Conformational analysis of some organic molecules by gas phase Raman spectroscopy

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Abstract - Gas phase Raman spectroscopy can frequently be used to obtain the conformational stability of monosubstituted four-membered rings. Similar data can also be quite useful in determining the barriers to internal rotation for many molecules which contain either the CH_3 or CF_3 groups by observation of the torsional overtones. By utilizing far infrared spectra along with low frequency Raman data for the gas it is possible to obtain the barriers to interconversion for several types of molecules which have asymmetric rotors. Several examples of each type of these studies are given and discussed.

INTRODUCTION

For many years, chemists as well as physicists have been interested in studying large amplitude, anharmonic vibrations (see, for example, ref. 1). From a spectroscopic standpoint, much information may be gleaned from the spectra of compounds which undergo these kinds of vibrations which depart radically from the "normal" harmonic description of molecular vibrations. Once this information is obtained, it is of immediate utility to thermodynamicists, theoreticians, organic and inorganic chemists -- those who can use the spectroscopic data to account for such basic molecular properties as enthalpy, entropy, structure, and bonding.

Since the anharmonic vibrations which will be considered here, i.e., ring bending vibrations and torsional oscillations, are usually low in frequency, several excited vibrational states are ordinarily populated at ambient temperature, and upper-stage transitions may be observed. Correct assignments of these "hot bands" can lead to a knowledge of the vibrational potential function and barriers to interconversion between molecular forms. In the case of ring compounds, or molecules with asymmetric rotors, knowledge of the molecular structure itself or the most stable conformation may often be determined.

Historically, these low frequency anharmonic vibrations have been studied by means of a number of techniques. In particular, techniques such as calorimetry, microwave spectroscopy, inelastic neutron scattering, nuclear magnetic resonance spectroscopy, and infrared spectroscopy have all been applied to the study of large amplitude vibrations with varying degrees of success. In addition, other techniques such as sound absorption, electron diffraction, and electron spin resonance spectroscopy have been used to obtain information on barriers to interconversion, but only to a lesser extent. Over the last few years gas phase Raman spectroscopy has been applied to this area of research, and we shall review the utility of this technique for conformational analysis of some organic molecules.

Since the anharmonic vibrations which we shall be discussing herein are those molecular vibrations which are the lowest in frequency, they make up the largest single contribution to the vibrational partition function and thus to all of the thermodynamic functions of the molecule as well. Therefore, it is not surprising that these vibrations were first studied by thermodynamic techniques from which it was possible to make some of the earliest estimates of vibrational potential functions. Another direct result of the low frequency anharmonic vibrations is the significant population of a large number of excited states. These vibrationally excited states can therefore lend themselves nicely to study by microwave spectroscopic investigations. Observations of intensities of rotational transitions of molecules in excited vibrational states which are commonly called vibrational satellites, when compared to intensities of ground state absorptions, can lead to estimates of vibrational frequencies within a potential well. However, more accurate knowledge about the vibrational potential function can frequently be obtained from microwave data by consideration of the variation of rotational constants with vibrational quantum number or rotation-vibration interactions, when observed. In fact, very accurate barriers can be obtained by this microwave "splitting method" under certain conditions. However, this technique is generally limited to barrier determinations of less than 3 kcal/mol for ground state "splittings" although barrier heights can be evaluated in the range of 3 to 4.5 kcal/mol if splittings in the excited vibrational states are measured.

Also, molecules which contain more than one chlorine, bromine, or iodine atom, as well as molecules which contain asymmetric rotors, do not readily lend themselves to the determination of barrier heights by this splitting method. Thus, most of the potential barriers determined by the microwave technique have been for methyl rotors of substituted ethanes and ethylenes or for methyl groups attached to a nonmetallic element.

None of the techniques initially used to study low frequency anharmonic vibrations, i.e., thermodynamics, microwave spectroscopy, inelastic neutron scattering, or nuclear magnetic resonance spectroscopy, involve direct observation of any vibrational frequencies, i.e., transitions between energy levels within the potential well governing that vibration. To this end, only infrared and Raman spectroscopy allow actual observation of the vibrational transitions themselves -- not just the effect of these transitions on some other physical property of the molecule. In the mid-infrared region, anharmonic vibrations were first observed as combination and difference bands of the anharmonic vibration with another normal mode of vibration. Quite often this led to a fairly complicated spectrum which was sometimes not resolvable. Once measurements in the far infrared region of the specturm became more commonplace, direct observation of fundamental transitions of these large amplitude vibrations became possible and considerable research effort was concentrated in this area.

Another technique which enables the direct observation of anharmonic vibrations, and has received comparatively little attention, is Raman spectroscopy. There are several reasons for this apparent neglect. In order to best study anharmonic vibrations, the molecules must be in the gas phase, where they are free from liquid phase or solid phase interactions. Since the number of scattering molecules per unit volume is considerably less in the gas phase than in the other phases, weak signal intensity prohibited observation of all but the stronger Raman lines of gases. Also, quite often anharmonic vibrations are not totally symmetric and do not, therefore, give rise to sharp, distinct Q branches in the Raman spectrum. Raman band contours of nontotally symmetric vibrations are ordinarily weak and broad, and little information can be obtained from them. Finally, it should be noted that overtones in the Raman spectrum, while being totally symmetric and thus giving rise to Q branches, are usually notoriously weak. Nevertheless, with high powered lasers and improved detection systems, observation of weak Raman peaks has become routine, and the technique of gas phase Raman spectroscopy has become commonplace. Thus, it was natural to use gas phase Raman spectroscopy to study these interesting anharmonic vibrations.

While the fundamentals of these large amplitude vibrations often yield broad, weak band contours in the gas phase Raman spectrum, if allowed at all, these overtones are of the proper symmetry to yield the desired Q branches. And by their very anharmonicity -- both electrical and mechanical -- these vibrational overtones are allowed and have sufficient intensity to be observed, even when the fundamentals may not be observable. Thus, gas phase Raman spectroscopy offers another method of directly observing anharmonic vibrations and has its own set of advantages and disadvantages as an adjunct to other techniques or as the primary technique for studying these large amplitude vibrations.

LOW FREQUENCY RING MODES

For a ring molecule containing n atoms in the ring itself, there are $n - 3$ out-of-plane ring bending vibrations. These vibrations are low frequency and large amplitude in nature and are derived from a strongly anharmonic potential function. When $n = 4$, as in four-membered rings, the one ring bending vibration resembles a "puckering" of the ring framework and has led to the general term "ring puckering mode".

It has been found (ref. 1) that cyclobutane and other four-membered rings of the formula $(CH_2)_3X$ where X = O, S, SiH_2, etc. have ring puckering motions which can be fit to a double minimum potential function. Since the ring can be bent either "above" the planar configuration, or "below" it, this means that there are two equivalent wells in the potential function, one on either side of the planar configuration, with a barrier to interconversion between the two forms. A potential function of the form $V(x) = Ax^4 - Bx^2$ describes this behavior, and barriers to attaining the planar configuration in $(CH_2)_3X$ molecules range from 5 to 510 cm^{-1} (refs. 2-5). For some of these molecules the vibrational ground state is above the barrier and these molecules are planar whereas others are permanently bent in the ground state. Studies of these types of compounds have been reviewed in the previous article by Professor Jaan Laane.

When there is no longer a symmetry plane in the planar configuration, the potential function becomes asymmetric and terms in x^3 have to be added. This leads to two possibilities. Two wells could exist with different energies (corresponding to two stable conformers) or there could be just one well (corresponding to only one stable form). These types of potential functions are found for substituted cyclobutanes and bicyclic ring molecules, where preferred conformations exist.

The use of Raman spectroscopy as a means of investigating the ring-puckering vibration in the gas phase of four-membered ring molecules having the general formula $(CH_2)_3X$ (where X = CH_2, S, O, SiH_2) is well documented (ref. 6). These earlier studies allowed for the determination of unexpected selection rules governing the observed intensities for the ring puckering vibration in the Raman spectrum of the gas phase. The development of these rules facilitated the assignment of the ring puckering vibration for many monosubstituted cyclobutane compounds. For this class of molecules where the substituent is either a single atom such as a halogen or a symmetric rotor such as a methyl group, the inversion of the ring can lead to two distinct conformational isomers, i.e., axial and equatorial orientations of the substituent to the ring. Such a substitution results in the observed frequency for the ring puckering vibration being particularly sensitive to the conformational equilibrium. An analysis of the observed ring puckering transitions, therefore, provides considerable information with regard to the equilibrium. Gas phase Raman spectroscopy, as compared to other means of investigating the ring puckering vibration, has been shown to be particularly suited to the investigation of this motion for monosubstituted cyclobutyl compounds. The reason for this lies not only in the contribution to the observed intensity of the $\Delta v = 2$ transitions from electrical anharmonicity but also from symmetry considerations. Regardless of the orientation of the ring (provided it is non-planar), or the substituent (provided the substituent is either a symmetric rotor or a single atom) the molecule belongs to the C_s point group with the ring puckering vibration falling into the A' symmetry block. Consequently, the fundamental ($\Delta v = 1$) transitions are not only Raman allowed, but will appear as sharp Q branch lines which facilitates the determination of the band centers.

From Raman spectra of the gas phase we have successfully determined the potential functions governing the ring puckering vibrations for the halocyclobutanes (refs. 7,8). These studies are consistent with the determination that the equatorial conformer is energetically favored over the axial form and that the energy difference between the two forms is relatively large (>1 kcal/mol). This result is in agreement with a recently reported _ab_ _initio_ study (ref. 9) where it has been determined that the equatorial conformation is preferred for both fluoro- and chlorocyclobutane with the energy difference between this form and the axial conformation being calculated to be 3.1 and 1.0 kcal/mol, respectively.

Additional _ab_ _initio_ studies (ref. 10) performed for cyclobutanol, cyclobutylamine and methylcyclobutane allowed for the conclusion to be drawn that the energy difference between the axial and equatorial conformers for a given monosubstituted cyclobutane compound is dependent on the electronegativity of the substituent. The calculated energy differences are consistent with the axial conformer becoming increasingly more stable in the series F < OH < NH_2 < Cl < CH_3 < Li.

Prior to the publication of these results we had investigated the low frequency Raman spectrum of methylcyclobutane in the gas phase (ref. 8). The data were interpreted to indicate that the molecule is permanently puckered in either the axial or equatorial conformation with a barrier to ring inversion of 700-900 cm^{-1}. However, with the assignment of only three puckering transitions, no attempt was made to obtain the potential function governing the ring puckering motion. Additionally, no investigation was carried out of other portions of the spectrum to determine whether a second conformer was present. In light of the results obtained from the _ab_ _initio_ investigation (ref. 10), where the energy difference between the axial and equatorial conformers of methylcyclobutane was determined to be 140 cm^{-1} (0.4 kcal/mol), it was clear that a reinvestigation of the conformational equilibrium present in this molecule was warranted. Similarly, because the electronegativity of the silyl group should be only marginally different from that of the methyl group, one expects to find a significant amount of axial conformer present in the fluid states of cyclobutylsilane at ambient temperature. Additional evidence to support such an equilibrium for cyclobutylsilane could be found from a combined electron diffraction and _ab_ _initio_ study (ref. 11) where energy differences of 191 and 100 cal/mol were determined from these methods, respectively. Therefore, we have chosen our recently published results obtained for methylcyclobutane (ref. 12) and cyclobutylsilane (ref. 13) to illustrate the use of gas phase Raman spectroscopy as a means of obtaining information with regard to the potential function governing ring inversion and the conformational analysis of four-membered ring compounds. These results are to be compared in a forthcoming publication with similar data obtained for cyclobutylgermane.

Methylcyclobutane

The Raman spectra of gaseous methylcyclobutane and methyl-d_3-cyclobutane in the region expected for the ring puckering mode are shown in Figs. 1A and B, respectively. In the spectrum of the "light" compound (Fig. 1A), well defined Q branches are observed at 161, 147.5 and 132 cm^{-1} with additional shoulders and weaker lines at 165, 154, 139.5 and 125 cm^{-1}. Similar lines at slightly lower frequencies are also observed for the d_3 compound (Fig. 1B). The three pronounced Q branches appear to form a reasonable series and are assigned as the first three transitions of the ring puckering mode for the more stable

equatorial conformer. The assignment of the other observed Raman lines is much more difficult and several alternatives were considered. The assignment given in Table 1 is based on the intensity expectations which govern the relative intensities of the various possible transitions for an asymmetric double-minimum potential function for ring inversions (refs. 14,15). This assignment, although not completely definitive, enabled the determination of the potential function shown in Fig. 2. This potential not only adequately reproduces the observed spectra but also gives reasonable puckering angles and a value of the energy difference between the equatorial and axial forms which is consistent with the experimentally determined value of 295 ± 75 cm^{-1} (ref. 12).

Cyclobutylsilane

The low frequency Raman spectrum of cyclobutylsilane in the vapor state is shown in Fig. 3. It is essential to the correct analysis of these transitions to have knowledge of whether or not a second conformation is present. From a detailed investigation of the Raman spectrum in the gas phase, as well as the corresponding spectra of the liquid and solid phases, it was determined that a significant amount of the axial conformer is present. Furthermore, from a variable temperature study of a "conformer pair" of Raman lines observed in the gas phase, the energy difference was determined to be 147 ± 50 cm^{-1} (420 cal/mol). The strong lines occurring at 287 and 257 cm^{-1} are assigned to the A' ring-SiH$_3$ bend of the equatorial and axial conformers, respectively. Relative intensity measurements between these lines and the weaker shoulders occurring at 274 and 246 cm^{-1} indicate that the shoulders are "hot bands" arising from the SiH$_3$ torsion or the ring puckering vibration
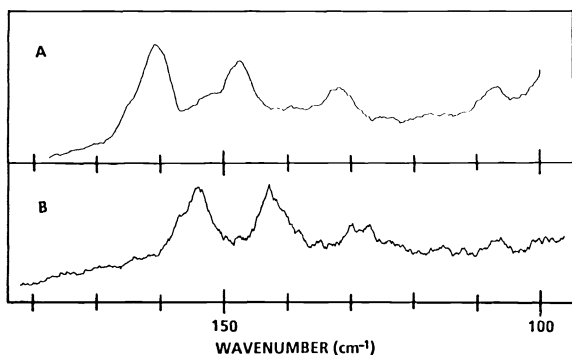

Fig. 1. Raman spectra of gaseous methylcyclo-
butane (A) and methyl-d$_3$-cyclobutane (B).
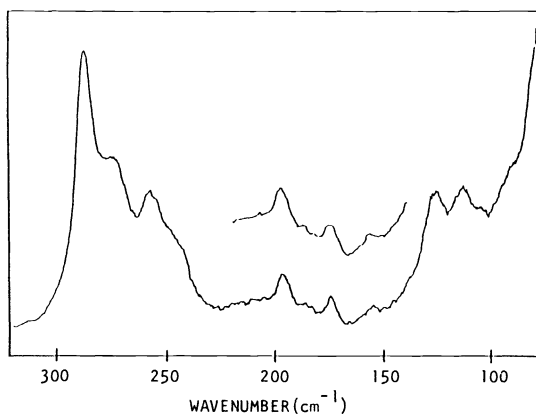Used by permission (ref. 8).

Fig. 3. Low frequency Raman spectrum of gaseous cyclobutylsilane, SBW = 5.5 cm^{-1}. Upper trace was collected with SBW = 6.5 cm^{-1}. Used by permission (ref. 13).
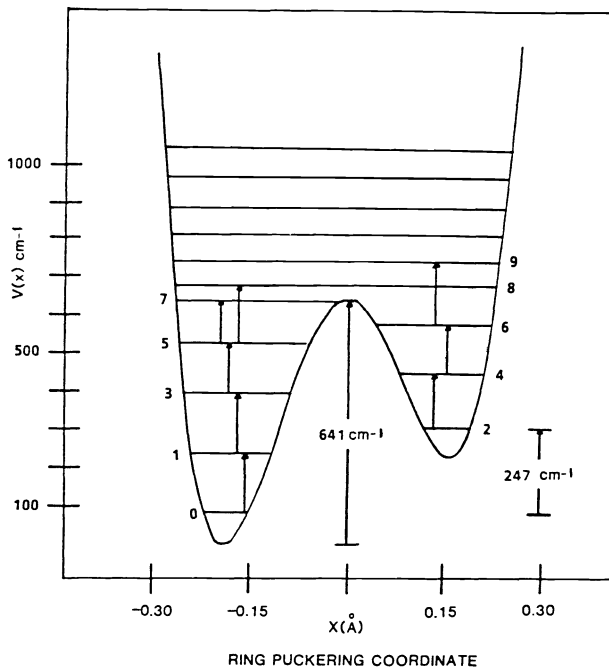

RING PUCKERING COORDINATE

Fig. 2. Potential function for the ring inversion of methylcyclobutane obtained with an assumed reduced mass of 160 amu.
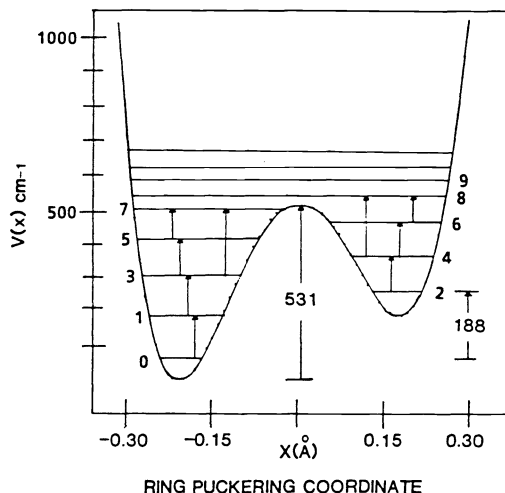Used by permission (ref. 8).

RING PUCKERING COORDINATE

Fig. 4. Potential function governing the ring puckering vibration of cyclobutyl-silane. $V(X) = (3.13 \pm 0.09) \times 10^5 X^4 + (1.36 \pm 0.04) \times 10^4 X^3 - (2.30 \pm 0.08) \times 10^4 X^2$ with a reduced mass of 198 amu.
Used by permission (ref. 13).

of each conformer. Analysis of combination band spectra arising in the 2300-2000 cm^{-1} region of the infrared spectrum in the vapor phase gives frequencies for the SiH$_3$ torsional fundamental of 124 and 139 cm^{-1} for the equatorial and axial conformers, respectively. The assignment of the SiH$_3$ torsion is significant to the analysis of the Q branches observed in the Raman spectrum of the vapor phase below 200 cm^{-1}. The reason for this is that it necessitates that all of the features observed in this frequency region arise from the ring puckering fundamental and not from $\Delta v = 2$ transitions of the SiH$_3$ torsional mode which, if in this region, would give rise to features similar in appearance. The irregular spacings and intensities, coupled with the existence of two conformers in the vapor phase, clearly suggests that the ring puckering motion in cyclobutylsilane should be characterized by an asymmetric double-minimum potential. Having determined the shape of the potential and knowing the energy difference between the two conformations, an assignment to the vapor phase Raman spectrum below 200 cm^{-1} can be made. One such assignment of the ring puckering transitions is listed in Table 2 and the corresponding potential function is shown in Fig. 4. This potential function yields puckering angles of 21.3 and 17.8° for the equatorial and axial forms, respectively. Although these values are at some variance with the angles of 32° (equatorial) and 23° (axial) determined from the electron diffraction data (ref. 11), they agree well with those calculated (ref. 11) from a mixed, extended basis set (21.8 (equatorial) and 20.3° (axial)).

TABLE 1. Observed and calculated frequencies (cm^{-1}) for the ring puckering vibration of methylcyclobutane (ref. 12)

Transition	observed	calculated[a]	obs-calc	Weight	Rel.Int. obs	calc
Equatorial
3 ← 0	306	(308.7)[b]				
1 ← 0	161	160.0	1.0	1.0	1.0	1.0
3 ← 1	147.5	148.8	-1.3	1.0	0.7	0.9
5 ← 3	132	133.9	-1.9	1.0	0.4	0.5
7 ← 5	107	109.8	-2.8	1.0	0.2	0.3
8 ← 5	165	163.1	1.9	1.0	0.1	0.1
Axial
4 ← 2	139.5	140.9	-1.4	1.0	0.1	0.3
6 ← 4	125	121.3	3.7	1.0	0.1	0.2
8 ← 6	107	(103.1)[b]	---	---	---	0.3
9 ← 6	154	153.8	0.2	1.0	0.1	0.1

[a]Calculated using a potential of the form $V(X) = (4.78 \pm 0.10) \times 10^5 X^4 - (3.08 \pm 0.04) \times 10^4 X^2 + (2.18 \pm 0.10) \times 10^4 X^3$ with a reduced mass of 160 amu. The barrier height was found to be 641 cm^{-1} (1.83 kcal/mol) and the ΔH was 247 cm^{-1} (706 cal/mol).

[b]Not used in the frequency fit.

TABLE 2. Observed and calculated frequencies (cm^{-1}) for the ring puckering vibration in cyclobutylsilane

Transition	obs[a]	calc[b]	Δ[c]	weight	calc. rel. int.
Equatorial
1 ← 0	126(124.8)	124.1	0.7	1.0	1.0
3 ← 1	113(116.0)	116.2	-0.2	1.0	1.0
5 ← 3	105(104.4)	106.2	-1.8	1.0	0.8
7 ← 5	90(91.4)	90.7	0.7	1.0	0.5
7 ← 3	197	196.8	0.2	1.0	
Axial
4 ← 2	113(112.1)	111.1	1.1	1.0	0.4
6 ← 4	98(97.7)	98.9	-1.1	1.0	0.4
8 ← 6	(78.8)	78.3	0.5	1.0	0.2
8 ← 4	177	177.2	-0.2	1.0	

[a]Frequencies given in parentheses are taken from the infrared spectrum of the gas whereas all other observed frequencies are taken from the Raman spectrum of the gas (ref. 13).

[b]Calculated by using a potential of the form $V(X) = (3.13 \pm 0.09) \times 10^5 X^4 + (1.36 \pm 0.04) \times 10^4 X^3 - (2.30 \pm 0.08) \times 10^4 X^2$ with a reduced mass of 198 amu. The barrier height was found to be 531 cm^{-1} and the ΔH is 188 cm^{-1} (538 cal/mol).

[c]Δ = obs - calc.

TABLE 3. Coefficients of the quartic, quadratic, and cubic terms[a] of the
potential function in the form $V = AZ^4 + ABZ^2 + ACZ^3$ for several
molecules[b]

Molecule	A	AB	AC	Reference
Cyclobutane	26	-232	--	17
Cyclobutylfluoride	17	-118	45	8
Cyclobutylchloride	16	-106	44	18
Cyclobutylbromide	19	298	119	18
Cyclobutylcyanide	19	288	122	18
Cyclobutanol	18	-255	4	19
Cyclobutylamine	17	-120	50	20
Cyclobutylsilane	13	-149	7	13
Methylcyclobutane	18	-186	10	12

[a]For several of the above investigations more than one possible potential has been reported
within the same publication. We have taken those coefficients from the potential for which
the authors had the most confidence.

[b]Coefficients as taken from the potential functions in the reduced form as given in
ref. 16.

Based on these recent studies of methylcyclobutane and cyclobutylsilane, it is interesting
to compare the results with other monosubstituted four-membered rings. In Table 3 a
comparison of the quartic term in the potential functions of a number of four-membered
rings is given, which should reflect the degree of "strain" in these rings.

Five-membered rings

Five-membered rings have two out-of-plane ring bending vibrations. In the limiting case of
cyclopentane, these two ring motions are actually degenerate. However, in the case of
five-membered rings with a double bond incorporated into the ring framework, one of these
ring bending modes, a twisting about the double bond, is considerably higher in frequency
than the other out-of-plane motion and the lower frequency vibration can be treated as a
ring puckering vibration of a pseudo four-membered ring, since the double bond will act as
a single unit. This results because it would require more energy to cause a twisting about
the double bond than that required to excite the puckering motion. As in the case of
$(CH_2)_3X$ molecules, five-membered ring molecules can be either planar or bent in the ground
state. Bicyclic ring compounds including five-membered rings can be treated as pseudo
four-membered rings also, since the second ring serves to make that bond in the ring rigid,
as in the case of a double bond. But in this case, cubic terms must also be added to the
potential function (ref. 21) since there is a preferred conformation -- the boat form --
and the two wells in the potential function are once again nonequivalent.

For saturated five-membered rings, the two out-of-plane ring modes have to be treated in a
two-dimensional fashion (refs. 4,22). These two motions can be thought of as a puckering
motion of the ring and a wave travelling around the ring representing the phase of the
puckering as it rotates around the ring. This gives rise to the term pseudorotation to
describe this motion. For cyclopentane, there is no barrier hindering the pseudorotational
motion around the ring, but for cyclopentane derivatives with heteroatoms in the ring,
barriers to pseudorotation range from 0.1 to 5.9 kcal/mol (ref. 4). This topic has been
thoroughly reviewed in the previous article but it should be noted that Raman spectroscopy
is the only reasonable method for obtaining frequencies for the higher frequency twisting
modes for many of these five-membered rings (refs. 23-25).

SYMMETRIC ROTORS

Torsional oscillations, or internal rotations, involve the twisting about a bond of one
part of the molecule (the top or internal rotor) with respect to the rest of the molecule
(the frame). Barriers hindering this type of molecular motion range from several tens of
kilocalories per mole for internal rotation about double bonds or bonds with partial
double-bond character, to a few kilocalories per mole or less for torsions about single
bonds.

Types of internal rotors fall into two categories -- symmetric tops and asymmetric tops.
For symmetric tops, a rotation about the top-frame bond of $2\pi/n$ (where n is an integer)
will bring the top to a position symmetrically equivalent to, or indistinguishable from,
the original configuration. It is, thus, possible to speak of the foldness of the top in

terms of n. For example, a methyl (CH_3) group is a threefold symmetric top (with local C_{3v} symmetry) since a rotation about the carbon-to-frame bond of 120° will result in an orientation completely superimposable upon the initial orientation. Twofold tops include phenyl, $-NO_2$, and $-BF_2$ groups (of local C_{2v} symmetry). When a rotation of 360° (i.e., when n = 1) is the only operation that results in a symmetrically equivalent position for the top, it is known as an asymmetric rotor. Examples of asymmetric tops include amino ($-NH_2$), phosphino ($-PH_2$), alcohol ($-OH$), and thiol ($-SH$) groups, when they are bonded to an asymmetric frame. In the case of a symmetric frame, the top with the highest degree of symmetry prevails, and when two tops of different foldness are bonded directly to one another, the resultant foldness is the product of the two individual tops' foldness. For instance, CH_3BF_2 would be classified as a sixfold internal rotor while ethane, CH_3CH_3, would be threefold.

The foldness of the internal rotor relates directly to the potential function governing the torsional oscillation. A threefold rotor implies that there are three symmetrically equivalent positions of minimum energy between 0 and 2π. Thus, a potential function which has three minima in this range is dictated in this case. Similarly, CH_3BF_2, being a sixfold rotor, would require a potential function with six minima.

Previously, the best information available on barriers to internal rotation was derived from either microwave spectroscopy (via the splitting technique) or by direct observation of the torsional fundamentals in the far infrared. This list now includes the technique of gas phase Raman spectroscopy in which either the overtones of the torsion or its fundamentals are observed.

We have presented numerous publications illustrating the use of Raman spectroscopy in the gas phase as a means of investigating internal rotation, and we have shown that, in some cases, this technique may be the only available means for such an investigation. For example, when the torsional modes of a given molecule give rise to infrared bands of poor contour and an assignment of the microwave spectrum has not been possible (a situation which frequently arises for a number of reasons), there are few additional sources of data which give a sufficient amount of information about the torsional mode to warrant their use solely for this purpose. Gas phase Raman spectroscopy is, however, not without its limitations as a tool for determining torsional barriers. One such limitation is the need for a sufficient vapor pressure to allow for enough scattering molecules in the focused beam to produce a detectable signal. Another frequently encountered problem is the presence of other fundamental vibrations in the region of the $\Delta v = 2$ transitions of the torsional motion. This latter problem can have severe consequences as it is the availability of the $\Delta v = 2$ transitions from the Raman spectrum of the gas phase which have been shown to provide some of the most useful and reliable torsional data. Before giving a few examples we will briefly review the theory needed to calculate the torsional barriers from the experimental data.

The potential function governing torsional oscillations has the form

$$2V = \sum_n V_n (1 - \cos n\phi),$$

where ϕ is the torsional angle and V_n's are the potential constants. For symmetric rotors only certain values of V_n will be allowed. For example, the potential function for a methyl rotor (C_{3v} symmetry) would only contain terms in V_3, V_6, V_9, and so forth. A twofold symmetric top would have only even terms in the potential function. Asymmetric rotors will have all terms allowed but, in general, only terms with $n \leq 6$ will be significant.

Using this potential function, the Hamiltonian for internal rotation can be formulated:

$$H = H_r + F(p - P)^2 + \tfrac{1}{2} \sum_n V_n (1 - \cos n\phi),$$

where H_r is the rigid rotor Hamiltonian, $F = h^2/2I_r$, I_r is the reduced moment of inertia for internal rotation, and $(p - P)$ is the relative angular momentum of the internal rotor and the frame. For symmetric tops, F will be a constant, but for asymmetric tops, I_r changes with torsional angle so F is also a function of ϕ, and is usually written,

$$F(\phi) = F_0 + F_1 \cos \phi + F_2 \cos 2\phi + \ldots,$$

where usually less than six values of F_i are needed to fit $F(\phi)$.

For symmetric tops, the wells in the potential function are all equivalent and occur every $2\pi/n$. Since the wells are equivalent, energy levels within each well will be n-fold degenerate as a result of quantum mechanical tunneling. In this case, the energy levels are split into an A component and a doubly degenerate E component. As the energy levels approach the top of the barrier, the splitting between A and E levels increases. This leads to different possible frequencies for A ← A, E ← A, and E ← E transitions. In some
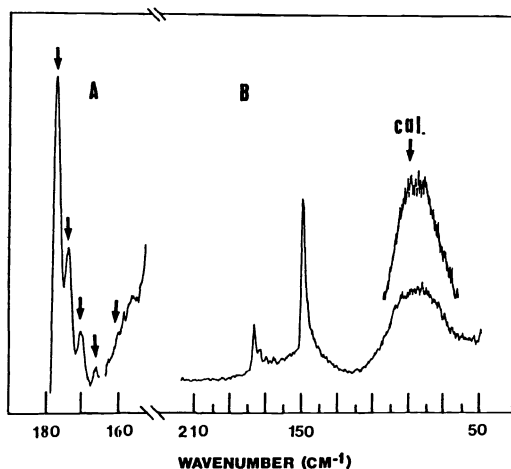
Fig. 5. Raman spectrum of gaseous phase CF_3CH_2Br using 3.5 cm-¹ SBW. Used by permission (ref. 27).
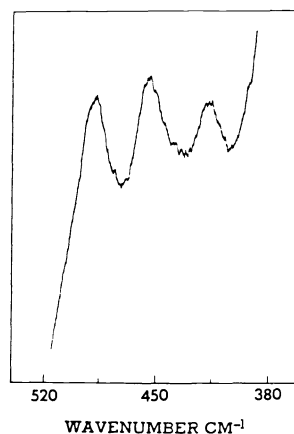

WAVENUMBER CM⁻¹

Fig. 6. Raman torsional overtones of ethyl chloride, recorded at room temperature with 5 cm-¹ spectral slitwidth. Used by permission (ref. 28).

cases, the barrier to internal rotation is low enough so that energy levels near the top of the barrier are populated and A-E splittings may be resolved in the vibrational spectrum.

For molecules which contain two symmetric tops, such as the presently examined 1-halo-2-methylpropane series, it has been shown (ref. 26 and references therein) that the potential function governing internal rotation of the CH_3 moieties is best described as a function of both coordinates. Assuming two coupled rotors, the internal Hamiltonian can be written as:

$$H = (\tfrac{1}{2})(g^{44}\hat{p}_0^2 + 2g^{45}\hat{p}_0\hat{p}_1 + g^{55}\hat{p}_1^2) + V(\tau_0,\tau_1).$$

The potential term in the above expression, $V(\tau_0,\tau_1)$, has the standard form:

$$2V(\tau_0,\tau_1) = V_{30}(1 - \cos 3\tau_0) + V_{03}(1 - \cos 3\tau_1) + V_{33}(\cos 3\tau_0 \cos 3\tau_1 - 1)$$

$$+ V'_{33} \sin 3\tau_0 \sin 3\tau_1 + V''_{33} \sin 3\tau_0 \cos 3\tau_1 + V'''_{33} \cos 3\tau_0 \sin 3\tau_1.$$

For the <u>trans</u> conformer of the 1-halo-2-methyl propane series, $V''_{33} = -V'''_{33}$, and we have neglected the V_{60} and V_{06} terms.

The Raman spectrum of gaseous CF_3CH_2Br in the region from 50 to 210 cm-¹ is shown in Fig. 5. Whereas the fundamental leads to a very broad Raman line with an ill-defined center, the overtone region has four well defined lines at 176.5, 173.0, 170.1 and 165.9 cm-¹ which have been assigned as the 2 ← 0, 3 ← 1, 4 ← 2 and 5 ← 3 transitions, respectively. From these data the barrier to internal rotation was calculated to have a value of 4.39 ± 0.07 kcal/mol and a V_6 term of 103 ± 25 cal/mol (ref. 27). Clearly, if these transitions had been obscured by the presence of an additional fundamental their assignment may or may not have been possible. It is significant to note the relative intensity of the 2 ← 0 transition to the successive double jumps which are more intense than would be expected from the Boltzmann factor. Such an intensity distribution has been shown (refs. 27-29) to arise primarily from the large electrical anharmonicity $\partial^2\alpha/\partial Q^2$ present in the higher vibrationally excited torsional states. In ethyl chloride (ref. 28), for example, the 3 ← 1 transition (488 cm-¹) is of even greater intensity than the 2 ← 0 transition (455 cm-¹) (see Fig. 6).

From these data it is clear that several advantages over infrared spectroscopy are apparent. No special instrumentation (e.g. far infrared) is required -- the low frequency Raman spectrum is as easy to obtain as any other portion of the Raman spectrum. In particular, when torsional overtones are observed, they are even further shifted away from the exciting line than the fundamentals, so that any possible interference from the Rayleigh scattering is minimized. Quite often torsional fundamentals are extremely weak in the infrared owing to an insignificant dipole moment change, or they may give rise to band contours containing no Q branches from which reliable frequencies may be obtained. In the Raman spectrum, both mechanical and electrical anharmonicity allow the torsional overtones to be active and also give them sufficient intensity to be frequently observed. Since the overtones (or in some cases, the fundamentals) are totally symmetric, only isotropic polarizability terms can exist and will lead to stronger Q branches than for anisotropic fundamentals. From these sharp Q branches, frequencies can be easily extracted. Finally, since $\Delta v = 2$ transitions are usually studied, the frequency spacing between peaks in a Raman torsional overtone series is approximately twice that in the infrared, where $\Delta v = 1$ selection rules are obeyed, and therefore resolution rarely presents a problem in the Raman spectrum.

ASYMMETRIC ROTORS

In general, for asymmetric rotors the wells are no longer symmetrically equivalent. However, for a molecule like 3-fluoropropene (allyl fluoride), the fluorine atom can align itself <u>cis</u> to the double bond or in either of the two equivalent <u>gauche</u> conformations. This equivalency of the two <u>gauche</u> forms makes energy levels doubly degenerate in the <u>gauche</u> wells while those in the <u>cis</u> well are nondegenerate. Depending on the relative magnitudes of the V_n terms, the various wells in the potential function of asymmetric rotors may be of different relative energies. This leads to the possibility of one conformer being more stable than other possible conformers. In a later section, the torsional potential function for 3-fluoropropene is discussed.

The utility of Raman spectral data from the gas phase for conformational analyses has its origins in situations where the corresponding infrared data are not completely definitive. An infrared band may not be observed at all due to a variety of reasons among which is a small absorption coefficient. A more typical problem arises as a result of the overlapping of "conformer peaks" or closely lying fundamentals in the infrared spectrum of the gas phase. For the determination of the thermodynamically preferred conformation, as well as the energy difference between this rotamer and other conformations, it is not only necessary to observe spectral features arising from each conformation but such spectral features need to be sufficiently spaced to allow for their complete analysis. Oftentimes a "conformer pair" observed in the infrared spectrum of the vapor is so extensively overlapped that the respective contours become distorted and it is difficult to ascertain the fundamental frequency for each form. If this fundamental is a totally symmetric vibration (for example, one which belongs to the A' symmetry block of a conformation of C_s symmetry) then this fundamental should give rise to a sharp, easily resolvable, Q branch in the Raman spectrum of the vapor. If this conformation is in equilibrium with a rotamer of C_1 symmetry then a pair of Q branches is typically observed. The "sharpness" of such Q branches makes a pair of "conformer peaks" lying as close as 10 cm^{-1} commonly resolved in the Raman spectrum of the vapor whereas the corresponding infrared spectrum is virtually useless. The ramifications of such resolution are obvious. This pair of Q branches lends itself to variable temperature studies from which not only the thermodynamically preferred conformation can frequently be inferred but also these data allow for the determination of the energy difference between this form and the high energy conformation.

Another frequently encountered situation is one in which a "conformer pair" of infrared bands is clearly resolved; however, the contour of one or both of these bands is such that little more than the fundamental frequency can be obtained. For example, if the out-of-plane axis, for a molecule which is C_s in symmetry, is the b-principal axis then the asymmetric torsion (A") for such a molecule will give rise to a B-type band in the infrared spectrum of the vapor phase. Torsionally excited states ($\Delta v = 1$), needed to accurately define the asymmetric potential function, are typically observed to be so extensively overlapped with the fundamental that a determination of their frequencies is not possible. For such a situation the $\Delta v = 2$ transitions should be observed in the infrared spectrum as A/C hybrid contour bands, thereby giving rise to Q branches and frequencies which are obtainable. However, these transitions are usually very weak and, in order to confidently assign them, the corresponding transitions from the Raman spectrum of the vapor, which are now Q branches themselves for $\Delta v = 2$ transitions, are required.

Similarly, for the <u>gauche</u> conformer belonging to the C_1 point group, the fundamental vibrations are expected to give rise to A/B/C hybrid type band contours in the infrared spectrum of the vapor phase. Depending on the degree of "pure" A-, B- or C-type present in the hybrid the fundamental and torsionally excited states may or may not be observed in the infrared spectrum of the vapor. For such a conformation the fundamental vibrations are totally symmetric and should thus give rise to readily assignable Q branches in the Raman spectrum of the vapor.

As an example of the use of Raman spectroscopy in the vapor phase for conformational analysis purposes, we have chosen our results obtained for 3-fluoropropene. Both the infrared and Raman spectra obtained for the vapor phase classically illustrate the combined use of such data for obtaining information regarding the conformational equilibrium existing in this molecule.

3-Fluoropropene

The far infrared and Raman spectra of gaseous 3-fluoropropene (allyl fluoride) in the region of the asymmetric torsional vibration are shown in Fig. 7A and B, respectively. From a microwave investigation (ref. 30) rotational lines were assigned as belonging to two separate conformations and the determined moments of inertia were found to be consistent with one conformer which has the fluorine atom <u>cis</u> to the double bond, giving this rotamer C_s symmetry, and another in which the fluorine atom is rotated out of the plane by 127° giving this conformer a <u>gauche</u> structure and C_1 symmetry. From variable temperature studies and <u>gauche</u>/<u>gauche</u> splittings observed in the microwave spectrum, a subsequent study (ref. 31) approximated the potential function which governs the internal rotation of the CH_2F moiety. The reported (ref. 31) uncertainty in the frequencies of the <u>gauche</u> transitions along with the accompanying uncertainty of the determined potential function
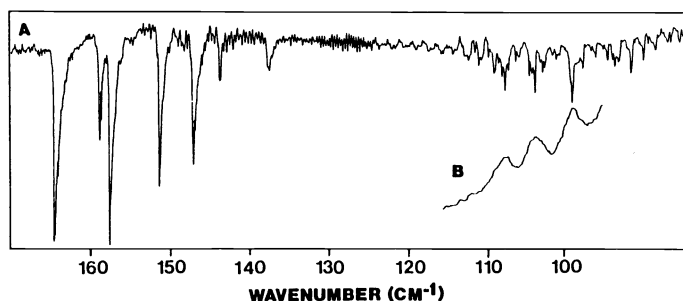
Fig. 7. Far infrared spectra of gaseous 3-fluoropropene (A)
between 170 and 80 cm^{-1} taken at 0.125 cm^{-1} resolution;
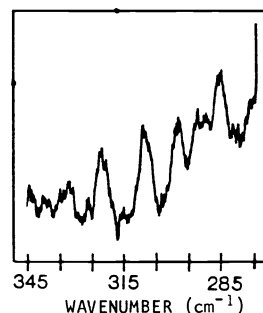(B) Raman spectrum of vapor. Used by permission (ref. 32).

Fig. 8. Two quantum transitions
observed in the Raman spectrum
of gaseous 3-fluoropropene.
Used by permission (ref. 32).

and reported value of ΔE were the principal reasons why we undertook our study. Because
the c-principal axis is perpendicular to the symmetry plane for the more stable cis
conformation the strong Q branches (beginning at 164 cm^{-1}) observed in the far infrared
spectrum (Fig. 7A) can readily be assigned as the asymmetric torsion of this rotamer;
however, the complexity of the spectrum below 120 cm^{-1} necessitated the collection of
additional data in order to identify the fundamental and associated "hot bands" of the
gauche conformer. Because the asymmetric torsion is an A" mode for the cis conformer only
a broad non-descript feature was observed in the Raman spectrum of the vapor for this
fundamental; however, the overtone region produced a very clear series of Q-branches at
323, 309, 299, 291 and 284 cm^{-1} (Fig. 8). These features could be used to verify the
assignment of the far infrared spectrum. All of the fundamentals arising from the gauche
conformer, being C_1 in symmetry, are expected to give rise to Q branches in the Raman
spectrum of the vapor. It is clear from Fig. 7 that the asymmetric torsion and associated
"hot-bands" are readily observable in the Raman spectrum of the vapor at 108, 104 and 99
cm^{-1}. The observation of these lines significantly facilitated the assignment of the far
infrared spectrum in this region.

In order to be able to characterize the asymmetric potential function, a value for the
approximate relative enthalpy difference between the high and low energy conformers is
needed since this is one of the constraints defining the potential function. The previous
investigation (ref. 31) reported the value of ΔH to be 166 ± 67 cal/mol; however, with such
a large uncertainty the determined potential function could be significantly affected. In
order to obtain a more accurate value for this parameter we carried out variable
temperature experiments of the Raman spectrum of the vapor (see Fig. 9) and concluded that
the lines observed at 920 and 905 cm^{-1} are a "conformer pair" and, based on the
disappearance of the 920 cm^{-1} line in the spectrum of the solid, this line was assigned to
the high energy gauche conformer. It should be mentioned that these two bands were
extensively overlapped in the infrared spectrum of the vapor and, therefore, from these
data it was not possible to perform a variable temperature study. The plot based on the
variable temperature measurements of these Raman lines in the gas phase is shown in Fig. 10
and a value of 263 ± 25 cm^{-1} (752 cal/mol), which is significantly different from that
previously proposed (ref. 31), has been determined from the slope of this line. From these
data and the torsional assignment, potential coefficients of V_2 = 459 ± 29, V_3 = 830 ± 9,
V_4 = 18 ± 8 and V_6 = -37 ± 5 cm^{-1} were obtained (ref. 32). The resulting potential
function (Fig. 11) has an enthalpy difference of 304 ± 20 cm^{-1} which is in reasonable
agreement with that obtained from the variable temperature study. The observed
frequencies, their assignments and fit to the potential function using the above constants
are summarized in Table 4.

Although the Raman data obtained for 3-fluoropropene in the vapor phase appears to serve no
purpose other than for the clarification of the infrared data it is a classic example of
the utility of this type of data. As previously mentioned, the out-of-plane axis for a
molecule which is C_s in symmetry can be the b-principal axis. The asymmetric torsion for
such a molecule would give rise to an infrared band of B-type contour, the minima of which
are difficult to determine. It is clear that the "double jump" data obtained from the
Raman spectrum of the vapor could easily clarify such assignments. Additionally, although
the c-principal axis may be perpendicular to the plane, oftentimes only a broad ill-defined
band will be observed in the infrared spectrum. Such was the case in n-butane (ref. 33)
where the assignment of the asymmetric torsion would not have been possible without the
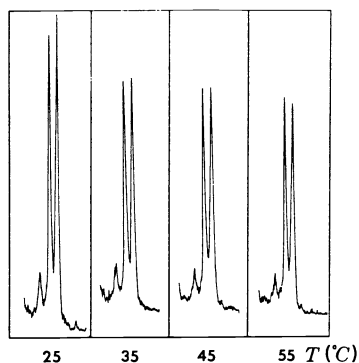data obtained from the Raman spectrum of the vapor.

Fig. 9

Fig. 10

Fig. 9. Representative Raman spectra for the temper-
ature dependence of gaseous 3-fluoropropene.
Used by permission (ref. 32).
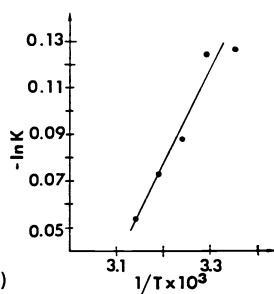
Fig. 10. Temperature dependence of the ratio of cis
to gauche conformers for gaseous 3-fluoropropene.
Used by permission (ref. 32).

TABLE 4. Observed Raman and infrared
frequencies of gaseous 3-fluoropropene
for the asymmetric torsional mode

	Transition[a]	Obs.	Calc.[b]	Δ
cis	2 ← 0	323	322	1.0
	3 ← 1	309	309	0.0
	4 ← 2	299	296	3.0
	5 ← 3	291		
	1 ← 0	164.62	163.88	0.74
	2 ← 1	157.66	158.15	-0.49
	3 ← 2	151.44	151.66	-0.22
	4 ← 3	147.17	142.20	2.97
	5 ← 4	143.75		
gauche	1∓ ← 0±	108.0	108.33	-0.33
	2∓ ← 1±	104.26	104.26	0.00
	3∓ ← 2±	99.62	99.06	-0.56
	4∓ ← 3±	92.10	94.58	-2.48

[a] Two quantum transitions were observed
in the Raman spectrum of the vapor and
frequencies are expected to be accurate
to ±2 cm^{-1}. All remaining transitions
were observed in the far infrared spect-
rum of the gas (ref. 32).

[b] Calculated using a potential function of
the form $V(\theta) = \sum_{i=1}^{6} (V_i/2)(1-\cos i\theta)$,
where $V_2 = 459 \pm 29$, $V_3 = 830 \pm 9$,
$V_4 = 18 \pm 8$, and $V_6 = -37 \pm 5$ cm^{-1}
and the following F series:
$F_0 = 2.6698$, $F_1 = 0.4514$, $F_2 = 0.2385$,
$F_3 = 0.0584$, $F_4 = 0.0184$, $F_5 = 0.0052$
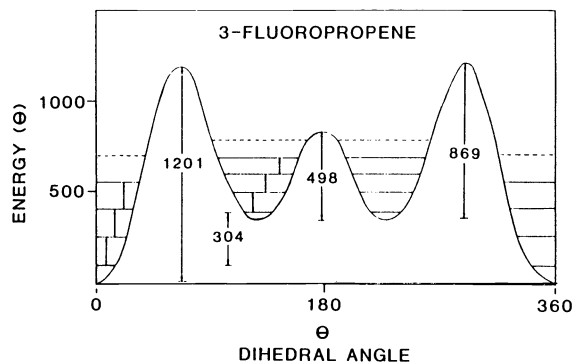and $F_6 = 0.0015$ cm^{-1}.

Fig. 11. Torsional potential function, including
the observed energy levels, for the asymmetric
torsion of 3-fluoropropene. The dihedral angle
of zero corresponds to the cis conformer. Calcu-
lated using the potential coefficients and F ser-
ies given in Table 4. Used by permission (ref.32).

1-Halopropanes

Among the most recent studies which we have carried out, and have used gas phase Raman
spectroscopy as a means of investigating the torsional motions, are a series of
investigations (refs. 34,35) on molecules having the general formula $CH_3CH_2CH_2X$ and
$(CH_3)_2CHCH_2X$ where X = F, Cl, and Br. As with most studies of torsional oscillations in
the gas phase, it has been found for these molecules that it is not solely the Raman or
infrared data which are useful but a combination of the two which provides the needed
information for the torsional analysis. The primary reason for this is that these
molecules exhibit a trans (C_s) ↔ gauche (C_1) conformational equilibrium in the vapor
phase. Consequently, the torsional fundamentals for the gauche conformer give rise to Q
branches in the Raman effect whereas the A" vibrations of the trans form exhibit pure A, B
or C-type contour, depending on the orientation of the principal axes, in the far infrared
spectra of the vapor. Therefore, the torsional frequencies for the gauche conformation are
typically best determined from the Raman data, whereas it is the infrared data which
provide the majority of the torsional data for the trans conformation (provided the
out-of-plane axis is a or c).

It is well established (refs. 36,37) that the 1-halopropanes, $CH_3CH_2CH_2X$, exist in both the
trans and gauche conformations in the fluid phases. As an example of the typical low
frequency Raman data which we have obtained (ref. 34) for the gas phase of these molecules,
that obtained for 1-bromopropane is shown in Fig. 12. The Q branches observed at 198, 193
and 186 cm^{-1} are assigned to the fundamental and first two excited state methyl torsional
transitions for the gauche conformer. These data lead to a barrier height governing
internal rotation of the methyl group of 1093 ± 8 cm^{-1} (3.13 kcal/mol). Similar

transitions were observed in the Raman spectra of the gas phase for the <u>gauche</u> conformers of both the corresponding fluoride and chloride molecules and these data and resulting barrier heights are summarized in Table 5. Note that the transitions for the corresponding motion of the <u>trans</u> conformers have been assigned from the infrared data. Similarly, the transitions arising from the internal rotation of the CH_2Br, or asymmetric top, can be assigned. The strong Q branch observed at 123 cm^{-1} (see Fig. 12) is assigned to the asymmetric torsion of the <u>gauche</u> conformer. Again, the corresponding assignment for the <u>trans</u> conformer can be made from the far infrared spectral data. These results obtained for the asymmetric torsion of the bromide, chloride and fluoride are summarized in Tables 6 and 7.

TABLE 5.   Observed methyl torsional transitions, assignments and internal rotational barriers for the 1-halopropanes (ref. 34)

Conformer	Infrared ν(cm^{-1})	Raman $\Delta\nu$(cm^{-1})	Assignment	Δ	F(cm^{-1})	V_3(cm^{-1})	V_6(cm^{-1})
1-fluoropropane							
trans	213.13		1(A,E)←0(A,E)	0.43	6.147	936 ± 4	--
	195.58		2(A,E)←1(A,E)	-0.45		(2.67 kcal/mol)	
gauche	209.91	210	1(A,E)←0(A,E)	1.12	5.559	986 ± 9	--
	193.15	∿194	2(A,E)←1(A,E)	-0.88		(2.82 kcal/mol)	
1-chloropropane							
trans	213.80		1(A,E)←0(A,E)	-0.14	6.277	929 ± 2	--
	197.55		2E←1E	0.51		(2.66 kcal/mol)	
	197.35		2A←1A	0.55			
gauche	210.60	211	1(A,E)←0(A,E)	-0.14	5.544	1123 ± 2	-43 ± 1
	201.90	202	2(A,E)←1(A,E)	0.21		(3.21 kcal/mol)	(123 cal/mol)
1-bromopropane							
trans	203.7		1(A,E)←0(A,E)		6.345	841	--
						(2.40 kcal/mol)	
gauche	198.15	198	1(A,E)←0(A,E)	0.65	5.573	1093 ± 5	-77 ± 3
	192.50	193	2(A,E)←1(A,E)	-0.94		(3.13 kcal/mol)	(220 cal/mol)
	186.15	186	3(A,E)←2(A,E)	-0.82			

TABLE 6.   Observed and calculated (cm^{-1}) asymmetric torsional transitions for the 1-halopropanes (ref. 34)

Molecule	Conformer	Assignment	Infrared	Raman	Calc.[a]	Δ
1-fluoropropane	trans	1 ← 0	128.88		129.69	-0.81
		2 ← 1	125.74		125.60	0.14
		3 ← 2	122.10		121.22	0.88
		4 ← 3	118.23		116.55	1.68
	gauche	1 ← 0	140.76	140	140.19	0.57
		2 ← 1	136.04		136.54	0.50
1-chloropropane	trans	1 ← 0	119.06		118.46	0.60
		2 ← 1	115.52		116.01	0.25
		3 ← 2	111.50		113.38	-1.88
	gauche	1 ← 0	132.75	133	133.55	0.83
		2 ← 1	130.60		130.62	0.02
		3 ← 2	128.00		127.63	0.37
1-bromopropane	trans	1 ← 0	112.68		113.72	-1.04
		2 ← 1	110.30		110.18	0.12
		3 ← 2	108.03		106.59	1.44
	gauche	1 ← 0	125.13	123	124.36	0.77
		2 ← 1	121.61		121.53	0.09
		3 ← 2	117.53		118.55	-1.02

[a]Calculated using the potential constants from Table 7, and for 1-fluoropropane: F_0=1.82184, F_1=-0.11048, F_2=0.083768, F_3=-0.0193855, F_4=0.0063965, F_5=-0.00182969, and F_6=0.0005553; for 1-chloropropane: F_0=1.361481, F_1=-0.158885, F_2=0.137314, F_3=-0.0403855, F_4=0.0164295, F_5=-0.0059455, and F_6=0.00223375; for 1-bromopropane: F_0=1.1855058, F_1=-0.1740488524, F_2=0.1804645, F_3=-0.05629194, F_4=0.02643425, F_5=-0.0104906, and F_6=0.00443742 cm^{-1}.
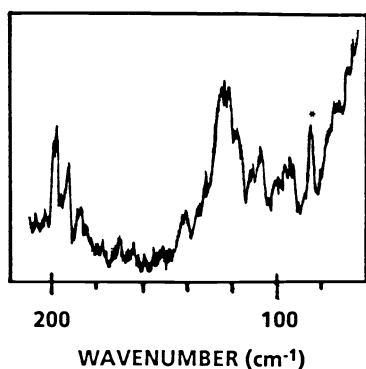
200   100

WAVENUMBER (cm⁻¹)

Fig. 12. Low frequency Raman spectrum
of gaseous 1-bromopropane.

TABLE 7. Potential constants and barriers (cm^{-1}) for the
asymmetric torsions of the 1-halopropanes (ref. 34)

Coefficient[a]	1-fluoropropane	1-chloropropane	1-bromopropane
V_1	77 ± 36	349 ± 26	942 ± 43
V_2	-239 ± 11	-493 ± 13	-844 ± 23
V_3	1280 ± 4	1578 ± 3	1560 ± 7
V_6	-12 ± 2	-47 ± 2	13 ± 3
ΔH	122 ± 10	127 ± 10	37 ± 10
Barriers			
gauche/trans	1245	1430	1190
trans/gauche	1125	1300	1135
gauche/gauche	1485	2060	2540
dihedral angle	117°	115°	112°

[a]Potential coefficients for a potential function of the form

$$V(\theta) = \sum_{i=1}^{6}(V_i/2)(1 - \cos i\theta).$$

1-Halo-2-methylpropanes

An investigation of the low frequency vibrational spectra of this series of molecules (ref. 35) follows the aforementioned investigation of the 1-halopropanes (ref. 34). From the data obtained for the gas phase of the 1-halopropanes it became clear that a combined use of the low frequency Raman and far infrared spectra could allow for a more complete analysis of the torsional oscillations than was previously available (refs. 36,37) It was only natural to assume that the 1-halo-2-methylpropanes (isobutyl halides) would give similar results from which it was hoped that barrier height trends could be established between this series, the 1-halopropanes, and the much earlier work on the 1-haloethanes (refs. 28,38,39).

As an example of the low frequency Raman data obtained for the gas phase of the 1-halo-2-methylpropanes, that obtained for the bromide is shown in Fig. 13. It should be mentioned that the presence of two symmetric tops in this series of molecules, as opposed to one in the 1-halopropanes, necessitates that this torsional motion be analyzed from a combined investigation of data obtained from both Raman and far infrared spectra. Previously shown (ref. 40) to exist in both trans and gauche conformations, the analysis of the symmetric torsional motions of the 1-halo-2-methylpropanes must begin with symmetry considerations.

The A' and A'' methyl torsions for the trans conformation of each isobutyl halide molecule are expected to exhibit A/C hybrid and B-type infrared band contours, respectively. In the Raman effect the A' methyl torsion should produce a polarized line, whereas the line due to the A'' torsional fundamental should be depolarized. Conversely, both methyl torsional fundamentals in the gauche conformer should be observed as polarized lines in the Raman effect, and as A/B/C hybrid bands in the infrared spectrum of the gas. Similarly, the C_s symmetry of the trans isomer requires that the asymmetric torsion be an A'' mode, which, based on the structure of these halides, exhibits B-type band contours in the infrared spectra of the gases and broad depolarized lines in the Raman effect. On the other hand, the asymmetric torsion for the gauche form is expected to give rise to a Q branch in the Raman spectrum of the gas. Utilizing this information, in addition to far infrared spectra obtained for both the gaseous and solid phases, a plausible assignment of the Raman spectra shown in Fig. 13 can be made. Of the Q branch features observed at ∿243 (vw), 205 (vw), 188 (w), 176 (w) and 103 cm⁻¹ (w,bd), only one (176 cm⁻¹ assigned to the A' CCBr bend) is assigned as arising solely from the trans conformer even though it is this conformation which is thermodynamically preferred in the gas phase (refs. 35,38). The weaker intensity of this line, relative to the corresponding fundamental of the gauche conformer at 188 cm⁻¹, can be explained by the double degeneracy of the gauche form; however, it is only through a study of the relative intensity of a pair of conformer lines over several temperatures which confirms the greater stability of the trans form. The Q branch features observed at 245 and 205 cm⁻¹ are assigned to the methyl torsional modes of the gauche conformer while that at 103 cm⁻¹ arises from this rotamer's asymmetric torsion. An assignment of the vibrational spectrum of 1-bromo-2-methylpropane below 250 cm⁻¹ is given in Table 8 and the gas phase data given therein was used to calculate the methyl torsional barriers given in Table 9. The asymmetric torsional potential function is shown in Fig. 14 as determined from the data in Table 10.

TABLE 8.   Observed frequencies[a] (cm^{-1}) below 300 cm^{-1} for 1-bromo-2-methylpropane (ref. 35)

INFRARED				RAMAN						ASSIGNMENT
Gas	Rel. Int.	Solid	Rel. Int.	Gas	Rel.Int. & Depol.	Liquid	Rel.Int. & Depol.	Solid	Rel. Int.	Approximate Description
243 Q	vvw			∿243	vvw			283	vw	methyl torsion
								∿266	vvw	
∿243 R										
240 ctr,B	vvw	(∿253)								methyl torsion (trans)
∿238 P										
204.5 Q	w	∿228	vvw	205	vvw	∿225	vvw	∿242	vvw	methyl torsion
								∿234	vvw	
191 R										
187 Q	mw	193	ms	188	mw,p	192	m,p	196	w	CCBr bend
181 P										
176 Q	mw	(∿186)	sh	176	mw,p	181	mw,p	(∿187)	sh	CCBr bend (trans)
∿169 P										
108 R										
107 ctr,B	mw									asymmetric torsion (trans)
105 P										
102 Q	mw	130	mw	∿103	w			152	vvw	asymmetric torsion
								113	w	
								89	w	
								73	vw	
								∿67	vvw	lattice modes
								46	w	
								41	w	
								32	vw	
								22	vw	

[a]Abbreviations used: v, very; s, strong; m, moderate; w, weak; bd, broad; sh, shoulder; p, polarized; dp, depolarized; A, B, and C refer to infrared gas phase band contours; R, Q, and P refer to rotational-vibrational branches; ctr, center of a B-type band. The assignment has been made on the basis of C_1 symmetry for the more stable gauche conformer. Frequencies in parentheses are taken from the spectra of the unannealed solid.

TABLE 9.   Observed methyl torsional transitions, assignments, and internal rotational barriers in cm^{-1} for the 1-halo-2-methylpropanes (ref. 35)

Conformer	Infrared (cm^{-1})	Raman (cm^{-1})	Assignment	g(cm^{-1})	V_{30}	V_{03}	V'_{33}	V_{eff}[a]
$(CH_3)_2CHCH_2Cl$								
trans	228.8		1,0 ← 0,0	$g^{44} = g^{55} = 10.9046$	1130	1130	-65	1130
	216.1		0,1 ← 0,0	$g^{45} = -0.0627$				
gauche	246.0	245	1,0 ← 0,0	$g^{44} = 11.1646$	1338	1092	-	1215
	218.1		0,1 ← 0,0	$g^{55} = 10.8732$				
				$g^{45} = -0.0494$				
$(CH_3)_2CHCH_2Br$								
trans	240.7		1,0 ← 0,0	$g^{44} = g^{55} = 10.8478$	1141	1141	-203	1141
	204.4	205	0,1 ← 0,0	$g^{45} = -0.0425$				
gauche	243.7	243	1,0 ← 0,0	$g^{44} = 11.1684$	1308	970	-	1139
	228.8		0,2 ← 0,1	$g^{55} = 10.8246$				
	204.4	205	0,1 ← 0,0	$g^{45} = -0.0379$				

[a]$V_{eff} = \frac{1}{2}(V_{30} + V_{03}) - V_{33}$

TABLE 10. Observed and calculated asymmetric torsional transitions, potential
          constants, and barriers (cm^{-1}) for 1-bromo-2-methylpropane (ref. 35)

Conformer	Assignment	Infrared	Raman	Calc.[a]	Δ
trans	1 ← 0	106.70		106.60	0.10
gauche	1 ← 0	103.94	∿103	103.80	0.14
	2 ← 1	102.44		102.44	0.27
	3 ← 2	100.57		100.46	0.11
	4 ← 3	98.43		98.71	-0.28

Potential constants[b]

V_1	-493 ± 16
V_2	595 ± 18
V_3	2006 ± 6
ΔH	44 ± 20

Barriers

gauche/trans	2280
trans/gauche	2325
gauche/gauche	1480
Dihedral angle	124°

[a]Calculated using the potential constants above and F_0 = 0.64152635, F_1 = -0.02514841,
F_2 = -0.06392857, F_3 = -0.00874565, F_4 = 0.00543084, F_5 = 0.00104208 and F_6 = 0.00037444.

[b]The uncertainties are the statistical uncertainties but the actual uncertainties are
probably much larger since the data are not sufficient to give independent values for
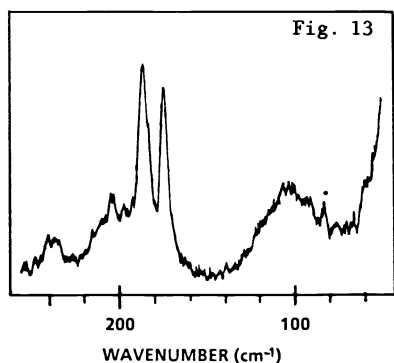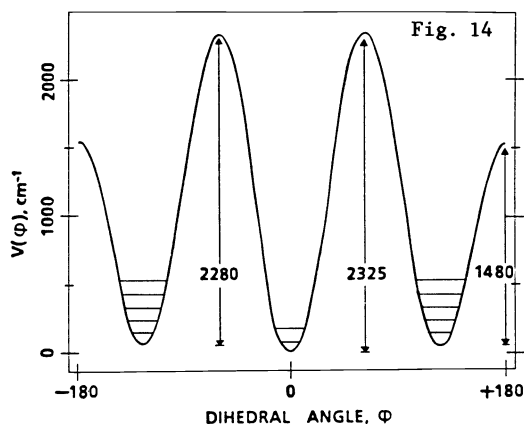the V_1 and V_2 terms.

Fig. 13. Low frequency Raman spectrum of gaseous 1-bromo-2-methylpropane.

Fig. 14. The asymmetric potential function of 1-bromo-2-methylpropane showing
    the energy levels of the observed transitions. The dihedral angle of zero
    corresponds to the low energy trans conformer. Used by permission (ref. 35).

These examples clearly illustrate the utility of gas phase Raman spectral data for
assigning the fundamental frequency for the asymmetric torsion of the gauche conformer. In
fact, not only do the data show the utility, but these examples demonstrate the necessity
of having the Raman data in order to be able to assign the fundamental frequency since the
far infrared gas phase data frequently are not definitive in this respect. For example, in
the case of 1-fluoropropane, there are a series of Q branches beginning at 140.76 cm^{-1} and
falling to lower frequencies. By utilizing the Raman data, it is clear that the first
observed Q branch is due to the gauche and not to the trans conformer. Many additional
examples could be given but it should be clear that, when one of the conformers has a plane
of symmetry, the asymmetric torsion for this conformer will not be active in the Raman
spectrum, whereas the other conformer without any symmetry will usually give rise to a
Raman line. Additionally, it has been shown that the Raman data can be utilized to
determine the frequency of the methyl torsion for the gauche conformer. Again, without
these data, it would not be possible to distinguish the methyl torsional frequencies for
the gauche and trans conformers of the 1-halopropanes. Therefore, the gas phase Raman data
are extremely valuable in correctly assigning the observed far infrared transitions for
molecules which have more than one conformer present in the gaseous state.

SUMMARY

Gas phase Raman spectroscopy can be used to obtain the conformational stability of mono-substituted four-membered rings. Similar data are also frequently needed to determine the twisting frequency of one of these low frequency modes of five-membered rings. The utility of gas phase Raman data for the determination of the internal rotation barrier for many molecules which contain either the CH_3 or CF_3 group has been demonstrated by the observation of the torsional overtones. Additionally, it is sometimes possible to distinguish between the methyl torsional transitions of molecules which have more than one conformer present in the gas phase by the gas phase Raman data. Finally, the utilization of far infrared spectra along with the low frequency Raman data for the gas has been used to otain the barriers to interconversion for several types of organic molecules which have asymmetric rotors. From the examples utilized, it is clear that the Raman data were indispensable in correctly assigning the asymmetric torsional frequencies to the correct conformer. From these results definitive potential surfaces for internal rotation have been obtained for a number of molecules, and barriers to internal rotation for asymmetric rotors have been elucidated.

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