aspect of molecular structure which has intrigued both theoreticians and experimentalists alike involves the orientation about a particular bond (or about several bonds) of one portion of the molecule with respect to the rest of the molecule; in other words, the molecular conformation about that bond (or those bonds). Physical or chemical properties, such as the molecular dipole moment or the inherent stability of the compound, depend intimately upon the three-dimensional arrangement of one fragment of the molecule with respect to the rest. For example, the *trans* conformer of 1,2-dichloroethane is non-polar, while the *gauche* conformer is decidedly polar. Furthermore, the *cis* conformer of this same compound is unstable, whereas the *trans* and *gauche* conformers are stable. In addition, the chemical reactivity of a given substance and its available reaction pathways are often critically sensitive to the geometry of the reactant (or its products) and are also dependent upon the energetics or processes in which the conformation of the molecule may be changed via an internal rotation about a conformationally sensitive bond.

Historically, conformational analyses of molecules have been carried out by a large number of techniques, both experimental and theoretical. Because of the recent advances in computer technology advanced *ab initio* calculations are commonly being employed to account for observed molecular structures. This necessitates that the experimentalist keep pace with the advancing theoretical methods by establishing new structures or verifying old ones by the most modern techniques. Such an approach will then provide the required definitive data which can then serve to verify or contradict theoretically predicted results.

The reason for the existence of a poor experimental data base with regard to the experimental determination of structures and conformational equilibria is basically threefold.

(1) *The absence of sufficient structural information.* Numerous potential functions governing internal rotation of both symmetric and asymmetric tops have been published without the knowledge of the structure of both conformers, particularly the high-energy conformer. It is extremely important for the accurate computations of energy levels, wavefunctions and potential functions that some reasonable structural information be known about all the exhibited conformations. Furthermore, in the absence of reliable structures determined from definitive techniques, such as those determined from microwave spectroscopy or analysis of the electron diffraction pattern, the reliability of optimized geometries determined from theory cannot be ascertained.

(2) *The lack of complementary experimental data.* In many cases, owing to symmetry and selection rules, both infrared and Raman spectroscopy results are needed to identify the high- and low-energy conformers. Almost always the Raman spectra of the gas are neglected and it is not unusual to find numerous studies for which spectra of all three phases are not reported.

(3) *The lack of high-resolution data.* It is now apparent that the highest possible resolution available should be used to record the low-frequency data because many torsional bands are extremely sharp and therefore may not be observed at low resolutions. Additionally, insufficient resolution may result in misleading relative intensities of the Q branches.

Vibrational spectroscopy is the most generally applicable method used in the study of the conformations of certain types of small molecule with few substituents. Infrared and Raman spectra can be recorded in all phases, and variable-temperature experiments may be conducted in all phases as well. Additionally, gas phase band contours observed for the infrared spectra, along with Raman de-polarization data, provide considerable structural information and lend confidence to spectroscopic assignments. Of course, the limitation of the vibrational spectroscopy technique is that it is best applied to relatively simple molecules which often contain an element of symmetry (or more), and one or perhaps no more than two portions of the molecule capable of producing different conformations upon internal rotation.

In spite of this limitation, vibrational spectroscopy has been successfully used to determine the conformational preferences and conformational equilibria in a number of chemically important systems. One such class of substances is the haloacetyl halides, which are the focus of this review.

The parent molecule of these compounds is of course acetaldehyde, CH_3CHO. The structural similarities between this parent molecule and others covered in this review are clear as they can all be represented by the general formula CH_2YCXO, where X and Y are the same or different halogens. These compounds have long been recognized as important biocide and chemical agents and reagents. Therefore their chemical nature, structure and conformational stabilities are of considerable interest.

To the structural chemist, all these compounds afford many interesting and important research opportunities, from both an experimental and a theoretical standpoint. The acetaldehyde and chloroacetaldehyde molecules have been used to develop or encourage development of theoretical models dealing with predictions of conformations, hyperconjugation and potential functions governing internal rotation. It is somewhat surprising that, in spite of the vast amount of both theoretical and experimental information which is known about acetaldehyde, considerably less (until fairly recently) is known about many of its important derivatives.

Among the more specific aims of this article is to show how a combined experimental and theoretical approach to the determination of the conformations of the molecules discussed is more useful than either method used exclusively. It will be shown that one or more of the three aforementioned problems associated with analysing the experimental data from vibrational spectroscopy apply in nearly all cases. Furthermore, these molecules have been shown to illustrate classically to what extent we should depend on the reliability of both the theoretical and the experimental techniques which have been applied.

It is hoped that the literature survey for this article has been reasonably complete up to 1988. Any pertinent articles overlooked represent errors of omission on our part, and we apologize in advance to the authors of any such papers. Finally, it is hoped that this review article can be of value not only to spectroscopists and structural chemists, but also to chemists in all areas who are interested in conformational analysis.

2. Background

A complete description of the theoretical background needed for the remainder of this review has been given elsewhere (Compton 1981, Fogarasi and Pulay 1985). At present, we shall only provide a brief summary of this theory and a description of the *ab initio* techniques which are used. Finally, examples which classically illustrate the specific problems associated with the experimental techniques are addressed.

2.1. Ab initio *methods*

Most of the results which are presented are from our most recent studies. For the *ab initio* calculations we have followed specific and consistent guidelines. By following such guidelines, comparisons between the results obtained for the various molecules in the series are more meaningful. We have not attempted to determine which theoretical technique best reproduces the results determined from experiment but rather to illustrate the usefulness of a combined theoretical–experimental approach to the type of studies presented. Some of the guidelines which we have followed include the use of the same basis set when comparisons between calculations and experiment are made for a series of molecules.

It is not unusual to find, for a given study, that the geometry optimization has been carried out with one basis set while frequency calculations or the potential surface determinations have been carried out with another. Such techniques are perfectly acceptable; however, more meaningful comparisons of calculated with experimental results for a molecular series are obtained when the calculations for all the molecules considered are carried out using the same basis sets.

Second, it is important to have definitive experimental data. If, for example, the conformations of a given molecule have been determined from experiment, the reliability of this determination must be ascertained. Such determinations when made solely from either infrared or Raman data can frequently be in error. Typically, complete analysis of the microwave spectrum or electron diffraction pattern may also be required. Even when these methods are employed, one must consider the type of structure provided (i.e. r_0, r_s, r_α or r_g) for comparison with optimized r_e geometries.

At present, we have chosen to describe the *ab initio* techniques which we have found to be the most commonly used and which we have most frequently used for related studies. For most of the theoretical results which are reviewed, linear-combination-of-atomic-orbitals molecular-orbital self-consistent field (LCAO-MO-SCF) restricted Hartree–Fock calculations have been performed with the programme Gaussian-82 and Gaussian-86 using Gaussian-type basis functions (Binkley *et al.* 1984, Frisch *et al.* 1988). The energy minima with respect to nuclear coordinates have been obtained by simultaneous relaxation of all geometric parameters using the gradient method of Pulay (1969). A variety of basis sets have been employed but typically the 3-21G, 3-21G*, 4-21G and 6-31G* basis sets are used. At such levels of calculations the angular parameters are usually determined with a relatively high degree of accuracy and bond distances should be in error only by small systematic amounts.

For the optimized geometries and potential surface calculations, optimization of the structure corresponding to the conformation which is most stable in the vapour is initially carried out at a given basis set level. From this structure the torsional dihedral angle under investigation is allowed to vary typically by 10° increments while all other structural parameters are held fixed. The minima and maxima which occur on this surface are subsequently optimized for obtaining the final potential function which is used for comparison with the experimentally determined potential functions. In some cases the structures corresponding to the minima on the potential surfaces have been relaxed further by inclusion of Møller–Plesset perturbation (Hehre *et al.* 1986).

For the normal coordinate analyses the force fields in Cartesian coordinates are calculated by the Gaussian-82 or Gaussian-86 programmes with the 3-21G or 3-21G* basis set. From previous studies, it has been found that the differences in the values of the force constants and frequencies are not significant when the smaller (3-21G), as opposed to the larger (6-31G*), basis set is used. For results from our laboratory the following procedure was used to transform *ab initio* results, which are in terms of Cartesian coordinates, into the form normally used for the iterative normal coordinate programmes. The Cartesian coordinates obtained for the optimized structures are input into the **G** matrix programme together with the complete set of internal coordinates. This complete set of internal coordinates is used to form the symmetry coordinates with the redundancies. The output of this **G** matrix programme consists of the **B** matrix and the unsymmetrized **G** matrix. The **B** matrix is used to convert the *ab initio* force field in Cartesian coordinates to a force field in the desired internal coordinates. All diagonal elements of the obtained force field in internal coordinates are assigned scaling factors. This force field is then used as input, along with the unsymmetrized **G** matrix and scaling factors, in the perturbation programme written by Schachtschneider (1964). Initially, all scaling factors are kept fixed at a value of 1·0 to produce the pure *ab initio* calculated vibrational frequencies. Subsequently, scaling factors of 0·9 for stretching coordinates, 0·8 for bending coordinates and 1·0 for torsional coordinates, and the geometric average of scaling factors for interaction force constants are used to obtain the 'fixed-scale' force field and resultant frequencies along with the potential energy distributions. Alternatively, the scaling factors can be varied so that the calculated frequencies agree with the observed experimental values.

2.2. *Determination of potential barriers*

A molecule undergoing hindered internal rotation about a single bond changes its overall energy as the torsional angle ϕ changes. This energy change is manifested in the torsional vibrational energy as well as the overall molecular energy. The change in the molecular rotational energy arises from the alteration in geometry of the molecule as ϕ changes, which in turn alters the principal moments of inertia which are dependent upon ϕ. The treatment used to obtain the potential function most often is a rigorous numerical method involving the calculation of torsional eigenfunctions and corresponding eigenvalues which are then iterated, in a least-squares manner, to give the best possible fit to the experimentally observed torsional transition frequencies (Compton 1981). The most common type of potential function, where at least one of the minima coincides with a plane of symmetry, is of the type

$$V(\phi)=\frac{1}{2}\sum_{i} V_i[1-\cos(i\phi)].$$

In general, it has been found that a six-term expansion in V_i is sufficient to handle almost any molecular system (Compton 1981). This is because V_1, V_2 and V_3 are, in general, larger than V_4, V_5 and V_6; thus terms greater than V_6 should be negligible. Calculation of the kinetic energy term requires evaluation of the internal rotation constant F, commonly called the 'F series', which is related to the reduced moment I_r of inertia of the top by $F=h/8\pi^2cI_r$. In order to determine the angular dependence of $F(\phi)$, F is calculated at various values of ϕ, the results of which are then curve fitted to a Fourier expansion in ϕ:

$$F(\phi)=\sum_{k=0}^{n} a_k\cos(k\phi).$$

via a least-squares method.

We have recently developed a programme (Groner *et al.* 1986) which allows for the incorporation of the relaxation of structural parameters into the expression for the angular dependence of $F(\phi)$ by assuming them to be small periodic functions of the torsional angle of the general type:

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

If complete r_0 or r_s structures for the stable conformations are available from microwave spectroscopy, then these can be employed. When such structures are not available, then the optimized structural parameters determined from *ab initio* calculations may be used to calculate the kinetic constants.

The structural stability and conformational preference of all molecules are determined by a balance of all the intramolecular forces. For the molecules discussed herein, typically one of several specific forces will predominate or be strongly influential. For example, in the haloacetyl halides, steric and/or conjugation contributions predominate; however, for the haloacetaldehydes, non-bonded intramolecular forces (similar to intermolecular hydrogen bonding) have been suggested to 'deform' the potential function governing internal rotation. The significance of the contribution of each of these effects determined from experimentally obtained structures, conformations, potential energy distributions among a set of symmetry coordinates and potential functions governing internal rotation are then compared with the corresponding quantities obtained from *ab initio* calculations.

3. Spectroscopic and *ab initio* results

In the ensuing text the far-infrared spectra of a series of haloacetyl halides, CH_2YCXO, recorded for the vapour phase at a resolution of 0·10 cm^{-1} in the 350–35 cm^{-1} region will be discussed. The fundamental asymmetric torsional frequencies of the more stable *trans* (two halogen atoms oriented *trans* to one another) and high-energy conformers have been observed. From these data the asymmetric torsional potential functions governing internal rotation about the C–C bond have been determined and are consistent with the conformation of the high-energy rotamer being *cis* or *gauche* depending on the halogens considered. For some of the molecules considered, previously reported results obtained from electron diffraction techniques and microwave spectroscopy were necessary in order to determine the high-energy conformer. For others, these data are not available and it can be shown that, although the vibrational data provide some information from which the structure of the high-energy conformer can be identified, they are not wholly definitive. When such cases arise we have shown that *ab initio* calculations at the 3-21G, 3-21G* and 6-31G* basis set levels of the optimized geometries, potential surfaces and vibrational frequencies can be used to support the conclusions made from the experimental results. We have shown that infrared band contour analyses of 'conformer peaks' observed in the spectra of the gases can provide additional support of the determination of the high-energy conformer but in some cases are inconclusive. Considerable discrepancies exist between the assignments of the fundamental vibrations which were previously reported and those which we have made. These discrepancies primarily arise from the lack of Raman spectra for the gas and solid phases in most of the earlier work. The revised assignments are, for most cases, supported by the vibrational frequencies calculated from theoretically determined force fields. In order to determine the reliability of the *ab initio* techniques at predicting trends in the optimized geometries, for some of the molecules, the rotational spectra have been re-analysed. From studies of the vibrational spectra of the vapour and liquid phases at variable temperatures the conformational energy differences have been determined. It will be shown that, although the barriers are frequently predicted rather accurately, with the basis sets considered, the energy differences have been poorly determined. For these cases, improvements in the calculated values will be compared with one another and with those for some similar molecules for the purpose of arriving at definitive structures, potential functions and vibrational assignments.

The examples cited here are results of our own studies on the conformational stability, barriers to internal rotation, vibrational assignments and, in some cases, the *ab initio* calculations of the haloacetyl halides which we have recently communicated (Durig *et al.* 1988a, b, 1989a, b, c, d, Durig and Phan 1989). From several previous investigations (Jones and Ladd 1970, Khan and Jonathan 1969, 1970, Nakagawa *et al.* 1952, Saegebarth and Wilson 1967, Steinnes *et al.* 1980, Szalanski and Ford 1974, Tanabe and Saiki 1972, 1974, van Eijck *et al.* 1978, van Eijck and Stolwijk 1985), it had been shown that this class of molecules exists in two different conformations in the fluid phases, and that the most stable conformation is *trans*; however, the structure of the high-energy conformation had been verified only for a few of these molecules (Steinnes *et al.* 1980, Khan and Jonathan 1970).

Although the Raman spectrum of the liquid had been previously investigated in many of the earlier studies, the spectra of the gas and solid were typically neglected. These data when combined with far-infrared spectra of the gas at moderately high resolution (0·10 cm^{-1}) have shown to be particularly useful for conformational analysis purposes.

Depending on the halogen involved, the structure of the high-energy conformer is one in which the two halogen atoms are oriented *cis* or *gauche*. From some of the earlier studies it had been determined that the high-energy conformer molecule was *gauche* but a large uncertainty in the value of the torsional dihedral angle persisted. We have shown that a reliable value for this parameter can sometimes be obtained from the direct observation of the fundamental and associated 'hot bands' of the torsional mode in the far-infrared spectrum of the gas and the subsequent calculation of the potential function governing the internal rotation. Such analyses of the torsional fundamentals of nearly all these molecules had not been carried out. Therefore, in order to obtain more reliable vibrational assignments and a better understanding of the asymmetric torsional potential functions for these molecules, we undertook a complete investigation of the vibrational spectra with special emphasis on the torsional modes. Additionally, we carried out *ab initio* calculations in order to obtain the force field and the frequencies for the normal modes as well as the asymmetric torsional potential barriers for comparison with the experimentally determined values. Some of these results will now be presented.

3.1. *Conformational analyses*

As an example of the utilities of the spectral data for conformational analysis purposes we have chosen some results from our recent investigations of chloroacetyl fluoride (Durig *et al.* 1988a), CH_2ClCFO, and bromoacetyl fluoride (Durig *et al.* 1989e), CH_2BrCFO. Included in this discussion will also be some results from the *ab initio* calculations which are used in the absence of definitive determinations of the structure of the high-energy conformer from the spectral data. Finally, the utilities of infrared band contour analysis will be presented.

If the *cis* conformation of either CH_2ClCFO or CH_2BrCFO were the high-energy rotamer, then this structure would have a symmetry plane, which allows for the separation of the irreducible representations of the fundamental vibrations into A' and A'' symmetry blocks, the latter of which leads to de-polarized lines in the Raman spectra of the fluid phases. In contrast, if the high-energy conformer has a *gauche* structure, then no symmetry plane would be present and all the Raman lines for this conformer must be polarized. For CH_2ClCFO (Durig *et al.* 1988a), the Raman line observed in the spectrum of the gas phase as a *Q* branch of medium intensity at 554 cm^{-1} (figure 1), although shifted to slightly higher frequency, remains in the corresponding spectrum of the liquid, disappears in the spectrum of the solid phase and therefore is assigned as arising from the less stable conformer. The corresponding 'conformer line' to this feature gives rise to a broad, very weak line in the spectrum of the liquid (figure 1 (*c*)) at 532 cm^{-1} which remains at 529 cm^{-1} in the spectrum of the solid phase (figure 1 (*d*)). Because the line at 532 cm^{-1} is clearly de-polarized in the liquid, it is assigned as arising from an out-of-plane bend of the *trans* conformer. However, the line observed at 562 cm^{-1} in the liquid is clearly polarized and gives rise to the *Q* branch in the Raman spectrum of the gas at 554 cm^{-1}. Therefore this feature cannot arise from an *A''* vibration of the *cis* former but must arise from the *gauche* conformer. The infrared spectrum of the vapour (figure 1 (*a*)) is also consistent with the

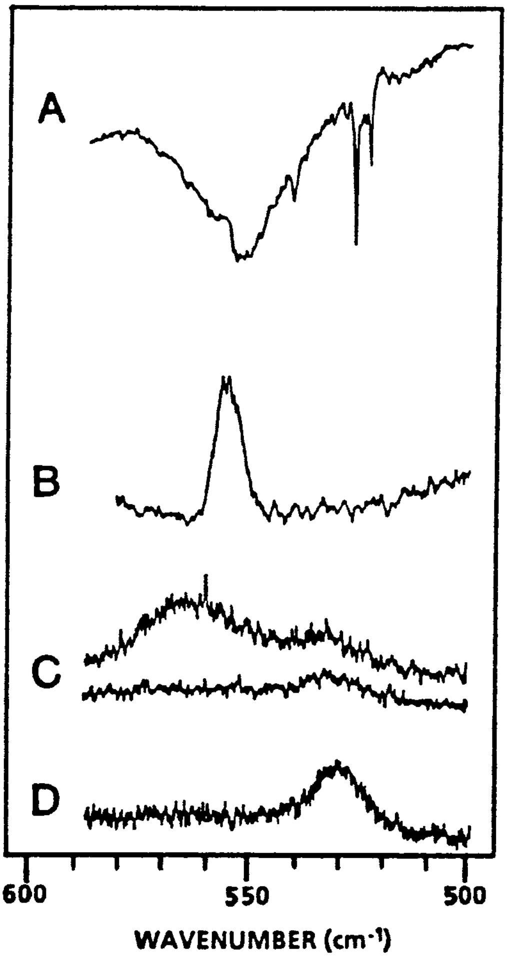

Figure 1. (*a*) Mid-infrared spectrum of gaseous chloroacetyl fluoride, (*b*) Raman spectrum of gaseous chloroacetyle fluoride, (*c*) Raman spectrum of liquid chloroacetyl fluoride and (*d*) Raman spectrum of solid chloroacetyl fluoride in the region of the CFO out-of-plane bending mode. Used by permission of Durig *et al.* (1988a).

assignments to the aforementioned Raman spectral features. The Raman line occurring at 554 cm^{-1} corresponds to a hybrid contour anticipated for a *gauche* conformer whereas the corresponding band for the *trans* conformer is a distinct *C*-type *Q* branch at 528 cm^{-1} characteristic of an out-of-plane mode.

In the corresponding region of the infrared spectrum of gaseous CH_2BrCFO (Durig *et al.* 1989e) a similar conformer doublet is observed for an out-of-plane mode at 531 and 521 cm^{-1} respectively (figure 2 (*a*)). The band at 521 cm^{-1} clearly remains in the solid (figure 2 (*b*)) and is thus assigned as arising from the *trans* conformation which can be shown (Durig *et al.* 1989e) to exist exclusively in this phase. The distinct *C*-type *Q* branch (521 cm^{-1}) arises from the out-of-plane fundamental (*c* principal axis perpendicular to the symmetry plane) for the *trans* form whereas the *gauche* conformer gives rise to an *A–B–C* hybrid band contour (531 cm^{-1}).

Oftentimes the spectral data are not as conclusive as in the aforementioned two examples. When such cases arise, it is necessary to rely on additional experimental or theoretical results to determine the structure of the high-energy conformation. From our recent investigation of fluoroacetyl chloride such was the case (Durig *et al.* 1989b).

The assignment of the microwave spectrum and partial r_s structure for the *trans* conformer of fluoroacetyl chloride are available (Szalanski and Ford 1974) and, using calculations previously described, structural optimizations were carried out for this conformer with the initial parameters taken from this investigation (Durig *et al.* 1989b). The final structure was then employed to obtain a potential surface scan in which only the FCCO torsional dihedral angle was allowed to vary from 0° (*trans* position) to 180°

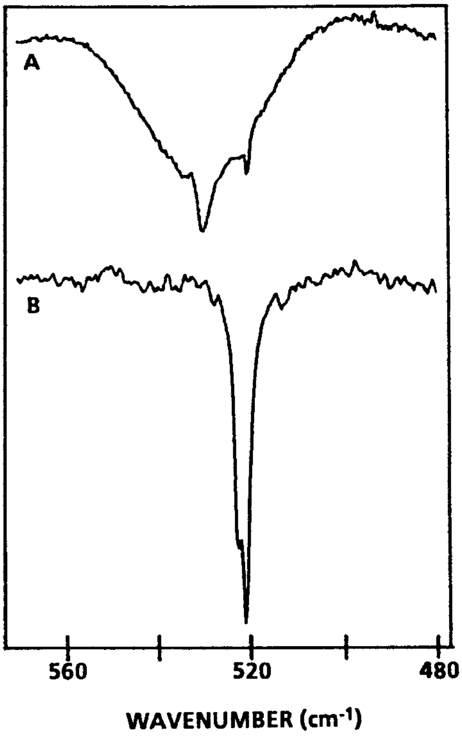

Figure 2. Mid-infrared spectrum of (*a*) gas and (*b*) solid bromoacetyl fluoride in the region of the CFO out-of-plane bending mode. Used by permission of Durig *et al.* (1989e).

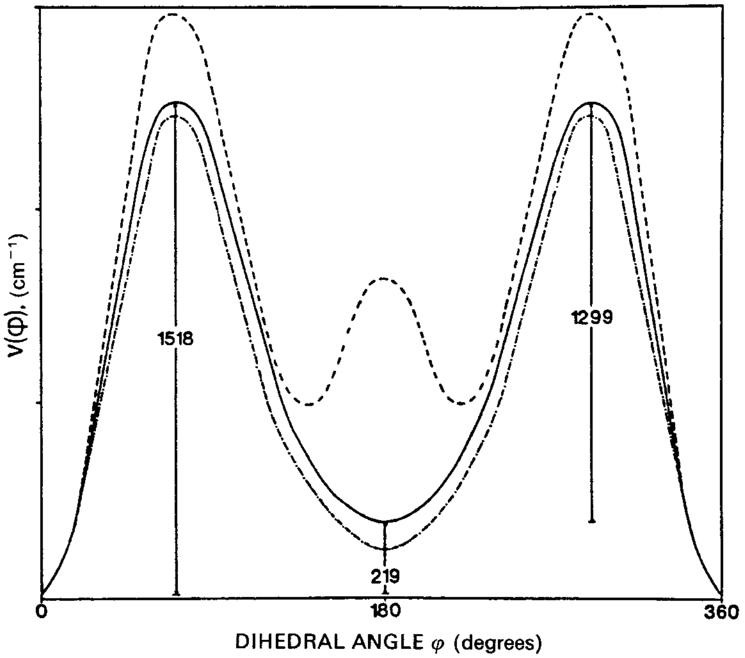

Figure 3. Potential function governing internal rotation of the CH_2F moiety of fluoroacetyl chloride as determined by *ab initio* calculations with the 6-31G* basis set. The potential surface given by the broken curve was obtained by allowing the torsional dihedral angle to vary by 10° increments while all other structural parameters were held fixed at the optimized values obtained for the *trans* conformer. The potential surface given by the chain curve was obtained by optimization at the *gauche* minimum and at the transition states by relaxation of all of the geometric parameters. The potential surface given by the solid curve was calculated using second-order perturbation configuration interaction at all minima and maxima on the surface. Used by permission of Durig *et al.* (1989b).

(*cis* position). Both the 3-21G* and the 6-31G* basis sets were employed and used in an identical manner. The potential surface obtained in this manner predicted another minimum located approximately 30° away from the *cis* position which corresponds to a *gauche* structure (figure 3, broken curve). The results obtained with the 6-31G* basis set give the *trans*-to-*gauche*, *gauche*-to-*gauche* and *gauche*-to-*trans* barriers of 1786, 389 and 1198 cm^{-1} respectively, with an energy difference of 588 cm^{-1}. A *trans*–*gauche* equilibrium was also obtained from initial calculations for fluoroacetyl fluoride (Durig *et al.* 1989c) but further optimizations at both the *cis* and the *gauche* positions, with either basis set, clearly indicated that the *gauche* minimum was a false minimum. Therefore, geometry optimizations at the *cis* and the *gauche* positions of fluoroacetyl chloride showed that the true minimum in the potential surface is at the *cis* position (figure 3, chain curve). The total energy calculated at the *cis* position was considerably reduced upon relaxation of the structural parameters. This structural relaxation is so significant that, at the 3-21G* basis set level, with these additional geometry optimizations, the total energy of the *cis* conformation is lower than that of the *trans* conformation.

With the structural parameters optimized at both the *trans* and the *cis* positions, the energy difference between the two rotamers of fluoroacetyl chloride was calculated. Numerical values of the energy difference were obtained with the 6-31G* (160 cm^{-1}, *trans* more stable) and the 3-21G* basis sets (146 cm^{-1}, *cis* more stable). These quantities are significantly smaller than the value obtained experimentally (509 ± 37 cm^{-1}, *trans* more stable) for the gas. In an attempt to improve the calculated energy difference, and the barriers, the Møller–Plesset perturbation treatments (Hehre *et al.* 1986) at the second order were included for optimized structures at the *trans* and the *cis* positions, as well as at the transition state. With MP2/6-31G*//6-31G*, the energy difference was calculated to be 219 cm^{-1} whereas values of 1518 and 1299 cm^{-1} were found for the *trans*-to-*cis* and the *cis*-to-*trans* barriers respectively (figure 3, solid curve). Values of 265, 1913 and 1648 cm^{-1} were obtained with MP2/3-21G*//3-21G* for the energy difference, *trans*-to-*cis* and *cis*-to-*trans* barriers respectively, with the *trans* conformer being the more stable form.

Although the vibrational data are suggestive of a high-energy *cis* form, the *ab initio* calculations add additional support to this conclusion. However, further experimental confirmation is desirable. We made a major effort to assign the additional microwave transitions which are observed but not assigned to the *trans* conformer but the large number of observed excited-state transitions along with the two isotopes of chloride rendered the task impossible with conventional microwave equipment. Therefore an electron diffraction study of fluoroacetyl chloride would be useful in confirming the structure of the high-energy isomer. Such a study should be aided by the *ab initio* structural parameters since the calculated differences of the parameters between the two conformers could be used in the analysis.

From a relatively recent theoretical study of acetaldehyde (Baba *et al.* 1985) it was found that the n–π* excited state has a structure similar to the *cis* conformation of fluoroacetyl chloride. The reason for the stability of this form in acetaldehyde is due to hyperconjugation between the methyl group and the carbonyl bond. This is evidenced by the increase in electron population on the C–C bond and on the methyl hydrogen atoms as the minimum-energy structure is approached. For fluoroacetyl chloride the changes in electron population are opposite to this effect as given in table 1. This means that the C(O)Cl moiety is drawing electrons from the methylene hydrogens and the C–C bond. This effect is accomplished by the hyperconjugating factor in the planar (i.e. *cis* and *trans*) forms. This effect contributes to the lower energy of these two structures compared with the *gauche* conformation or the transition state.

Table 1. Selected atomic and Mulliken overlap populations for fluoroacetyl chloride as determined by the 6-31G* basis set.

Structure†	C–C‡	2H§	C(O)Cl‖
trans (0°)	0·289	1·586	31·102
cis (180°C)	0·295	1·576	31·111
Transition (72°)	0·311	1·603	31·098
gauche (140°C)	0·311	1·587	31·094

† Values in parentheses represent the FCCO dihedral angle.

‡ Represents the Mulliken overlap population for the C–C bond.

§ Represents the sum of the net atomic populations on both hydrogens.

‖ Represents the sum of the net atomic populations on the carbon, oxygen and chlorine atoms.

Finally, let us consider the use of infrared band contour analysis for the determination of the high-energy conformer in these type studies. From the discussion above (Durig *et al.* 1989b), the microwave, vibrational and theoretical studies of fluoroacetyl chloride were interpreted on the basis that the *trans* conformer is thermodynamically preferred in the vapour phase but the structure of the high-energy conformer remained unverified from experimental results. From the Raman spectrum of the liquid the CH_2 twist of the high-energy conformer occurred as a de-polarized line and disappeared in the spectrum of the solid, which suggests a *cis* conformer; the possibility remained that this line was 'accidentally' de-polarized. Therefore we had to rely heavily on the *ab initio* results which gave the *cis* conformer as the high-energy form. In the presence of such limited experimental evidence we investigated the infrared band contours for the vapour phase of fluoroacetyl chloride to see whether we could obtain additional experimental evidence of the *trans–cis* equilibrium for this molecule (Durig *et al.* 1989f).

The rotational constants were taken from the microwave data (Szalanski and Ford 1974) for the *trans* conformer and from the calculated values obtained from the 6-31G* *ab initio* results for the *cis* conformer. For the *gauche* conformer bond lengths and valence angles were taken from the *cis* conformer, but with an FCCO dihedral angle equal to 120°. Pure *A*-, *B*- and *C*-type transitions for each of the conformers were calculated in the harmonic rigid-rotor approximation at 293 K, with J ranging from 0 to 150 and with a slit width of 0·5 cm^{-1} and at 0·25 cm^{-1} intervals. For both stretching vibrations considered (i.e. ν(C=O) and ν(C–Cl)), the dipole change vector $\partial\mu/\partial Q$ was assumed to be parallel to the corresponding chemical bond. Theoretical hybrids corresponding to these dipole changes were calculated as usual (van der Veken 1986) and were convoluted in order to take into account excited-state contributions, with mixed Gauss–Lorentz slit functions.

In the first instance, the ν(C=O) contours were simulated. The direction cosines of the $\partial\mu/\partial Q$ in their respective principal axes are given in table 2. The final hybrids for all three conformers are shown in figure 4, together with the carbonyl stretching region of the experimental spectrum. For the latter it is clear that both conformers give rise to a contour that is predominantly *B* type, *Q* branches in both cases being barely visible. As a criterion for the convolutions on the theoretical hybrid band, the intensity dip between *P* and *R* branches of the high-frequency component was used. The relatively wide Lorentzian slit that has to be used (full width at half-height, 4 cm^{-1}) to reproduce this dip causes the weak *Q* branches in the hybrid bands to disappear, so that, as is clear from figure 4, all conformers give rise to a predominantly *B*-type contour. Consequently, the simulations of ν(C=O) are of no help in determining the symmetry of the conformers.

Table 2. Direction cosines for fluoroacetyl chloride.

		$\cos\alpha$	$\cos\beta$	$\cos\gamma$
ν(C=O)	*trans*	−0·143 34	0·989 67	0·0
	cis	0·484 90	−0·874 57	0·0
	gauche	0·230 72	−0·943 16	−0·239 21
ν(C–Cl)	*trans*	0·927	0·0	—
	cis	0·485 48	0·874 25	0·0
	gauche	0·678 00	0·734 47	−0·029 74

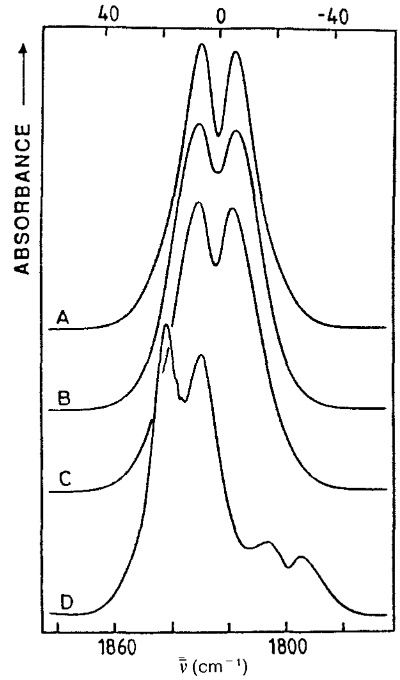

Figure 4. Comparison of experimental ν(C=O) stretches of CH_2FCClO with simulated contours: (*a*) *trans* conformer; (*b*) *cis* conformer; (*c*) *gauche* conformer; (*d*) experimental contours. All simulated contours were convoluted with a Lorentzian slit of 4 cm^{-1} (full width at half-height). Used by permission of Durig *et al.* (1989f).

Similar band contour calculations for the C–Cl stretching mode are indicative that the high-energy conformer of fluoroacetyl chloride is *gauche* which is contrary to the *ab initio* calculations (Durig *et al.* 1989b). Using the MP2/6-31G*//6-31G* basis set the high-energy conformer is predicted to be the *cis* form which is only 219 cm^{-1} higher in energy than the *trans* form. Additionally, it should be noted that the experimentally determined barriers to internal rotation were reasonably well reproduced by the *ab initio* calculations. Therefore one must question the validity of conclusions from the contour analysis and an electron diffraction study of fluoroacetyl chloride is badly needed to determine experimentally the structure of the high-energy conformer of this molecule.

3.2. *Asymmetric torsional vibrations*

Once the structure of the high-energy conformer has been determined, an assignment to the torsional fundamentals and associated excited states can usually be made from the far-infrared spectra of the gas. In order to show the differences in the observed far-infrared spectra between a *trans*↔*cis* and a *trans*↔*gauche* equilibrium we have chosen fluoroacetyl fluoride, CH_2FCFO, which exists in the former equilibrium, and chloroacetyl chloride, $CH_2ClCClO$, which exists in the latter (Durig *et al.* 1988b, 1989c).

From a complete analysis of the vibrational spectra of fluoroacetyl fluoride (Durig *et al.* 1989c) we have determined, in agreement with previously reported results from microwave spectroscopy (van Eijck *et al.* 1978, Saegebarth and Wilson 1967), that this molecule exists in a *trans*↔*cis* equilibrium. The asymmetric torsional fundamentals for both the *trans* and the *cis* conformers are assigned to the features observed at 118·90 and 52·06 cm^{-1} respectively in the far-infrared spectrum of the gas (figure 5). In addition to the torsional fundamentals, a number of torsional excited-state transitions for both conformers have been observed.

Similarly, the asymmetric torsional fundamentals and a number of associated 'hot bands' for both the low-energy *trans* and the high-energy *gauche* conformers of chloroacetyl chloride have been observed in the far-infrared spectrum of the gas (figure 6). The bands occurring at 82·7 and 50·7 cm^{-1} can readily be assigned to the torsional fundamentals for the *trans* and *gauche* conformers respectively.

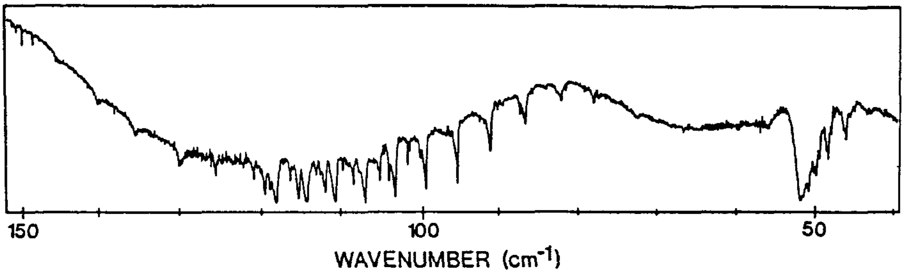

Figure 5. Far-infrared spectrum of gaseous fluoroacetyl fluoride in the region of the asymmetric torsional mode. Used by permission of Durig *et al.* (1989c).

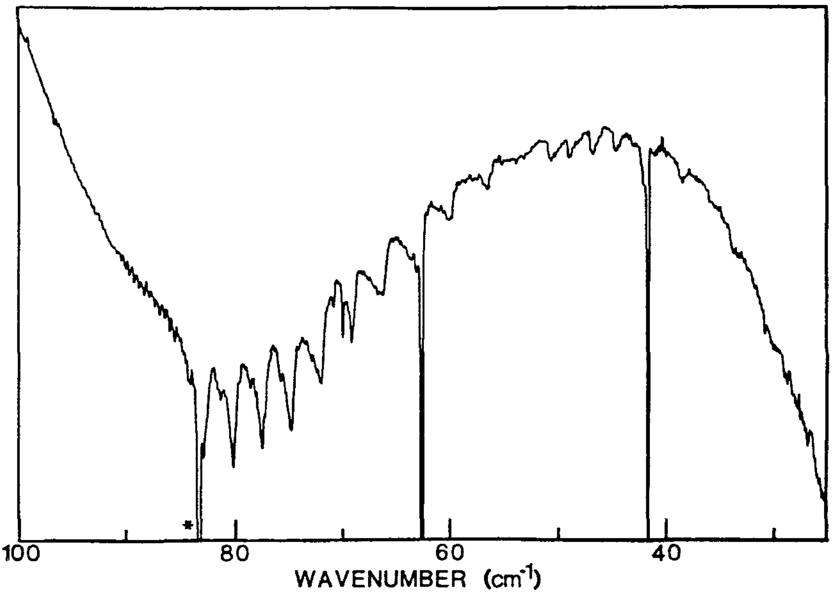

Figure 6. Far-infrared spectrum of gaseous chloroacetyl chloride in the region of the asymmetric torsional mode. The sharp intense lines observed at 83·4 (denoted with an asterisk), 62·6 and 41·7 cm^{-1} are attributed to three of the rotational lines of the HCl impurity. Used by permission of Durig *et al.* (1988b).

Although both molecules give rise to an intense *C*-type band for the preferred *trans* conformation, only fluoroacetyl fluoride gives rise to a distinct *C*-type band for the high-energy (*cis*) form. It should be mentioned, however, that the relatively less intense transitions arising from the asymmetric torsion of the *gauche* (see 50·7 cm^{-1} in figure 6) conformer of chloroacetyl chloride is not definitive evidence that the high-energy conformer for this molecule is *gauche*. This evidence must be supported from other spectral features in the vibrational spectra or from other more definitive structural studies such as microwave spectroscopy or an electron diffraction investigation.

Using the assignments for the asymmetric torsional transitions for chloroacetyl chloride and chloroacetyl fluoride given in table 3 and methods previously described (Compton 1981), we can determine the torsional potential as a cosine-based function in the torsional dihedral angle ϕ. The potential function shown in figure 7 is consistent with the potential constants given in table 4 (calculation I) for chloroacetyl chloride. Also given in table 4 are the corresponding results for chloroacetyl fluoride (Durig *et al.* 1988a) and chloroacetyl bromide (Durig and Phan 1989) which have been determined from similar experimental data (i.e. far-infrared spectra of the gas).

A comparison of the potential functions calculated for the three chloroacetyl halides shows that the *trans-to-gauche* barriers increase from 796 cm^{-1} for CH_2ClCFO to 944 cm^{-1} for $CH_2ClCClO$ and finally to 963 cm^{-1} for $CH_2ClCBrO$. The increase in this barrier can be attributed to the increased steric interaction between the carbonyl halogen atom and the hydrogen atoms in the transition state. Since the size of the bromine atom is only slightly larger than that of the chlorine, the *trans*-to-*gauche* barrier is calculated to increase only slightly from $CH_2ClCClO$ to $CH_2ClCBrO$. On

Table 3. Observed torsional transitions of gaseous chloroacetyl fluoride and chloroacetyl chloride (cm^{-1}).

		$CH_2ClC(O)F$			$CH_2ClC(O)Cl$		
			Observed-calculated†‡			Observed-calculated†‡	
Conformer	Transition	Observed	I	II	Observed	I	II
trans	1←0	86·5	−0·02	−0·13	82·7	0·05	0·22
	2←1	83·2	0·00	0·09	80·1	0·05	0·10
	3←2	79·8	0·02	0·26	77·4	0·00	−0·05
	4←3	76·2	−0·03	0·31	74·7	0·00	−0·12
	5←4	72·6	0·08	0·46	71·9	−0·03	−0·20
	6←5	68·6	−0·02	0·33	69·0	−0·08	−0·26
	7←6	64·4	−0·04	0·17	66·1	−0·03	−0·19
	8←7	59·9	0·00	−0·06	63·0	−0·05	−0·15
	9←8	54·8	0·00	−0·56	59·8	−0·02	0·01
	10←9	48·7	0·01	−1·50	56·5	0·13	0·37
	11←10	—	—	—	52·6	−0·02	0·55
gauche	∓1←±0	47·8	−0·04	−1·01	50·7	−0·11	0·36
	±2←∓1	45·2	0·08	0·23	49·0	0·06	0·24
	∓3←±2	42·0	−0·04	1·23	47·0	0·08	−0·01
	±4←∓3	—	—	—	44·7	−0·01	−0·33
	∓5←±4	—	—	—	42·2	−0·02	−0·44

† Calculated using the corresponding potential coefficients (i.e. I) given in table 4.

‡ Calculated using the corresponding potential coefficients (i.e. II) given in table 4 which are determined by using the torsional dihedral angle determined from *ab initio* as a constraint on the calculated potential.

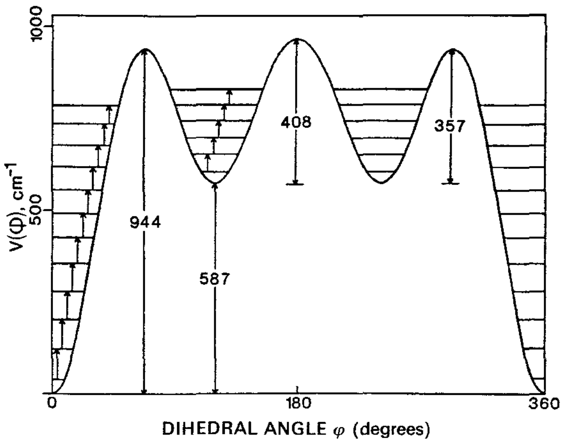

Figure 7. Asymmetric torsional potential function for chloroacetyl chloride as determined from far-infrared spectral data. The dihedral angle of 0° corresponds to the *trans* conformer. Used by permission of Durig *et al.* (1988b).

the other hand, this barrier increases significantly from CH_2ClCFO to $CH_2ClCClO$. At the transition state between the two *gauche* wells (the two halogen atoms eclipse each other), repulsive interactions increase and the *gauche*-to-*gauche* barrier increases dramatically. The increase in this barrier as one proceeds from chloroacetyl chloride to chloroacetyl bromide has a significant effect on the fundamental frequencies and the observed spacing of the torsional transitions for the *gauche* conformer. Trends in the torsional dihedral angle are also evident from table 4. The smaller angles determined for the chloride and bromide compared with the fluoride are indicative of larger Cl···Cl and Cl···Br repulsions than the corresponding Cl···F steric repulsion.

Also included in tables 3 and 4 are the fits of the observed frequencies and resulting potential coefficients and barriers to internal rotation which are determined if the torsional dihedral angle calculated for the *gauche* conformer from the *ab initio* results is used as a constraint on the determined potential function. These results are tabulated as calculation II in these tables. Several factors should be noted from these calculations. Although the fit of the observed transitions is not as good as that obtained when the torsional dihedral angle is allowed to vary, it is still satisfactory for both $CH_2ClC(O)F$ and $CH_2ClC(O)Cl$. For the potential parameters, the V_1 term is the poorest determined, and the V_2 constant the next poorest. Additionally, it should be noted that these two parameters are highly correlated when one has only the frequencies from the torsional transitions to use in a potential calculation for a molecule going from a *trans* or *cis* to a *gauche* configuration. The V_2 term essentially moves the potential well for the *gauche* conformer and, consequently, the dihedral angle places a very large restriction on the value of this parameter. Consequently, the determined uncertainties for the calculation using the dihedral angle are considerably smaller for the V_1 and V_2 terms compared with the uncertainties where the dihedral angle is permitted to vary.

Since structural information is not available for the high-energy conformers of these molecules, the angles determined from *ab initio* calculations must be considered tentative. Clearly, the determination of the structural parameters from the microwave spectrum of the high-energy conformers should be carried out in order to determine the dihedral angles which would certainly place a considerable restriction on the values of

Table 4. Comparison of potential coefficients, barriers to interconversion and torsional fundamental frequencies for $CH_2ClC(O)X$ (X ≡ F, Cl and Br) as determined from far-infrared spectral data, *ab initio* calculations and a combination method.

	X≡F		X≡Cl		
Parameter	I†	II‡	I†	II‡	X≡Br§
V_1 (cm^{-1})	350(12)	313(3)	438(16)	528(4)	336(11)
V_2 (cm^{-1})	306(6)	375(3)	278(8)	176(3)	73(10)
V_3 (cm^{-1})	420(1)	406(3)	557(1)	569(2)	757(7)
V_4 (cm^{-1})	44(1)	20(2)	67(2)	100(1)	103(3)
V_6 (cm^{-1})	2(1)	11(2)	6(1)	−4(1)	5(2)
trans-to-*gauche* barrier (cm^{-1})	796 [730]‖	826	944 [883]	914	963
gauche-to-*gauche* barrier (cm^{-1})	245 [280]	195	408 [591]	510	709
ΔH (cm^{-1})	525 [136]	524	587 [493]	587	373
Dihedral ∢XCCO (degrees)	122 [126]	126	118 [113]	113	115
ν_{obs}(*trans*)	86·5 [85]		82·7 [82]		80·2
ν_{obs}(*gauche*)	47·8 [61]		50·7 [62]		53·8

† Parameters determined from the assignment given in table 3. Values taken from Durig *et al.* (1988).

‡ Parameters determined from the assignment given in table 3 and using the torsional dihedral angle determined from *ab initio* as a constraint on the calculated potential.

§ Parameters taken from Durig and Phan (1989).

‖ Values given in brackets are those calculated with the 6-31G* basis set except for the torsional frequencies which were calculated using the 3-21G and 3-21G* basis set for the fluoride and chloride respectively.

the V_2 terms. The use of electron diffraction data for this purpose is probably not possible, since this parameter is typically poorly determined since the high-energy conformations have a large-amplitude torsional vibration. For example, the torsional dihedral angle was found to have an uncertainty of ±7·7° from the electron diffraction investigation of chloroacetyl chloride (Steinnes *et al.* 1980).

The chloroacetyl halides have considerably different potential functions from the fluoroacetyl halides (table 5), in that the *gauche* conformer is not the higher-energy form in fluoroacetyl fluoride or fluoroacetyl chloride. Nevertheless, we can still compare the potential wells obtained for the *trans* conformer. The large chlorine atom in the CH_2Cl moiety in the chloroacetyl halides brings about a stronger chlorine–oxygen steric hindrance than the corresponding fluorine–oxygen steric hindrance present in the fluoroacetyl halides. This strong steric hindrance presumably raises the energy of the *trans* minimum in the chloroacetyl halides which in turn reduces the depth of the *trans* potential wells in the chloroacetyl halides. Therefore the *trans* potential wells are only 796 and 944 cm^{-1} 'deep' in chloroacetyl fluoride and chloride (Durig *et al.* 1988a, b) respectively, whereas they are about 1314 and 1455 cm^{-1} 'deep' in fluoroacetyl fluoride and chloride (Durig *et al.* 1989c).

For all the molecules thus far presented, there has been little if any uncertainty associated with the assignment of the torsional fundamentals. For the haloacetyl halide molecules, such definitive assignments result in reliably determined potential functions from experimental data which can then be used to determine the accuracy of the theoretical techniques. Let us now consider a situation for which such assignments are

Table 5. Comparison of energy parameters of fluoroacetyl fluoride and fluoroacetyl chloride.

	CH_2FCFO†			CH_2FCClO‡		
		Ab initio			*Ab initio*	
	Infrared	3-21G	6-31G*	Infrared	3-21G*	6-31G*
Torsional frequency (*trans*) (cm^{-1})	118·90	127		116·18	124	
Torsional frequency (*cis*) (cm^{-1})	52·06	28		49·42	34	
Potential constants						
V_1 (cm^{-1})	86±11			43±6		
V_2 (cm^{-1})	946±33			1039±36		
V_3 (cm^{-1})	407±4			498±3		
V_4 (cm^{-1})	138±20			149±21		
V_6 (cm^{-1})	−14±7			−10±7		
ΔH (cm^{-1})	494±48	616	305	541±45	265	219
trans-to-*cis* barrier (cm^{-1})	1297±26	1502	1435	1455±25	1913	1518
cis-to-*trans* barrier (cm^{-1})	803±26	886	1130	914±24	1648	1299

† Values taken from Durig *et al.* (1989c). Theoretically calculated values were determined using MP2/3-21G//3-21G and MP2/6-31G*//6-31G* calculations.

‡ Values taken from Durig *et al.* (1989b). Theoretically calculated values were determined using MP2/3-21G*//3-21G* and MP2/6-31G*//6-31G* calculations.

less definitive and the results obtained from the *ab initio* technique are employed to facilitate the analysis of the experimental results. Such is the case for the related molecule chloroacetaldehyde, CH_2ClCHO (Durig *et al.* 1990).

The most stable conformation of chloroacetaldehyde is that with the chlorine atom eclipsing the aldehyde hydrogen except there is a small 'bump' at the exact planar conformation which causes a zig-zag in the rotational constants with excited torsional states (Ford 1976). From this variation in the rotational constants with torsional state, the barrier height at the *cis* conformation has been estimated as approximately 60% of the zero-point energy for the torsion (Malloy and Carreira 1977). Using *ab initio* Hartree–Fock gradient calculations employing the 6-31G* basis set, this barrier was calculated to be 12 cm^{-1} (34 cal mol^{-1}) but with electron correlation (MP2) the calculated barrier was less than 1 cm^{-1} (figure 8) (Durig *et al.* 1990). In order to see what effect this small barrier has on the torsional transitions, we recorded the far-infrared spectrum of chloroacetaldehyde at a resolution of 0·10 cm^{-1} from 350 to 25 cm^{-1}.

A strong broad band is observed below 100 cm^{-1} which is attributed to the asymmetric torsion for both conformers. An expansion of this spectral region is shown in figure 9. Two sets of *Q* branches are observed with the first set assigned as beginning at 26·9 cm^{-1} and the second at 58·9^{-1}, both of which apparently proceed to higher frequencies. This first *Q* branch at 26·9 cm^{-1} is assigned to the 2←1 transition of the asymmetric torsional fundamental of the *cis* conformer (see below) whereas that at 58·9 cm^{-1} is assigned to the asymmetric torsional fundamental of the *trans* conformer. The remaining observed features are assigned as reported in table 6. The assignment of these torsional transitions was greatly aided by the *ab initio* calculations where the torsional fundamental for the less stable *trans* conformer was predicted at a significantly higher frequency (154 cm^{-1}) than that for the more stable *cis* form (74 cm^{-1}) (Durig *et al.* 1990).

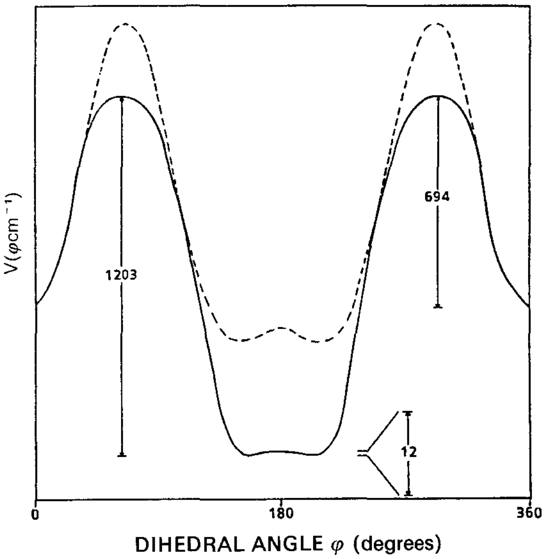

Figure 8. Potential function governing internal rotation of the CH_2Cl moiety of chloroacetaldehyde as determined by *ab initio* calculations with the 6-31G* basis set. The potential surface given by the broken curve was obtained by optimizations at the *s-trans* minimum and then rotation of the CH_2Cl group. The potential surface given by the solid curve was calculated using optimization at the *s-trans* minimum, the minimum about 25° away from the *s-cis* conformer, at 180° and at the transition state by relaxation of all of the geometric parameters. Used by permission of Durig *et al.* (1990).

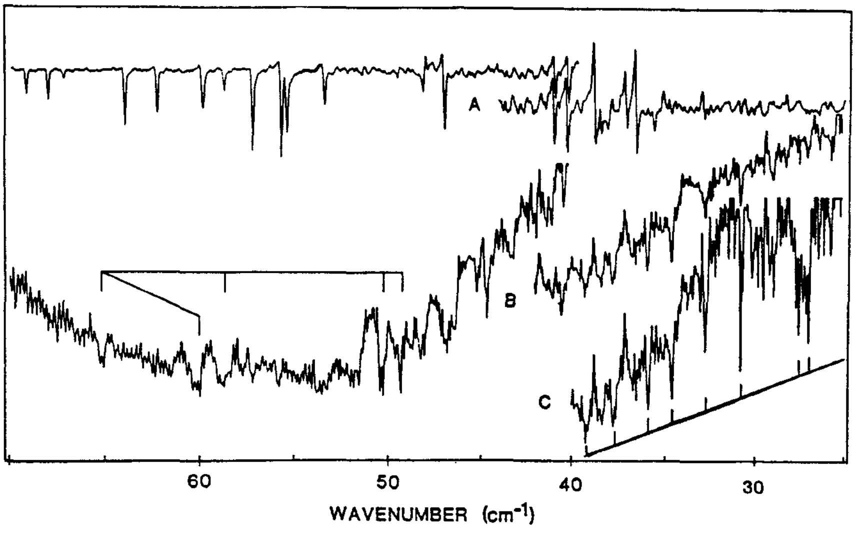

Figure 9. Far-infrared spectrum of gaseous chloroacetaldehyde in the region of the asymmetric torsional mode: (*a*) background with water vapour; (*b*) sample at maximum vapour pressure in 1 m path length cell with 12·5 μm beam splitter; (*c*) sample at maximum vapour pressure, 1 m path length call and 25 μm beam splitter.

Table 6. Observed and calculated† asymmetric torsional transitions for gaseous chloroacetaldehyde.

Conformer	Transition	ν_{obs} (cm^{-1})	$\nu_{obs}-\nu_{calc}$ (cm^{-1})‡
cis	1←0	(15·60)§	
	2←1	26·90	0·09
	3←2	27·50	−0·03
	4←3	30·80	0·11
	5←4	32·80	0·03
	6←5	34·60	−0·14
	7←6	36·00	−0·40
	8←7	37·70	−0·06
	9←8	39·20	0·40
trans	1←0	58·90	0·19
	2←1	65·20	−0·78
	3←2	60·30	0·51

† Value calculated from the potential coefficients given in table 7.

‡ The calculated frequencies are consistent with the potential coefficients and '*F* numbers' given in table 7.

§ Calculated with the potential coefficients given in table 7.

Since there is a small 'bump' in the well of the *cis* rotamer, we expect perturbation of the first few energy levels. For this reason the 1←0 transition is expected to be relatively low in frequency compared with the other transitions, and the difference between the first excited-state transition and the next is expected to be much smaller than the difference in frequency between the higher-state transitions. The assignment used for the observed transitions is consistent with these expectations. The fit of the observed to calculated transitional frequencies is remarkably good, which leads to very small uncertainties in the potential coefficients. The resultant values of the potential constants are listed in table 7, and the potential function is shown in figure 10. The *cis*-to-*trans* and the *trans*-to-*cis* barrier heights are $500 \pm 5\,\mathrm{cm}^{-1}$ ($1{\cdot}43 \pm 0{\cdot}01\,\mathrm{kcal\,mol}^{-1}$) and $233 \pm 5\,\mathrm{cm}^{-1}$ ($0{\cdot}67 \pm 0{\cdot}01\,\mathrm{kcal\,mol}^{-1}$) respectively, with an enthalpy difference of $267 \pm 19\,\mathrm{cm}^{-1}$ ($0{\cdot}76 \pm 0{\cdot}05\,\mathrm{kcal\,mol}^{-1}$).

The assignment of the torsional modes could not have been made without the *ab initio* calculations. We initially assumed that the lower-frequency transitions were due to the high-energy conformer and that both series proceeded from higher to lower frequencies. With such an assignment, the observed transitions could be fitted reasonably well except for those in the 60–70 cm^{-1} region but it was not possible to introduce a 'bump' at the *cis* conformation. We knew that this potential function could not be correct since the 'bump' had been clearly demonstrated from the microwave data (Ford 1976). However, the *ab initio* calculations indicated that the torsional transitions for the high-energy conformer should be at higher frequencies than those for the more stable conformer; so the assignment was switched. Of course, there is some question concerning the correctness of the proposed assignment for the individual Q branches, but there are several pieces of supporting data. First, the assignment provides a 'bump' with a value consistent with that predicted from the analysis of the zig-zag behaviour of the experimental rotational constants (Ford 1976). Malloy and Carreira (1977) estimated the value to be 60% of the zero-point energy which we have calculated to be 10·9 cm^{-1}; this gives a value of 6·5 cm^{-1}. The value from the potential function is 11 cm^{-1} so that the agreement is satisfactory. Second, the relative appropriate spacings

Table 7. Potential coefficients, barriers to internal rotation, and '*F* numbers' for chloroacetaldehyde.

		Ab initio‡			
Parameter	Value†	RHF 3-21G*	RHF 6-31G*	MP2 6-31G*	MP4 6-31G*
V_1 (cm^{-1})	414±11				
V_2 (cm^{-1})	191±3				
V_3 (cm^{-1})	−203±5				
V_4 (cm^{-1})	44±1				
V_6 (cm^{-1})	−26±1				
cis-to-*trans* barrier (cm^{-1})	500±5	1060	1203	1039	—
trans-to-*cis* barrier (cm^{-1})	233±5	903	694	767	—
Enthalpy difference, *cis*-to-*trans* (cm^{-1})	267±19	157	509	272	279
'Bump' (cm^{-1})	11	86	12	0	

† Parameters as determined from the assignment given in table 6 where $F_0 = 2{\cdot}850\,381$, $F_1 = 0{\cdot}206\,146$, $F_2 = 0{\cdot}018\,360$, $F_3 = 0{\cdot}001\,730$, $F_4 = 0{\cdot}000\,323$, $F_5 = 0{\cdot}001\,730$ and $F_6 = 0{\cdot}018\,360$.

‡ Results taken from Durig *et al.* (1990).

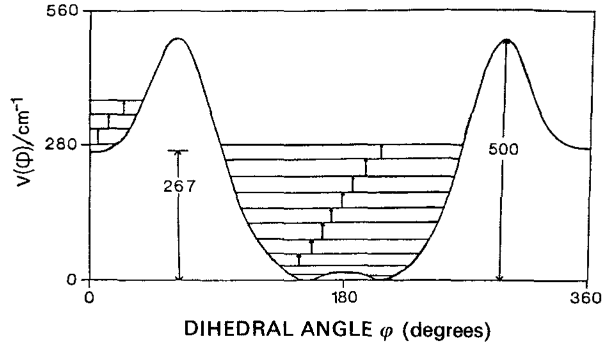

Figure 10. Asymmetric torsional potential function for chloroacetaldehyde as determined from far-infrared spectral data. The dihedral angle of 0° corresponds to the *trans* conformer (chlorine atom eclipsing the oxygen atom). Used by permission of Durig *et al.* (1990).

are found among the first three excited-state torsional transitions for the *cis* conformer. Third, all the observed transitions are really accounted for along with their relative intensities. Finally, the proposed assignment is consistent with the relative values for the torsional fundamentals based on the *ab initio* calculations. Although the assignment cannot be considered completely definitive, it appears to be consistent with all the observed experimental data.

The barriers calculated at the 6-31G* basis set level are more than twice the values obtained experimentally. One is tempted to attribute the difference to possible misassignment of the torsional transitions but the barrier is not drastically altered by reversing the assignment or by placing successive upper-state transitions going from higher to lower frequencies rather than lower to higher frequencies. Reversing the order of successive transitions lowered the *cis*-to-*trans* barrier by about 10%. The barrier is essentially fixed by the frequency difference between successive transitions when the fundamental is assigned in the same general frequency range. At this point it appears that the *ab initio* values may not be in agreement with the experimental values better than a factor of two. For example, the calculated barriers at the 6-31G* basis set level for fluoroacetone were found to be 50% larger than those obtained experimentally (Durig *et al.* 1989a). This result is in marked contrast with the aforementioned results for the haloacetyl halides where the calculated barriers are usually within 10% of the experimentally determined values. These latter results may have been fortuitous and the expected agreement between calculated barriers at the 6-31G* level and those experimentally determined may in fact be only within a factor of two or so for those within the 500–1000 cm^{-1} range.

3.3. *Structure determinations*

Among the more interesting aspects of molecular dynamics is the change in structural parameters which occur with change in conformation. Such changes can then be attributed to the differing intramolecular forces for the two conformers. These changes are often subtle and can be in error from microwave spectroscopy particularly if, for example, one of the heavy atoms lies on the inertial axis. Similarly, if only partial r_s structures are presented, the ‘fixing’ of structural parameters between the conformations may lead to erroneous changes in those parameters which are allowed to vary. *Ab initio* calculations can be particularly useful for elucidating these subtle changes. However, it is only through a systematic combined experimental–theoretical approach that verification of such changes can be ascertained.

As an example of this combined approach we have chosen the fluoroacetyl fluoride molecule (Durig *et al.* 1989c). The investigation of the microwave spectrum included five isotopically substituted derivatives which allowed for the determination of mixed r_0–r_s structures for both conformations (van Eijck *et al.* 1978). Particular attention was given to the transitions arising from the high-energy *cis* conformer from which it was concluded that the torsional motion for this form was essentially harmonic as for the more stable *trans* form.

Except for the methylene C–F and C–C distances, trends in the structural parameters between the two conformers established from the microwave investigation (van Eijck *et al.* 1978) compare reasonably well with the *ab initio* results (tables 8 and 9) if one disregards the uncertainties given in the reported values. For example, in the *trans* conformer the proximity of the methylene fluorine atom to the oxygen atom gives rise to a repulsion between these atoms. The result of this repulsion is an opening of the CCO angle for the *trans* rotamer as opposed to the *cis* form where this repulsive force is minimized. Similarly, both of the FCC angles and the C–C bond distance have been determined to be larger in the *cis* conformer than in the *trans* form in order to minimize the repulsive energy arising from eclipsing the two fluorine atoms in the high-energy *cis* conformation. However, it is clear from these *ab initio* data that there is a problem with the value of the C–C bond distance for the *trans* conformer obtained from the microwave data (van Eijck *et al.* 1978). Although the absolute values for the C–C bond distances obtained from the *ab initio* calculations may be in error by a significant amount (about 0·01 Å), the relative values for this parameter between the two conformers should be reasonably accurate. At the 6-31G* level the C–C bond distance is calculated to be 0·006 Å longer for the *cis* conformer whereas this difference is 0·024 Å from the values obtained from the microwave data. Therefore the C–C distance of 1·483 Å reported from the microwave study for the *trans* conformer is undoubtedly too short.

Table 8. Structural parameters for the *trans* conformer of fluoroacetyl fluoride.

Parameter	Microwave† r_s	*Ab initio* 3-21G	*Ab initio* 6-31G*	r_0 least-squares adjusted value
r(C=O) (Å)	1·194±0·013	1·177	1·163	1·182±0·004
r(C–F) (Å)	1·351±0·014	1·358	1·324	1·353±0·008
r(C–C) (Å)	1·483±0·007	1·495	1·504	1·510±0·006
r(H_2C–F) (Å)	1·366±0·007	1·388	1·348	1·364±0·008
r(C–H) (Å)	1·096±0·003	1·079	1·082	1·092±0·001
∢CCO (degrees)	129·9±0·7	131·0	129·0	129·7±0·5
∢CCF (degrees)	110·3±0·5	109·0	109·8	108·6±0·3
∢H_2CCF (degrees)	109·6±1·0	107·4	108·8	109·9±0·2
∢CCH (degrees)	109·2±0·4	108·9	109·0	109·3±0·4
∢HCH (degrees)	109·0±0·4	108·7	108·9	110·1±0·3
A (MHz)	10 508·91	10 482	10 826	10 509·38
B (MHz)	3855·06	3882	3944	3855·24
C (MHz)	2870·71	2883	2944	2871·14
μ_a (D)	046±0·01	0·45	0·35	0·35
μ_b (D)	2·63±0·05	3·14	3·09	3·09
μ_c (D)	0·0	0·0	0·0	0·0
μ_t (D)	2·67±0·05	3·17	3·11	3·11
$-E$ (hartrees)		348·707 713 6	350·635 521 8	

† Values are from van Eijck *et al.* (1978).

Table 9. Structural parameters for the *cis* conformer of fluoroacetyl fluoride.

Parameter	Microwave† r_s	*Ab initio* 3-21G	*Ab initio* 6-31G*	r_0 least-squares adjusted value
r(C=O) (Å)	1·195±0·005	1·183	1·168	1·185 (fixed)
r(C–F) (Å)	1·322±0·016	1·342	1·309	1·335±0·006
r(C–C) (Å)	1·507±0·007	1·503	1·510	1·514±0·008
r(H_2C–F) (Å)	1·362±0·010	1·388	1·352	1·372±0·004
r(C–H) (Å)	1·097±0·07	1·079	1·081	1·091 (fixed)
∢CCO (degrees)	123·8±0·9	125·2	124·1	123·53±0·70
∢CCF (degrees)	112·3±0·5	110·3	111·6	111·61±0·78
∢H_2CCF (degrees)	113·8±0·5	113·0	113·4	113·52±0·65
∢CCH (degrees)	108·5±1·1	108·7	108·4	108·10±0·95
∢HCH (degrees)	109·1±1·3	108·6	109·0	108·55±0·80
A (MHz)	10 223·84	10 253	10 528	10 222·02
B (MHz)	4110·53	4184	4212	4112·09
C (MHz)	2991·99	3027	3066	2988·25
μ_a (D)	1·18±0·03	1·26	1·46	
μ_b (D)	1·68±0·04	2·32	1·56	
μ_c (D)	0·0	0·0	0·0	
μ_t (D)	2·05±0·06	2·64	2·14	
$-E$ (hartrees)		348·705 542 5	350·634 699 0	

† Values are from van Eijck *et al.* (1978).

Additionally, the methylene C–F distance does not follow the trend given by the *ab initio* calculations between the two conformers. The determination of an unreasonably short C–C bond distance for the *trans* conformer and a rather short (O)C–F bond distance in the *cis* conformer can, at least in part, be attributed to the very small substitution coordinates of the sp^2 carbon atom in both conformations. We therefore determined an r_0 structure compatible with the previously reported rotational constants (table 10) for each conformation using a programme which consists of direct iterative adjustments of structural parameters to the observed rotational constants.

The calculations of the r_0 structure for the *trans* form presented no difficulties. As input to the programme, we used the previously reported r_s values except for the C–C bond distance which was taken as the value from the *ab initio* calculations. The values which were determined agree fairly well with the previously published r_s values, with the exception of the C=O and C–C bond distances (table 9). Our value of 1·182 Å for the C=O distance is slightly smaller than the r_s value of 1·194 Å; however, it is still within the reported uncertainty. Our determined value of 1·510 Å for the C–C bond distance is a more reasonable value. However, it should be noted that there is a very high correlation between the (O)C–F bond and the C–C bond distances as expected.

For the *cis* rotamer, on the other hand, there were difficulties in the determination of the r_0 structure using the published rotational constants. We subsequently noticed the discrepancies between the substitution coordinates for the hydrogen atoms derived from 'single' and 'double' substitution. Therefore, for the initial calculations, a decision was made to incorporate the rotational constants obtained for the d_1 and d_2 derivatives with very low weights in the determination of the structural parameters. Additionally, we fixed the C=O bond distance at 1·185 Å which is only slightly larger than the value obtained for this parameter for the *trans* conformer. This action seemed reasonable since there is a very high level of correlation of the C–C, (O)C–F and C=O bond distances. The determined values were not significantly different from the r_s values previously reported except that the carbonyl bond was 0·010 Å shorter and the (O)C–F bond was found to be 0·013 Å longer than the r_s value. The fit to the rotational constants was quite good except for A and C rotational constants of the d_1 and d_2 species. By gradually increasing the weight for these rotational constants we obtained a satisfactory fit (2 MHz) but the fits for the other rotational constants were significantly degraded (0·6 MHz) and the C–H distance appeared to be entirely too long, that is 1·106 Å. Additionally, the C–C bond distance was 1·501 Å which is too short compared with the *ab initio* calculations.

At this point we then let all parameters vary but placed fairly large uncertainties on the reported rotational constants for each successive isotopic species. There was no indication that any one particular set of rotational constants were in error. Using the reported experimental uncertainties, all the rotational constants and the r_0 parameters reported in table 9 were obtained. All the heavy-atom parameters appear to be very reasonable and they follow the trends relative to the corresponding values for the *trans* conformer as predicted from the *ab initio* calculations.

One is then left with r_0 structural parameters for the *cis* conformer which are not totally satisfactory and the fit of the rotational constants must be considered to be quite poor (table 10). It is possible that the reported rotational constants for two of the species are for excited states or, alternatively, that the very low frequency for the asymmetric torsion has led to an unusually large anharmonicity. It would be useful to check the assignment of the microwave transitions for the *cis* form.

Table 10. Comparison of the observed with calculated rotational constants for *trans* and *cis* fluoroacetyl fluoride from diagnostic least-squares adjusted structural parameters.

Molecule	Rotational constant	*trans* Observed†	*trans* Calculated	*trans* Δ	*cis* Observed†	*cis* Calculated	*cis* Δ
$^{12}CH_2F^{12}CF^{16}O$	*A* (MHz)	10 508·90	10 509·38	−0·48	10 223·84	10 222·02	1·82
	B (MHz)	3855·06	3855·24	−0·19	4110·53	4112·09	−1·57
	C (MHz)	2870·71	2871·14	−0·43	2992·00	2988·25	3·75
$^{12}CH_2F^{12}CF^{18}O$	*A* (MHz)	8817·68	9817·58	0·11	10 054·38	10 057·30	−2·92
	B (MHz)	3834·78	3834·40	0·37	3936·10	3934·61	1·49
	C (MHz)	2805·59	2805·77	−0·18	2884·72	2880·05	4·67
$^{13}CH_2F^{12}CF^{16}O$	*A* (MHz)	10 397·78	10 397·71	0·07	10 094·64	10 092·61	2·02
	B (MHz)	3839·62	3839·39	0·23	4092·93	4095·61	−2·68
	C (MHz)	2853·86	2854·00	−0·14	2971·71	2968·44	3·27
$^{12}CH_2F^{13}CF^{16}O$	*A* (MHz)	10 505·37	10 504·96	0·41	10 222·16	10 220·05	2·11
	B (MHz)	3848·17	3848·08	0·09	4098·17	4098·82	−0·66
	C (MHz)	2866·63	2866·84	−0·21	2985·30	2981·07	4·23
$^{12}CD_2F^{12}CF^{16}O$	*A* (MHz)	9486·89	9486·87	0·02	9188·80	9191·72	−2·91
	B (MHz)	3778·04	3778·30	−0·27	4015·42	4020·33	−4·91
	C (MHz)	2796·99	2796·46	0·52	2901·97	2900·22	1·75
$^{12}CHDF^{12}CF^{16}O$	*A* (MHz)	9967·70	9967·79	−0·09	9672·06	9674·56	−2·50
	B (MHz)	3817·73	3817·71	0·02	4065·36	4067·40	−2·04
	C (MHz)	2832·29	2832·30	−0·01	2944·53	2942·39	2·14

† Values are from van Eijck *et al.* (1978).

Another example of a structural problem which can be solved using a combination of microwave data and *ab initio* calculations is that for the fluoroacetyl chloride molecule (table 11). The structural parameters for this molecule were estimated from six rotational constants determined from the assignment of the ^{35}Cl and ^{37}Cl microwave spectra (Szalanski and Ford 1974). *Ab initio* calculations were carried out at the 6-31G* basis set level, and optimized structural parameters were obtained for the *trans* conformer which was the one identified in the microwave study (Szalanski and Ford 1974). Clearly, the C–H distance and HCC angles will have little effect on the observed rotational constants and therefore these parameters were fixed using the *ab initio* values. The C–H distances, which are expected to be calculated slightly too short, were fixed at values of 0·008 Å greater than the *ab initio* values. Additionally, it is known that the carbonyl distance is too short by about 0·020 Å for these molecules and thus this parameter was fixed at a value 0·020 Å longer than that calculated. A least-squares adjustment was then carried out employing the six rotational constants to permit the C–F, C–C and C–Cl distances to change along with the FCC, the OCC and the ClCC angles. The major difference between the r_0 values obtained and the *ab initio* values is that the C–F distance is determined to be 0·04 Å longer than that calculated and about 0·01 Å longer than that estimated in the previous microwave study. Also, the C–C distance is approximately 0·005 Å longer than the calculated value as expected. Interestingly the C–Cl distance agrees with the *ab initio* value. The angles show little difference except for the ClCC angle which is approximately 1·7° smaller than the calculated value. It is believed that these structural parameters with the indicated uncertainties which are listed in table 11 represent good values for the *trans* conformer of fluoroacetyl chloride.

The microwave data obtained for chloroacetyl fluoride (van Eijck and Stolwijk 1985) can also be used along with the results from theoretical calculations to provide structural information (table 12). From the analysis of the microwave spectrum, six rotational constants (^{35}Cl and ^{37}Cl species) were obtained for the *trans* conformer but

Table 11. Structural parameters and rotational constants for the *trans* conformer of fluoroacetyl chloride.

Parameter	Microwave†	3·21G*	6-31G*	r_0 least squares
r(C–F) (Å)	1·379	1·390	1·348	1·387 ± 0·009
r(C–C) (Å)	1·499	1·506	1·512	1·517 ± 0·008
r(C–H) (Å)	1·094	1·079	1·082	1·090 (fixed)
r(C=O) (Å)	1·185	1·182	1·163	1·183 (fixed)
r(C–Cl) (Å)	1·789	1·789	1·775	1·774 ± 0·007
∢FCC (degrees)	110·00	108·53	109·25	109·80 ± 0·74
∢HCC (degrees)	111·28	109·14	109·19	109·19 (fixed)
∢OCC (degrees)	129·95	128·43	126·98	127·65 ± 0·82
∢ClCC (degrees)	109·78	109·31	111·04	109·30 ± 0·27
∢HCH (degrees)	—	109·51	109·32	109·70 (fixed)
A (MHz)	9025·82 (4)	9105	9414·61	9025·93
B (MHz)	2403·92 (4)	2406	2420·10	2404·07
C (MHz)	1920·70 (2)	1926	1948·50	1921·40

† Parameters estimated by Szalanski and Ford (1974). Rotational constants are those determined from the assignment of the ground state ^{35}Cl spectrum.

the structural parameters had not been calculated. The initial structural parameters were taken from those calculated using the 6-31G* basis set except for the C=O distance which, again, was increased by 0·02 Å and held fixed at this value. The rotational constants were then used to obtain r_0 least-squares values. The C–F and C–Cl distances are determined to be essentially equivalent to the *ab initio* values as is the C–C distance which is calculated to be only 0·002 Å longer.

Another molecule for which we have recently investigated the structural parameters, using *ab initio* calculations, is the chloroacetyl chloride molecule. This molecule had been previously studied by both microwave (van Eijck and Kaleveld 1976) and electron diffraction (Steinnes *et al.* 1980) techniques; however, in the case of the microwave study, no structural parameters were given. It should be noted that the isotopic species $^{35}Cl^{35}Cl$, $^{37}Cl^{37}Cl$ and $^{35}Cl^{37}Cl$ were all found to give microwave spectra which could be readily assigned for the *trans* conformer. Therefore there are nine rotational constants which can be used to obtain six structural parameters. Again the C–O bond was fixed at a value of 0·020 Å longer than the *ab initio* value from the 6-31G* basis set. The six heavy-atom structural parameters were then permitted to vary and the final determined structure was obtained by the least-squares method. From the electron diffraction study (Steinnes *et al.* 1980) the (O)C–Cl distance was determined to be shorter than the (H_2)C–Cl distance by 0·01 Å. This order was reversed from the *ab initio* calculations where the (O)C–Cl distance is calculated to be 0·01 Å longer. Employing the rotational constants from the microwave data (van Eijck and Kaleveld 1976) the relative lengths of these two bonds are now in agreement with the *ab initio* results except the (O)C–Cl bond is only slightly (0·005 Å) longer than the (H_2)C–Cl bond distance. The only other parameter that is significantly different from that obtained from the *ab initio* calculations is the C–C bond distance which is 0·009 Å longer than the *ab initio* value. The results of the determination of these r_0 values are listed in table 13 with the relative uncertainties.

Based on the structural parameters calculated by *ab initio* methods for chloroacetyl fluoride we have determined the structural parameters for bromoacetyl fluoride using

Table 12. Comparison of structural parameters and rotational constants for the *trans* conformer of chloroacetyl fluoride.

Parameter	Initial†	3-21G*	6-31G*	r_0 least squares
r(C=O) (Å)	1·183	1·178	1·163	1·183 (fixed)
r(C–F) (Å)	1·324	1·358	1·324	1·326 ± 0·009
r(C–C) (Å)	1·506	1·499	1·506	1·508 ± 0·009
r(C–Cl) (Å)	1·763	1·774	1·763	1·764 ± 0·009
r(C–H) (Å)	1·088	1·079	1·080	1·088 (fixed)
∢CCO (degrees)	130·1	131·0	130·1	130·12 ± 0·97
∢CCF (degrees)	108·1	107·8	108·1	107·73 ± 0·69
∢CCCl (degrees)	113·2	112·0	113·2	113·28 ± 0·74
∢CCH (degrees)	108·6	108·9	108·6	108·6 (fixed)
∢HCH (degrees)	110·7		110·7	110·74 (fixed)
A (MHz)	10410·20		10691·69	10410·20
B (MHz)	2296·53		2301·27	2296·65
C (MHz)	1903·84		1915·81	1904·11

† The rotational constants are from the microwave data (van Eijck and Stolwijk 1985) and are those determined from the assignment of the ground state ^{35}Cl spectrum.

Table 13. Comparison of structural parameters and rotational constants for the *trans* conformer of chloroacetyl chloride.

Parameter	Electron diffraction†	3-21G*	6-31G*	r_0 least squares
r(C=O) (Å)	1·182(4)	1·182	1·163	1·183 (fixed)
r(C–Cl′) (Å)	1·772(16)	1·789	1·775	1·777±0·007
r(C–Cl) (Å)	1·521(9)	1·509	1·513	1·522±0·008
r(C–Cl) (Å)	1·782(18)	1·780	1·765	1·772±0·009
r(C–H) (Å)	1·062(30)	1·079	1·079	1·087 (fixed)
∢CCO (degrees)	126·9(9)	128·9	128·4	127·80±0·81
∢CCCl (degrees)	112·9(17)	111·7	112·5	111·96±0·59
∢CCCl′ (degrees)	110·0(7)	109·5	110·3	109·22±0·23
∢CCH (degrees)	108·8	109·2	108·8	108·8 (fixed)
∢HCH (degrees)	109·5	109·1	108·6	109·94 (fixed)
A (MHz)	9030·255(7)	9098·7	9317·9	9030·29
B (MHz)	1503·976(1)	1498·0	1500·7	1504·41
C (MHz)	1299·588(1)	1296·5	1302·8	1299·97

† The structural parameters are from the electron diffraction data (Steinnes *et al.* 1980).

‡ The prime (′) denotes the chloride atom bonded to the sp^2 carbon.

§ The rotational constants are from the microwave data (van Eijck and Kaleveld 1976) and are those determined from the assignment of the ground-state ^{35}Cl^{35}Cl spectrum.

Table 14. Structural parameters and rotational constants for the *trans* conformer of bromoacetyl fluoride.

Parameter	Initial†	r_0 least squares
r(C=O) (Å)	1·183	1·183 (fixed)
r(C–F) (Å)	1·326	1·324±0·009
r(C–C) (Å)	1·508	1·505±0·008
r(C–Br) (Å)	1·950	1·946±0·008
r(C–H) (Å)	1·088	1·088 (fixed)
∢CCO (degrees)	130·1	129·84±0·97
∢CCBr (degrees)	113·3	112·45±0·69
∢CCF (degrees)	107·7	107·28±0·41
∢HCC (degrees)	108·6	108·60 (fixed)
∢HCH (degrees)	110·7	110·7 (fixed)
A (MHz)	10381·38	10381·36
B (MHz)	1465·14	1465·20
C (MHz)	1294·48	1294·47

† The initial structural parameters are taken from the r_0 values calculated for chloroacetyl fluoride except for r(C–Br), and the rotational constants (^{79}Br values) are from the microwave data of bromoacetyl fluoride (van Eijck and Stolwijk 1985).

Table 15. Structural parameters for the *trans* conformer of chloroacetyl fluoride and bromoacetyl fluroide determined with the STO-3G* basis set.

Parameter	$CH_2ClC(CO)F$	$CH_2BrC(O)F$
r(C=O) (Å)	1·209	1·209
r(C–F) (Å)	1·355	1·355
r(C–C) (Å)	1·556	1·555
r(C–X) (Å)	1·770	1·871
r(C–H) (Å)	1·094	1·092
∢CCO (degrees)	126·81	127·08
∢CCF (degrees)	111·44	111·41
∢CCX (degrees)	110·82	111·78
∢CCH (degrees)	109·53	108·92
∢HCH (degrees)	109·80	110·01

an initial C–Br distance of 1·95 Å, previously assumed from the microwave study, and all other initial parameters taken from the r_0 values calculated for chloroacetyl fluoride. The six rotational constants determined for the ^{79}Br and ^{81}Br species (van Eijck and Stolwijk 1985) were used for this calculation. The final structure which was obtained is given in table 14. This structure is analogous to that determined for chloroacetyl fluoride (table 12). From *ab initio* calculations of these two molecules with the STO-3G* basis set, it can be shown that the structural parameters calculated for these two molecules are very similar (table 15). Of course, the C–X (X ≡ Cl and Br) distances and the CCX (X ≡ Cl and Br) angles are different but all other parameters are in agreement supporting the least-squares r_0 structures obtained for these two molecules.

4. Concluding remarks

Replacement of the halogen on the sp^3 carbon of the haloacetyl halides by a methyl group forms the propionyl halides which have the *trans*↔*gauche* equilibria. The *trans* conformer is the more stable rotamer and the far-infrared spectrum for this conformer, for these molecules, is quite rich with many excited states. Fewer excited states are observed on the asymmetric torsional transition for the *gauche* conformers but there are sufficient transitions observed so that good potential functions should be obtained. To date, only the potential function for propionyl fluoride has been determined from the far-infrared data (Guirgis *et al.* 1983). The potential function for propanal should be re-investigated, since the earlier far-infrared studies were carried out at only moderately high (0·25 cm^{-1}) resolution (Durig *et al.* 1980) and there is a strong possibility that there is strong coupling between the CH_3 and CHO rotors. Therefore an investigation of the far-infrared and *ab initio* calculation for the propionyl halides including propanal should provide very interesting conformational stability data. These data could be compared with the corresponding data for the haloacetyl halides to establish trends and relative importance of steric and other intramolecular forces in determining the relative conformational stabilities.

Similarly, the replacement of the halogen on the sp^2 carbon of the haloacetyl halides by a methyl group gives the haloacetone (1-halo-2-propanone) molecules. Only fluoroacetone of this series of molecules has been extensively studied to determine the conformational stability and potential function governing the internal rotation. In the vapour state this molecule exists predominantly with the fluorine atom oriented *cis* to the methyl group but a second conformer having a *trans* orientation is present in the liquid and the only conformer present in the spectrum of the annealed solid (Durig *et al.* 1989a). From the far-infrared data the asymmetric torsional potential function governing the internal rotation was determined and these experimental barriers were compared with the corresponding data obtained from *ab initio* calculations at the 3-21G and 6-31G* basis set levels. Further conformational studies of the other haloacetones would be of interest as would those for the 1,1-dihaloacetones where there are few conformational stability data available. Similar studies of the corresponding isopropyl compounds $(CH_3)_2CHCXO$, would be of interest where the conformational equilibria is expected to be *gauche–trans* equilibria, with the *gauche* form being more stable in the vapour state.

The torsional dihedral angles of *gauche* conformers, obtained from *ab initio* calculations, can be used as a constraint on calculated asymmetric torsional potential functions determined from far-infrared and low-frequency Raman spectra of gases. If such potential functions are characterized by two equivalent *gauche* minima and a minimum corresponding to a planar form, the use of this constraint has its largest effect on the V_1 and V_2 potential constants and the resulting *gauche*-to-*gauche* barrier. Since the V_1 and V_2 terms are correlated when only torsional frequencies are available for the determination of the asymmetric potential functions, additional constraints are needed to determine the potential coefficients for *cis*- or *trans*-to-*gauche* conformational equilibria.

Similarly, the structural parameters obtained from *ab initio* calculations can be used for restricting the differences in bond distances and angles between conformational isomers. These calculations are particularly useful when the structural parameters obtained from either microwave or electron diffraction studies are of limited certainty. For electron diffraction studies it is quite difficult to obtain structural parameters for a molecule which has two conformers present. However, by using the *ab initio* information, constraints can be placed on the differences between the parameters for the two conformers which usually improves the determination of the structural parameters significantly. Also the *ab initio* results can provide an excellent guide to what parameters might be expected to differ between the two conformers. From microwave studies, there are seldom sufficient rotational constants to obtain all the r_0 structural parameters; so *ab initio* calculations can be used for fixing the values of some of the parameters with confidence. However, for such cases it is usually necessary to do a series of molecules with one of them having the structural parameters well determined experimentally. Finally, in many cases, more reliable structures can be determined from the combined use of microwave data with the electron diffraction results along with the theoretical results as opposed to the use of the methods independently.

The theoretical techniques at present discussed do not provide good estimates for the frequencies of the low-frequency torsional modes nor for the enthalpy differences between conformational isomers when these values are small as for the molecules discussed herein. Nevertheless, such calculations can be quite useful for establishing trends and relative values of structural parameters, force constants and barriers to internal rotation which can then serve as constraints on the experimental values of these parameters.

References

BABA, M., NAGASHIMA, U., and HANAZAKI, I., 1985, *J. chem. Phys.*, **83**, 3514.

BINKLEY, J. A., FRISCH, M. J., DEFREES, D. J., RAGHAVACHARI, K., WHITESIDE, R. A., SCHLEGEL, H. B., FLEUDER, E. M., and POPLE, J. A., 1984, *Gaussian-82* (Carnegie Mellon University, Quantum Chemistry Publishing Unit, Pittsburgh, Pennsylvania).

COMPTON, D. A. C., 1981, *Vibrational Spectra and Structure*, Vol. 9, edited by J. R. Durig (Amsterdam: Elsevier), p. 255.

DURIG, J. R., COMPTON, D. A. C., and MCARVER, A. Q., 1980, *J. chem. Phys.*, **73**, 719.

DURIG, J. R., HARDIN, J. A., PHAN, H. V., and LITTLE, T. S., 1989a, *Spectrochim. Acta* A, **45**, 1239.

DURIG, J. R., and PHAN, H. V., 1989, *Struct. Chem.*, **1**, 61.

DURIG, J. R., PHAN, H. V., HARDIN, J. A., and LITTLE, T. S., 1989b, *J. chem. Phys.*, **90**, 6840.

DURIG, J. R., PHAN, H. V., HARDIN, J. A., BERRY, R. J., and LITTLE, T. S., 1989c, *J. molec. Struct.*, **198**, 365.

DURIG, J. R., PHAN, H. V., and LITTLE, T. S., 1989d, *Chem. Phys.*, **138**, 391; 1989e, *J. molec. Struct.*, **197**, 187.

DURIG, J. R., PHAN, H. V., LITTLE, T. S., and TOLLEY, C. L., 1990, *Struct. Chem.* (to be published).

DURIG, J. R., PHAN, H. V., LITTLE, T. S., and VAN DER VEKEN, B. J., 1989f, *J. molec. Struct. Theochem.*, **202**, 143.

DURIG, J. R., ZHAO, WENYUN, LEWIS, D., and LITTLE, T. S., 1988a, *J. chem. Phys.*, **89**, 1285, and references therein; 1988b, *Chem. Phys.*, **128**, 353.

FOGARASI, G., and PULAY, P., 1985, *Vibrational Spectra and Structure*, Vol. 14, edited by J. R. Durig (Amsterdam: Elsevier), p. 125.

FORD, R. G., 1976, *J. chem. Phys.*, **65**, 354.

FRISCH, M. J., BINKLEY, J. S., SCHLEGEL, H. B., RAGHAVACHARI, K., MELIUS, C. F., MARTIN, R. L., STEWART, J. J. P., BOBROWICZ, F. W., ROHLFING, C. M., KAHN, L. R., DEFREES, D. J., SEEGER, R., WHITESIDE, R. A., FOX, D. J., FLEUDER, E. M., and POPLE, J. A., 1988, *Gaussian-86* (Carnegie-Mellon University, Quantum Chemistry Publishing Unit, Pittsburgh, Pennsylvania).

GRONER, P., JOHNSON, R. D., and DURIG, J. R., 1986, *J. molec. Struct.*, **142**, 363.

GUIRGIS, G. A., BARTON, B. A. JR, and DURIG, J. R., 1983, *J. chem. Phys.*, **79**, 5918.

HEHRE, W. J., RADON, L., SCHLEYER, P. V. R., and POPLE, J. A., 1986, Ab initio *Molecular Orbital Theory* (New York: Wiley).

JONES, V. I. P., and LADD, J. A., 1970, *J. chem. Soc.* B, 1237.

KHAN, A. Y., and JONATHAN, N., 1969, *J. chem. Phys.*, **50**, 1801; 1970, *Ibid.*, **52**, 148.

MALLOY, T. B. JR., and CARREIRA, L. A., 1977, *J. chem. Phys.*, **66**, 4246.

NAKAGAWA, I., ICHICHIMA, I., KURATANI, K., MIYAZAWA, T., SHIMANOUCHI, T., and MIZUSHIMA, S., 1952, *J. chem. Phys.*, **20**, 1720.

PULAY, P., 1969, *Molec. Phys.*, **17**, 197.

SAEGEBARTH, E., and WILSON, E. B., 1967, *J. chem. Phys.*, **46**, 3088.

SCHACHTSCHNEIDER, J. H., 1964, *Vibrational Analysis of Polyatomic Molecules*, V and VI, Technical Reports Nos. 231–64 and 57–65, (California: Shell Development).

STEINNES, O., SHEN, Q., and HAGEN, K., 1980, *J. molec. Struct.*, **64**, 217.

SZALANSKI, L. B., and FORD, R. G., 1974, *J. molec. Spectrosc.*, **53**, 428.

TANABE, K., and SAEKI, S., 1972, *Spectrochim. Acta* A, **28**, 1083; 1974, *Bull. chem. Soc. Japan*, **47**, 2754.

VAN DER VEKEN, B. J., 1986, *Vibrational Spectra and Structure*, Vol. 15, edited by J. R. Durig (Amsterdam: Elsevier), p. 313.

VAN EIJCK, B. P., BRANDTS, P., and MAAS, J. P., 1978, *J. molec. Struct.*, **44**, 1.

VAN EIJCK, B. P., and KALEVELD, E. W., 1976, *J. molec. Struct.*, **34**, 161.

VAN EIJCK, B. P., and STOLWIJK, V. M., 1985, *J. molec. Spectrosc.*, **111**, 164.