Determination of Molecular Conformation from Large Amplitude Vibrations in Electronic Spectra of Organic Molecules in a Supersonic Jet

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1 Introduction

The more dramatic examples of the double helical conformation of DNA and the science of drug design demonstrate the great importance of molecular conformation in chemistry and biochemistry. At the other end of the scale of molecular size, the discovery that the equilibrium conformation of ethane is eclipsed rather than staggered, and a theoretical understanding of the nature of the energy barrier between equivalent staggered conformations, stimulated comparable investigations of similar molecules such as methyl alcohol and acetaldehyde.

There tends to be some confusion regarding the use of the words 'conformation' and 'structure' in the context of polyatomic molecules. Structure usually refers to quantitative bond lengths and angles, as might be obtained in a microwave spectroscopic or electron diffraction experiment. On the other hand, conformation is usually concerned with more qualitative properties such as planarity or non-planarity, eclipsed or staggered. However, what we may regard as conformational studies are also concerned with energies: for example, how much energy is required to go from the staggered to the eclipsed form of ethane, or from *cis*- to *trans*-1,2-difluoroethylene? They may be concerned also with structural parameters such as the distance out-of-plane of the hydrogen atoms of the NH_2-group in aniline.

So, the confusion remains to some extent and even the Oxford English Dictionary gives one of the meanings of conformation as 'structure'! In this Review, though, I shall be concerned more with molecular conformation, as we understand it generally, than with details of bond lengths and angles.

Carbon suboxide, C_3O_2, is an example of a polyatomic molecule which might be linear, rather than bent, about the central carbon atom. One method of finding out is to identify as many as possible of the vibrational levels of the corresponding bending vibration. These can be fitted to an appropriate potential function and, if the potential shows a minimum at a bending angle of 180°, it is linear. If it is a W-shaped potential, with a symmetrical double minimum, the molecule is bent. In the case of C_3O_2 it is linear but very floppy and easily bent. However, this linear conformation cannot be referred to, strictly, as the equilibrium conformation. It is the equilibrium conformation so far as the bending vibration is concerned but the zero-point conformation so far as all other vibrations are concerned. We must also be careful to appreciate that this bending potential will be affected when other vibrations in the molecule are excited. This is what is generally referred to as anharmonicity, but it is of a rather special kind.

In non-linear polyatomic molecules two particularly important aspects of conformation are (i) whether a molecule is planar, or has a planar skeleton, as in the examples of aniline (1) and 9,10-dihydrophenanthrene (2): (ii) whether a substituent attached to an aromatic ring is coplanar, eclipsed, or staggered with respect to the ring, as in the examples of styrene (3), toluene (4), and 3-aminobenzotrifluoride (5).

2 Experimental and Theoretical Methods

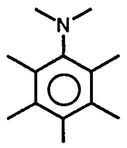
We are all familiar with the general shape of the potential function for a bound diatomic molecule: the Morse potential provides a reasonable approximation. To determine this potential from experimental data requires as many vibrational energy levels as possible to be known – preferably including levels close to the dissociation limit. If the electronic state concerned is the ground state these levels are usually obtained by emission from an excited electronic state. This excited state should have an appreciably different equilibrium bond length so that the Franck–Condon principle results in appreciable intensity of transitions from vibrational levels of the excited state to high-lying levels of the ground state. To determine vibrational levels in an excited electronic state absorption from the ground state may be used and the Frank–Condon principle again relied upon to allow access to high-lying vibrational levels.

In polyatomic molecules the same general methods apply but, particularly in larger molecules, the determination of vibrational potentials is usually confined to the ground singlet state S_0 and the first excited singlet state S_1, for closed shell molecules. For molecules in which spin–orbit coupling is appreciable, investigation of vibrational potentials in the first excited triplet state T_1 may also be possible.

Large polyatomic molecules have many vibrational degrees of freedom, $3N - 6$ where N is the number of atoms, and small rotational constants. This results in crowded, low-lying rotational and vibrational energy levels, which are relatively highly populated at room temperature, and a gas phase absorption spectrum which is increasingly likely to be so congested as to appear almost featureless. For example, although rotational fine structure can be observed in the $S_1 - S_0$ absorption spectrum of (1), (3), and (4) only broad vibrational structure is shown by (2) and (5).

An extremely successful way of getting round the problem of spectral congestion is to seed the molecules into a supersonic jet.[1] If a noble gas, which is often helium, at a pressure of the order of 1 atm is pumped through a small pinhole or slit with a diameter or width of the order of 100 μm into a low pressure chamber the atoms attain an extremely low translational temperature. This may be around 1 K, or less if the backing pressure is higher. When the molecules of interest are seeded into this so-called supersonic jet of helium they are drastically cooled. Rotational cooling is more efficient than vibrational cooling, because of the relative closeness of the energy levels. Typical

Dr. Hollas studied for his B.Sc. degree at University College London, where he went on to a Ph.D. under the supervision of Professor G. W. King and then Professor D. P. Craig. In 1959 he was awarded a Postdoctoral Fellowship at the National Research Council in Ottawa in the Division of Pure Physics headed by Dr. G. Herzberg. From 1961—64 he was a Senior Research Fellow in the Basic Physics Division of the National Physical Laboratory (Teddington) whose Superintendant was Professor J. A. Pople. In 1964 he was appointed as a Lecturer at the University of Reading where he is now a Reader. His interests are in applying the techniques of high resolution electronic spectroscopy to what are, by usual standards, large organic molecules.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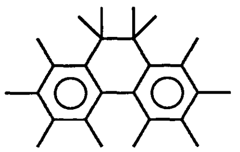
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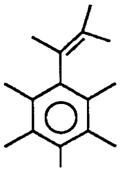
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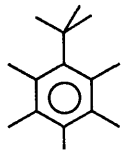
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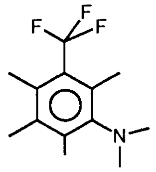
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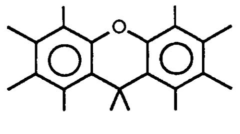
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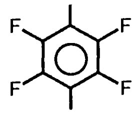
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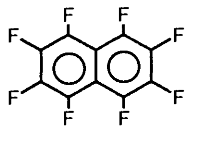
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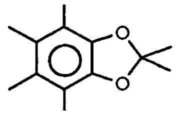
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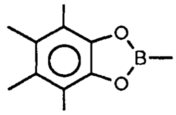
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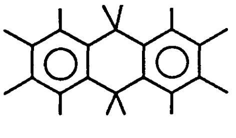
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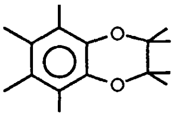
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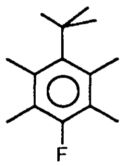
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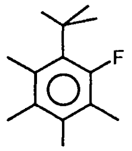
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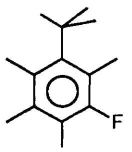
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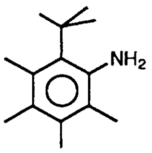
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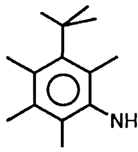
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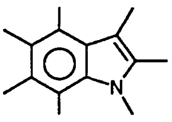
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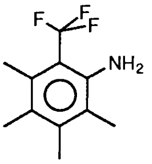
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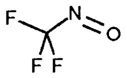
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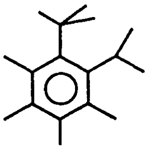
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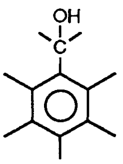
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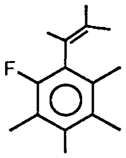
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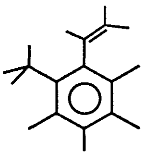
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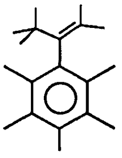
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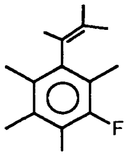
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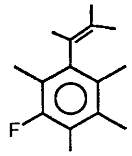
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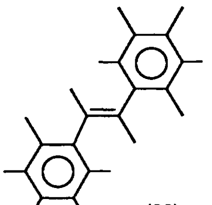
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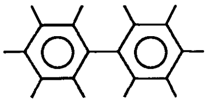
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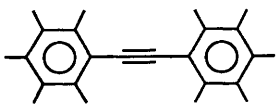
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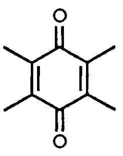
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rotational and vibrational temperatures achieved are 10 K and 100 K, respectively, but these may be lower with a higher pressure of helium. If argon is used instead of helium there is a tendency, because of the greater polarizability of argon, for van der Waals complexes to be formed. These are of great interest in their own right but will not be considered in this Review.

A supersonic jet may flow continuously or be pulsed. A pulsed jet is particularly appropriate if a pulsed laser is being used to obtain spectra and it also conserves material. The outer parts of the jet may be skimmed away if particularly narrow ranges of rotational temperatures and molecule velocities are required.

The rotational and vibrational cooling removes much of the congestion in the electronic spectra of molecules seeded into a supersonic jet. As a result, S_1–S_0 absorption and fluorescence spectra are mostly very sharp, but this is not always the case. Rotational and vibrational levels may be broadened due to efficient, competing processes which occur on a time scale which is short compared to the fluoroscence lifetime of the S_1 state. Examples of such processes are vibrational predissociation and intramolecular vibrational relaxation.

The absorption and fluorescence processes are investigated by laser irradiation, the laser beam intersecting the jet about 1 cm downstream from the pinhole or slit. Direct absorption has been used in supersonic jets but it is more usual to use an indirect method of monitoring absorption The two most common methods, fluorescence excitation (FE) and resonant multiphoton ionization (REMPI), are illustrated in Figure 1

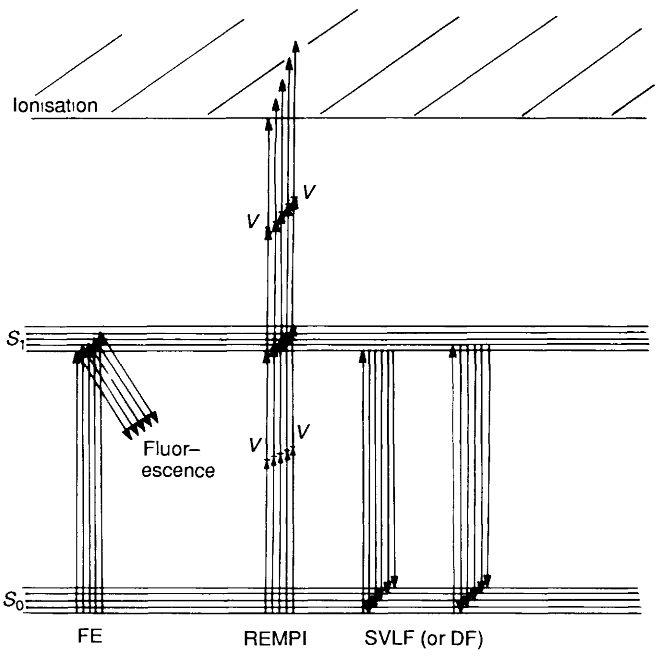

Figure 1 Fluorescence excitation (FE), 2 + 2 resonant multiphoton ionization (REMPI) and single vibronic level fluorescence (SVLF), or dispersed fluorescence (DF), processes

To obtain a FE spectrum the laser wavelength is tuned across the S_1–S_0 absorption system and the intensity of total, undispersed fluorescence monitored The FE spectrum corresponds exactly to an absorption spectrum if the quantum yield of fluorescence is constant for all vibronic levels of S_1 More often, the quantum yield declines with increasing vibrational excitation so that fluorescence intensities decrease compared to absorption intensities

The possibility of obtaining REMPI spectra depends on the high radiation density provided by a laser source Because of this high density a molecule may absorb more than one photon Such a multiphoton process may take several forms and all depend on an intermediate step, prior to ionization, in which the molecule is excited to the S_1 state this is the reason why it is called a resonant process Figure 1 illustrates the case where the molecule absorbs two photons to take it to S_1 The first photon takes it to a virtual state V, just as in a Raman scattering process, and the second takes it to S_1 Two more photons are absorbed to ionize the molecule and the complete process is sometimes referred to as a 2 + 2 multiphoton ionization process Alternatively, a 1 + 1 process may be used in which one photon takes the molecule to S_1 and a second ionizes it When the S_1–S_0 system is in the near ultraviolet the single photon is a visible photon in the 2 + 2 process but an ultraviolet photon in the 1 + 1 process In either process the laser radiation is tuned so that one or two photons scan the S_1–S_0 system while the total number of ions is collected and counted These ions may be passed into a time-of-flight mass spectrometer to ascertain that the REMPI spectrum corresponds to the correct molecular species

Both FE and REMPI spectra provide information on vibrational levels in S_1

To obtain vibrational levels in S_0 the technique of single vibronic level fluorescence (SVLF), alternatively called dispersed fluorescence (DF), is used This is illustrated in Figure 1 The laser wavelength is tuned to match a particular absorption band to take the molecule into a single vibronic level This may be the zero-point level or an excited vibrational level within S_1

Apart from the very low vibrational and rotational temperatures produced in a supersonic jet, there is a further great advantage in that the molecules are in collision-free conditions As a result, molecules excited to a single vibronic level are not transferred to other vibronic levels due to collisions occurring during the fluorescence lifetime

In a SVLF spectrum the fluorescence from the single vibronic level of S_1 that has been populated is dispersed to give vibrational levels in S_0

The observation of progressions in SVLF, FE, or REMPI spectra, allowing access to higher vibrational levels of S_0 or S_1 is highly desirable and depends on there being an appreciable change of curvature of the potential energy curve or of the equilibrium conformation of the molecule between S_0 and S_1

Figure 2 illustrates a typical experimental arrangement for obtaining FE and SVLF spectra The pulsed tunable dye laser is pumped by a Nd YAG or excimer laser but a high resolution CW ring dye laser may also be used In the figure the supersonic jet is directed vertically downwards into the vacuum pumping system The dye laser radiation may have to be frequency doubled when working in the near ultraviolet region but the beam of visible or ultraviolet radiation intersects the supersonic jet in the centre of the vacuum chamber Fluorescence is collected in a direction perpendicular to the laser and molecular beams In the arrangement in Figure 2 a set of four concave mirrors is used to collect the fluorescence more efficiently but other optical arrangements may be used The collected fluorescence is directed into a spectrometer with photomultiplier detection For a FE spectrum the laser is tuned through the S_1–S_0 absorption system and, with the angle of the grating in the spectrometer set to zero, the total undispersed fluorescence is collected For REMPI spectra ion collection plates are used or the ions are directed into a time-of-flight mass spectrometer For a SVLF spectrum the laser wavelength is fixed on a particular absorption band and the grating of the spectrometer rotated to scan through the region of the dispersed fluorescence Calibration of SVLF spectra may be achieved with an iron hollow cathode source

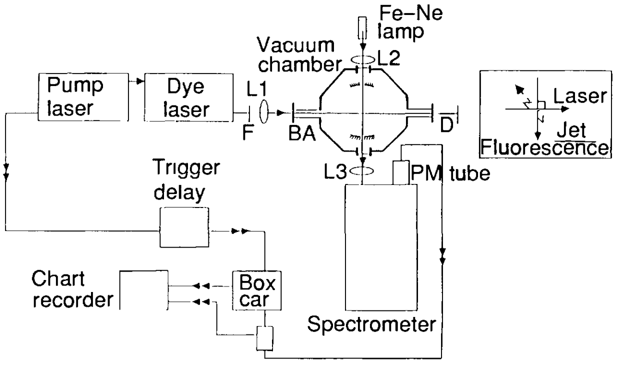

Figure 2 Typical experimental arrangement for obtaining FE and SVLF spectra of molecules in a supersonic jet

When the exciting laser radiation is pulsed the photomultiplier detects pulsed fluorescence, the length of the pulses being determined by the lifetime of the fluorescence These pulses are integrated by the boxcar and the signal output to a chart recorder or microcomputer

Other techniques for observing vibrational levels by laser excitation, such as fluorescence depletion and stimulated emission pumping (SEP), are used but will not be discussed here

There are two general types of vibration that we shall be concerned with One of these is inversion, as in the well-known inversion vibration of ammonia Examples are the out-of-plane bending vibration of the hydrogen atoms of the amino group of aniline (1) and the out-of-plane bending of the two benzene rings about the central carbon and oxygen atoms joining them in xanthene (6) The second type is a torsional vibration, examples of which are the torsional motion of the vinyl group relative to the benzene ring in (3) and of the CF_3 group relative to the benzene ring in (5)

For an inversion vibration, also called a ring-puckering vibration in the case of a closed ring system, as in (6), the form of the potential energy function which is adopted must be able to show a symmetrical double minimum, as it does[2] in the S_0 state of (1) There have been several suggested forms for this potential $V(Q)$, where Q is the inversion vibrational coordinate, but

$$V(Q) = \tfrac{1}{2}aQ^2 + b\exp(-cQ^2) \qquad (1)$$

is one of the more successful The first term is that of a harmonic oscillator and the second term introduces an energy barrier of height b, at $Q = 0$, between the two equivalent minima of the W-shaped potential

A useful alternative W-shaped potential to that in equation 1 is

$$V(Q) = AQ^2 + BQ^4 \qquad (2)$$

If A is zero the potential is a steep-sided quartic but the addition of the AQ^2 term, with negative A, introduces an energy barrier at $Q = 0$ of height

$$b = A^2/4B \qquad (3)$$

For a molecule which may be non-planar, or have in it a non-planar group, the determination of the barrier height, or showing that it is zero, is vital in determining molecular conformation

For torsional motion the most useful general form of the potential is

$$V(\phi) = \tfrac{1}{2}\sum_{n} V_n(-\cos n\phi) \qquad (4)$$

where ϕ is the torsional angle and n is a non-zero integer Which terms are dominant in the summation depends on the molecule concerned For example, in the planar (3) it is V_2 and, in (4), it is V_6 In these cases the barrier height between equivalent conformations is V_2 and V_6, respectively

3 Examples

3.1 Inversion Vibrations

When conformational investigations using spectroscopic techniques were confined mostly to small molecules the use of inversion vibrations in structure determination was applied to molecules such as ammonia (NH_3) and formaldehyde (H_2CO) Ammonia is pyramidal in its ground state but planar in several of the lower energy excited states, while formaldehyde is planar in its ground state but pyramidal in its S_1 excited state

These examples illustrate a possible source of ambiguity regarding what we call an inversion vibration Strictly, an inversion vibration is one which can take a non-planar molecule through an energy barrier to an equivalent configuration, related to the initial one by a reflection through the plane of the planar, high energy configuration If the energy barrier in the resulting W-shaped vibrational potential function is reduced to zero the molecule is planar and the inversion vibration becomes an out-of-plane bending vibration For example, the inversion vibration of pyramidal ammonia in S_0 and of non-planar formaldehyde in S_1 become out-of-plane bending vibrations in planar excited states of ammonia and in the S_0 state of formaldehyde

Now that larger molecules can be investigated, by the techniques described in Section 2, we encounter a wider variety of inversion vibrations although a similar example to those of ammonia and formaldehyde is the inversion, or out-of-plane bending, vibration of the amino hydrogens in aniline (1) which can be regarded as a phenyl derivative of ammonia The molecule is non-planar in S_0, with a barrier to planarity of 547 cm ^{1} (6 54 kJ mol^{-1}), and planar in S_1 with an almost purely quartic potential[2]

Symmetry arguments and selection rules will not be discussed here in detail but it is important to realize that, when splitting of vibrational levels occurs due to tunnelling through an inversion barrier, the symmetry classification of the split levels must be according to the point group of the planar structure For example, for pyramidal ammonia we must use the D_{3h}, and not the C_{3v}, point group and, for non-planar aniline (1), the C_{2v}, and not the C_s, point group[a] Then, in the absence of vibronic coupling, the vibrational selection rule is

$$\Delta v = 0, 2, 4, 6,$$

except in molecules which have very low symmetry, such as those belonging to the C_1 point group in these cases Δv is unrestricted

Some rather different types of inversion, or out-of-plane bending vibrations, which have been investigated by supersonic jet electronic spectroscopy are (a) the symmetrical (b_{3u}) out-of-plane bending vibration of the four fluorine atoms in 1,2,4,5-tetrafluorobenzene (7), (b) the symmetrical (b_{3u}) out-of-plane bending vibration of all the fluorine atoms in perfluoronaphthalene (8), (c) the out-of-plane b_1 bending variation of the CH_2 group in position-2 in 1,3-benzodioxole (9), (d) the out-of-plane b_1 bending vibration of the BH group in catecholborane (10), and the out-of-plane b_1 bending vibration about the central carbon and oxygen atoms in xanthene (6) All of these are important vibrations in respect of molecular conformation If any of them shows a potential energy minimum corresponding to a non-planar structure of the molecular skeleton it will also show a second, identical minimum corresponding to the mirror image non-planar structure, just as for the ground state of ammonia If the energy barrier separating the two minima in the W-shaped potential is sufficiently low, and the reduced mass for the vibration sufficiently small, quantum mechanical tunnelling through the barrier results in splitting and gross anharmonicity of the energy levels in each well of the potential

For out-of-plane ring vibrations, such as those referred to above in (9) and (10), an alternative description as ring-puckering vibrations is often used A simple example of a ring-puckering vibration is the out-of-plane vibration of the CH_2 group in position-3 in cyclopentene This vibration could equally well be called an inversion vibration or an out-of-plane bending vibration if the molecular skeleton is non-planar or planar, respectively

Supersonic jet electronic spectroscopy has opened up the possibility of investigating many vibrations of this type and of relating them to conformation in much larger molecules than previously and there have been many surprises among the results One example is illustrated by part of the FE spectrum of (7) in a supersonic jet[4] shown in Figure 3 There is a long progression, with Δv even, in ν_{11}, the symmetrical (b_{3u}) out-of-plane bending vibration of the four fluorine atoms Application of the Franck–Condon principle to this unexpected observation indicates an appreciable change of geometry, in the direction of motion of ν_{11}, from S_0 to S_1 Therefore, since the molecule is planar in S_0 it must be non-planar in S_1 The observed vibrational levels in S_1 have been fitted to the potential of equation 1 and are shown in Figure 4 The molecule is non-planar in S_1 Although the barrier to planarity is only 78 cm^{-1} (0 93 kJ mol ^{1}), corresponding to an out-of-plane angle of about 11°, the effect on the spectrum is seen in Figure 3 to be dramatic and is an excellent illustration of how sensitive this technique is in detecting changes of geometry

A simple rationalization, based on qualitative valence theory arguments, of why such a geometry change occurs between the ground and an excited electronic state is not often possible but, in this case, there is a convincing argument It has been shown

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[a] More rigorously the symbolism employing the permutation inversion symmetry introduced by Longuet-Higgins[3] may be used

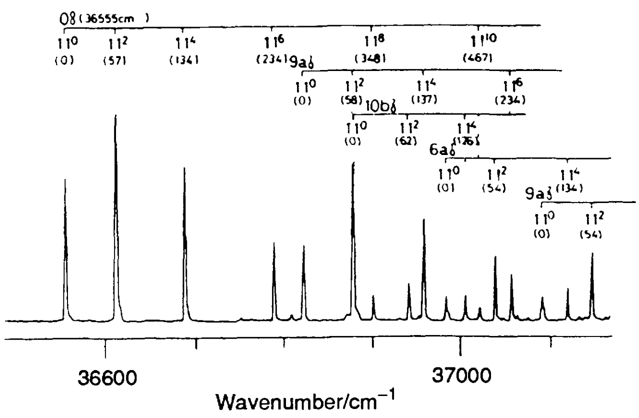

Figure 3 Part of the S_1–S_0 fluorescence excitation spectrum of 1,2,4,5-tetrafluorobenzene
(Reproduced by permission from *J Phys Chem* , 1986, **90**, 3948)

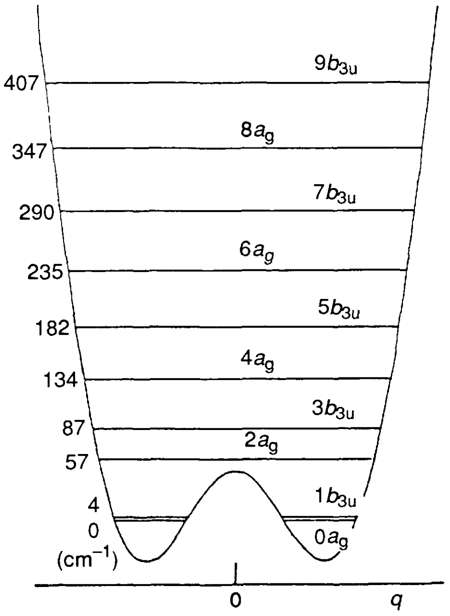

Figure 4 The b_{3u} fluorine inversion potential for 1,2,4 5-tetrafluorobenzene in S_1
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that, as more hydrogen atoms of benzene are substituted by fluorine atoms, the energy of a $\pi\sigma^*$ state is successively lowered in energy When four fluorines are present it is lowered so much that it is involved in strong vibronic coupling with the S_1, $\pi\pi^*$ state, conferring on it C—F antibonding character

A similar geometry change from S_0 to S_1 has been found in perfluoronaphthalene (8), which is planar in S_0 In the FE spectrum in a supersonic jet[5] there is a progression, with Δv even, in the symmetric (b_{3u}) out-of-plane bending vibration of all the fluorine atoms The energy levels of this vibration in S_1 are anharmonic and were fitted to the potential in equation 1 The barrier to planarity is 14 cm^{-1} (0 17 kJ mol^{-1}) Although this barrier is very small it can be determined accurately because of the extreme sensitivity of the lower vibrational levels to the perturbing effect of the barrier It is probable that the reason for the barrier is, again, the mixing, by vibronic coupling, of the $\pi\pi^*$ with a $\pi\sigma^*$ state, lowered in energy by the fluorine atoms

The inversion vibration of xanthene (6) is very strongly active in the FE spectrum,[6] part of which is shown in Figure 5 This indicates an appreciable change of geometry from S_0 to S_1 Figure 6 shows the inversion potentials calculated for both electronic states with the potential in equation 1 using the inversion energy levels obtained from the FE spectrum, for S_1, and various SVLF spectra for S_0 The molecule is non-planar in S_0, with a 49 cm^{-1} (0 59 kJ mol^{-1}) barrier to planarity, but planar in S_1

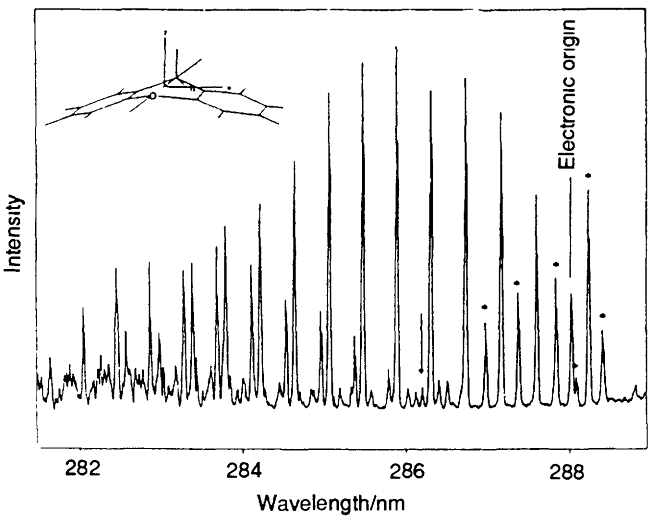

Figure 5 Part of the S_1–S_0 fluorescence excitation spectrum of xanthene
(Reproduced by permission from *J Chem Phys* , 1993 **98**, 836)

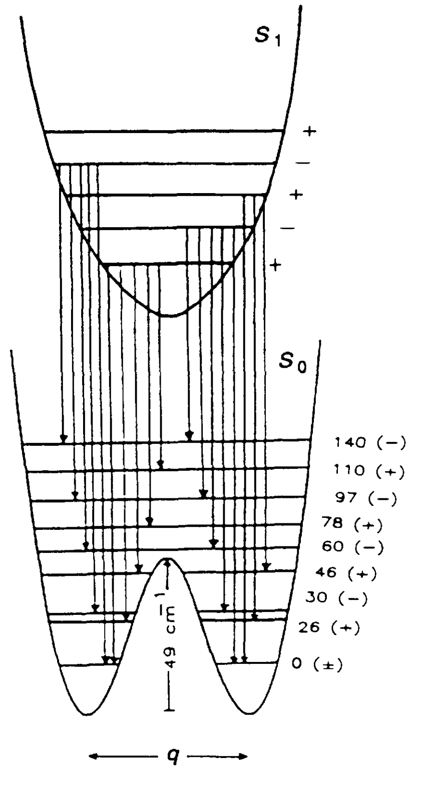

Figure 6 Inversion potentials for xanthene in S_0 and S_1
(Reproduced by permission from *J Chem Phys* , 1993, **98**, 836)

Because of the barrier in S_0, and the large reduced mass for this inversion motion, there is no observed doubling of the $v = 0$ level in S_0 One important result of this is that, in the progression from this level observed in the FE spectrum, the molecule behaves as if it has a rigidly non-planar skeleton and belongs to the C_s point group, with only a plane of symmetry The inversion vibration is then an a', totally symmetric, vibration and Δv can be even and odd On the other hand, transitions in the SVLF spectra from the planar, C_{2v}, S_1 state obey the Δv even selection rule because the inversion vibration is now a non-totally symmetric, b_1, vibration Transitions obeying this selection rule are shown in Figure 6

There is an interesting comparison between the geometry of xanthene and that of 9,10-dihydroanthracene (11) which has a non-planar skeleton in both the S_0 and S_1 electronic states [7] The barrier decreases from 615 cm^{-1} (7 36 kJ mol^{-1} in S_0 to 80 cm^{-1} (0 96 kJ mol^{-1}) in S_1 corresponding to an increase in the angle between the two benzene rings from 144 6° in S_0 to 164 1° in S_1 The structural differences in xanthene, compared to (11), in S_0 and S_1 are in agreement with the expectation that the replacement of CH_2 by oxygen favours a planar conformation

9,10-Dihydrophenanthrene (2) has a strongly non-planar, twisted conformation in S_0, with a barrier of 2460 cm ^{1} (31 6 kJ mol ^{1}), and in S_1, with a barrier of 1430 cm ^{1}) (17 1 kJ mol^{-1}) [8] The reason for this is that the CH_2 groups in the 9- and 10-positions strongly favour a staggered conformation This has been shown to be the case in benzodioxan (12) also,[9] which has a twisted, C_2, structure with a barrier to planarity in both electronic states which is too high to be determined but which is probably more than 4000 cm^{-1} (48 kJ mol ^{1})

The molecules 1,3-benzodioxole (9) and catecholborane (10) are interesting examples of partly saturated five-membered rings attached to a benzene ring and the question is whether the skeletal atoms of the five-membered ring are coplanar with the benzene ring

Figure 7 shows the SVLF spectrum[10] of (9) with excitation in the 0^0_0 band (the pure electronic transition, from the zero-point level of S_0 to that of S_1) There is a strong band, labelled 20^0_2, involving two quanta of ν_{20} in S_0, which is 102 cm^{-1} to low wavenumber of 0^0_0 but no band at twice this interval The vibration responsible, ν_{20}, must therefore be anharmonic indicating non-planarity in S_0 Interpretation of the gas phase far infrared spectrum[11] apparently showed that the levels of the puckering vibration of the CH_2 group in the 2-position are more or less harmonic and that the molecule is planar The 102 cm ^{1} interval in the SVLF spectrum could not involve the b_1 bending vibration about the central C—C bond and the only remaining possibility seemed to be that it involves two quanta of the a_2 twisting vibration of the oxygen atoms Therefore, the non-planarity in S_0 was attributed to a C_2 twisted conformation [10] The barrier to planarity is 157 cm^{-1} (1 88 cm kJ mol ^{1})

However, this is not the end of the story Investigation of the microwave spectrum of (9) in the zero-point level and several low-lying vibrational levels[12] has shown that the anharmonic vibration is the puckering vibration of the CH_2 group and that the non-planarity involves this group only It is the values of the rotational constants in the excited vibrational levels which allow this assignment of the vibration concerned The far infrared spectrum has also been reinterpreted satisfactorily and a slightly modified barrier to planarity of 126 cm ^{1} (1 51 kJ mol ^{1}) obtained

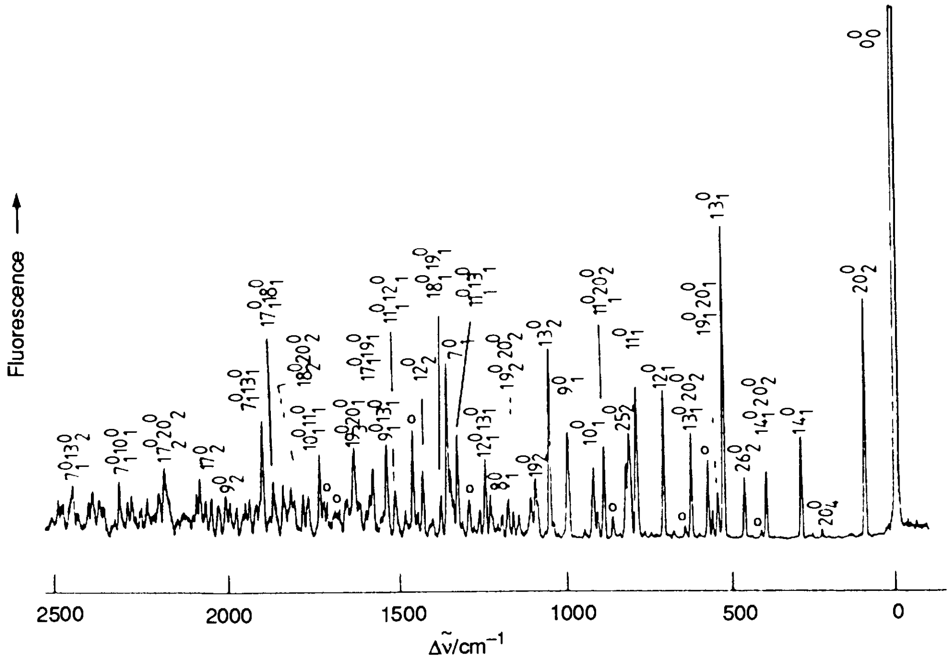

Figure 7 The 0^0_0 SVLF spectrum of 1,3-benzodioxile
(Reproduced by permission from *Chem Phys Lett*, 1989, **157** 183)

Catecholborane (10) has proved rather less of a problem SVLF spectra show[13] no low wavenumber anharmonic vibrations and, together with the gas-phase absorption spectrum, these show that the molecule is planar in both S_0 and S_1 The rationalization of this is that there is some π-electron conjugation around the five-membered ring, involving the otherwise empty $2p_x$ orbital on the boron atom, stabilizing the planar conformation

3.2 Torsional Vibrations

The energy barrier to torsional motion generally decreases as the number of times the equivalent equilibrium configuration is encountered during a 360° rotation increases In the case of toluene (4) this number is six, and the six-fold energy barrier is indeed very low It has been found, from the microwave spectrum,[14] to be 4 875 cm ^{1} (0 058 kJ mol^{-1}) in S_0

The torsional potential and energy barrier of (4) in S_1 have been determined from a REMPI spectrum [15] With the toluene in a supersonic jet weak transitions from the zero-point level of S_0 to various torsional levels in S_1 were observed and fitted to a potential like that in equation 4 but with only V_6 non-zero

The molecular symmetry group[3] to which toluene belongs is G_{12} but this is isomorphous with the D_{3h} point group, and it is that which we shall use here The torsional vibrational levels are labelled, in the free internal rotation limit, with the quantum number $m = 0, 1, 2, 3,$, all levels with $m > 0$ being doubly degenerate When a sixfold barrier is introduced the degeneracy of the $m = 3, 6, 9,$ levels is split For example the $m = 3$ level is split into a $3a_1''$ and $3a_2''$ pair It has been shown[16] that the order of these two levels depends on the sign of V_6 The $3a_1''$ level is the higher one if V_6 is negative, and this is the case only for a staggered, as opposed to an eclipsed, equilibrium configuration In the case of toluene V_6 is negative in both S_0 and S_1 (its value is $-$ 25 cm^{-1} in S_1) showing that the staggered configuration is the more stable in both electronic states, but not by very much

The situation is similar in 4-substituted toluenes For example, in 4-fluorotoluene[17] (13), V_6 is $-$ 4 8 cm^{-1} ($-$ 0 057 kJ mol^{-1}) in S_0 and −33.7 cm^{-1} (−0.403 kJ mol^{-1}) in S_1. It is not surprising that the equilibrium configuration is staggered in both states and that the barrier to be surmounted in going to the eclipsed configuration is very similar to that in toluene, in both electronic states.

When the substituent is in the 2- or 3-position, as in 2-fluorotoluene (14) and 3-fluorotoluene (15), the methyl torsional potential is dramatically different.[17] Figure 8 shows the methyl torsional bands associated with the 0_0^0 band in the FE spectrum of (14). The high intensity of these bands indicates, from the Franck–Condon principle, an appreciable change of torsional potential from S_0 to S_1. This molecule belongs to the G_6 molecular symmetry group, isomorphous with the C_{3v} point group. In the supersonic jet, nearly all the molecules are frozen down into the $0a_1$ and $1e$ levels (0 and 1 are the m quantum numbers); transitions from the upper $1e$ to the lower $0a_1$ level are nuclear spin forbidden and can never occur, even on collision. The selection rules are that only a_1–a_1, a_2–a_2, and e–e transitions are normally allowed except that a_1–a_2, a_2–a_1 transitions may occur weakly due to interaction between torsional and overall rotational motion. In Figure 8 several transitions to a_1 and e torsional levels in S_1, and a weak one to the $3a_2$ level are clearly observed. These have been fitted to a torsional potential for S_1, for which V_3 = 16.9 cm^{-1} and V_6 = −5.3 cm^{-1}, and SVLF spectra allow the torsional potential to be obtained for S_0, for which V_3 = 228.1 cm^{-1} and V_6 = −26.4 cm^{-1}.

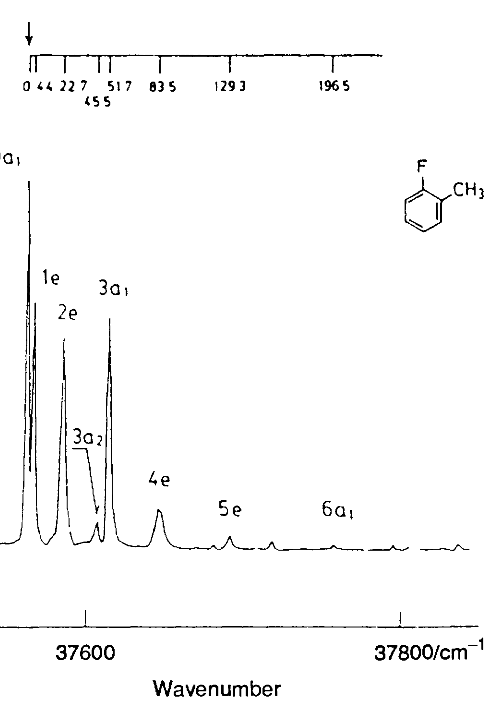

Figure 8 FE spectrum of 2-fluorotoluene showing methyl torsional bands in the region of the 0_0^0 band
(Reproduced by permission from *J. Phys. Chem.* 1985, **89**, 5617.)

The potentials for S_0 and S_1 are shown in Figure 9. In S_0 the molecule is eclipsed with a surprisingly high barrier of 228.1 cm^{-1} (2.728 kJ mol^{-1}) in going to the staggered configuration for which ϕ = 0°. In S_1 the fact that V_3 and V_6 are similar in magnitude leads to a complex potential showing that the molecule is quasi-staggered: there is a small energy barrier of 2.9 cm^{-1} at ϕ = 0° but it is below the zero-point level. The larger barrier, at ϕ = 60° is only 24.7 cm^{-1} (0.295 kJ mol^{-1}) above the minimum. It is because the molecule goes from an eclipsed ground state to an essentially staggered excited state that the Franck–Condon factors for the torsional transitions in Figure 8 are so large. The methyl torsional potential in S_1 is very similar to that of toluene but completely different in S_0.

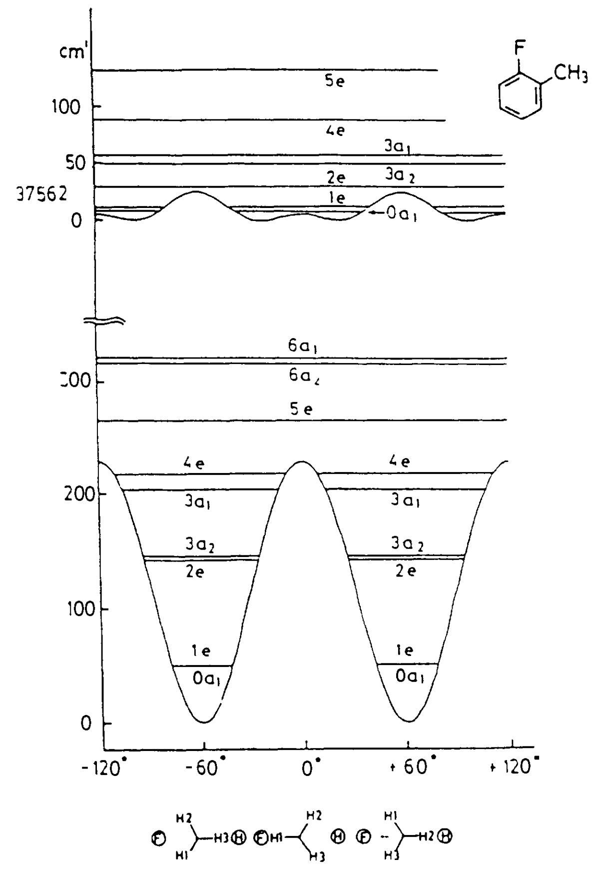

Figure 9 Methyl torsional potentials and energy levels for 2-fluorotoluene in S_0 and S_1
(Reproduced by permission from *J. Phys. Chem.* 1985, **89**, 5617.)

The methyl torsional potential in 3-fluorotoluene (15)[17] is very different from that in (16). In S_0, V_3 = 16.9 cm^{-1} and V_6 = −5.3 cm^{-1} so that the equilibrium configuration is staggered with a barrier of only 16.9 cm^{-1} (0.202 kJ mol^{-1}) to go to the eclipsed configuration. In S_1, however, V_3 = 123.7 cm^{-1} and V_6 = −26.4 cm^{-1}: the equilibrium configuration is also staggered but with a much higher barrier of 123.7 cm^{-1} (1.479 kJ mol^{-1}).

The methyl torsional potentials are rather similar when the substituent in the ring is an amino-group instead of a fluorine atom.[18] In 2-aminotoluene (16) the equilibrium configuration is eclipsed in S_0 and S_1 with barrier heights of 703 cm^{-1} (8.41 kJ mol^{-1}) and 40 cm^{-1} (0.48 kJ mol^{-1}) respectively. In 3-aminotoluene (17) there is a very low barrier in S_0 for which V_3 = 9 cm^{-1} and V_6 = −10 cm^{-1} and a barrier of 317 cm^{-1} (3.79 kJ mol^{-1}) in S_1, for which V_3 = 317 cm^{-1} and V_6 = −19 cm^{-1} and the equilibrium configuration is eclipsed.

The effect on the CH$_3$ torsional potential of the position of substitution in the indole molecule (18) has been investigated for 1-, 4-, 5-, 6-, and 7-methylindole.[19] The changes in the potential are appreciable, in both S_0 and S_1, and are a useful probe of the electronic structure of the indole molecule in the region of substitution.

Until recently, very little was known about the torsional potential for the CF$_3$ group attached to a benzene ring. Two examples that have been investigated through their supersonic jet fluorescence spectra are 2- and 3-aminobenzotrifluoride (19) and (5).

Figure 10 shows the FE spectrum of (5) close to the 0_0^0 band.[20] There is almost no similarity between this and the corresponding spectrum of 3-aminotoluene, even though the torsional potentials in S_0 and S_1 are remarkably similar for both molecules. The

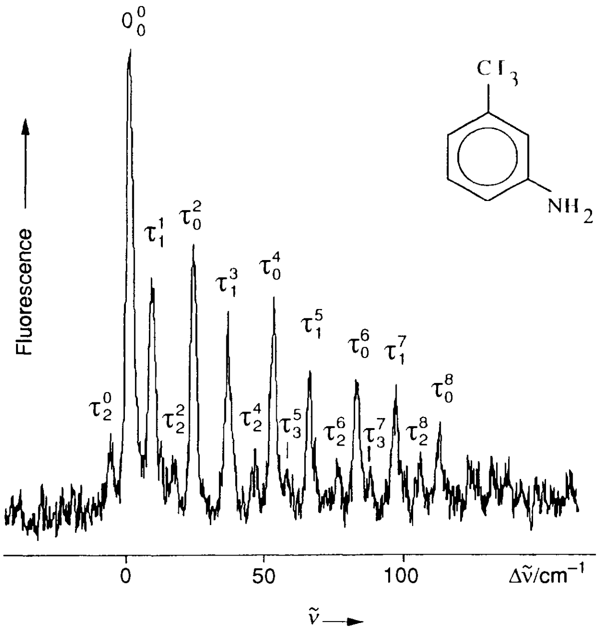

Figure 10 FE spectrum of 3-aminobenzotrifluoride showing CF_3-torsional bands in the region of the 0^0_0 band
(Reproduced by permission from *Chem Phys Lett*, 1991 **183** 377)

differences in the spectra are due mainly to the fact that the CF_3 group is very much heavier than the CH_3 group The internal rotation constant F, which is inversely proportional to the moment of inertia for internal rotation, is about 0 29 cm^{-1} for CF_3 and 5 cm^{-1} for CH_3 An important consequence of this is that, for the same torsional potential, the energy levels for CF_3 are very much more closely spaced than they would be for CH_3 In other words, the torsional motion of CF_3 tends to behave much more like a torsional vibration, with little tunnelling through energy barriers, whereas CH_3 torsional motion more often resembles free internal rotation, with a much greater tendency for tunnelling

The torsional potentials for (5) in S_0 and S_1 are shown in Figure 11 In S_0, $V_3 = 9$ cm^{-1} and $V_6 = -10$ cm^{-1} giving a very shallow potential with the equilibrium configuration about 25° from the eclipsed configuration In S_1, $V_3 = 155$ cm^{-1} and $V_6 = -40$ cm^{-1}, resulting in an eclipsed configuration The change in equilibrium geometry from S_0 to S_1 results in the long progressions in the torsional vibration, ν_τ, which dominate the spectrum in Figure 10 The S_1 potential in Figure 11 shows that, due to the large reduced mass of the CF_3 group, appreciable tunnelling through the torsional barrier occurs only at the $\nu_\tau = 10$ level This figure also shows why, even under the extremely low temperature conditions of the jet, progressions are observed in the FE spectrum with $\nu_\tau = 1$, 2, and 3 in S_0 The reason, again, is that the massive CF_3 group causes these levels to be so low-lying that they are appreciably populated

The comparison between the torsional potentials for 3-aminotoluene[18] and 3-aminobenzotrifluoride[20] shows them to be remarkably similar Those for S_0 are identical both molecules show a very low barrier In S_1, both are eclipsed with quite a high barrier, although it is twice as high in 3-aminotoluene These observations parallel the effect of substituting fluorine in the 3-position in toluene [17]

Long CF_3-torsional progressions are also observed in the fluorescence spectra of (19) These have been assigned[21] to give the torsional parameters $V_3 = 450$ cm^{-1} and $V_6 = 83$ cm^{-1}, in S_0, and $V_3 = 220$ cm^{-1} and $V_6 = -65$ cm^{-1}, in S_1 The equilibrium configuration is eclipsed in both states with barrier heights of 450 cm^{-1} (5 38 kJ mol^{-1}) in S_0 and 220 cm^{-1} (2 63 kJ mol^{-1}) in S_1 The fairly high barrier in S_0 is comparable with that of 703 cm^{-1} in (16) and 228 cm^{-1} in (14) In S_1, however, the barrier in (19) is much higher than in (16) and (14) which are much more nearly freely rotating Weak hydrogen bonding between an amino hydrogen and a fluorine atom may be responsible

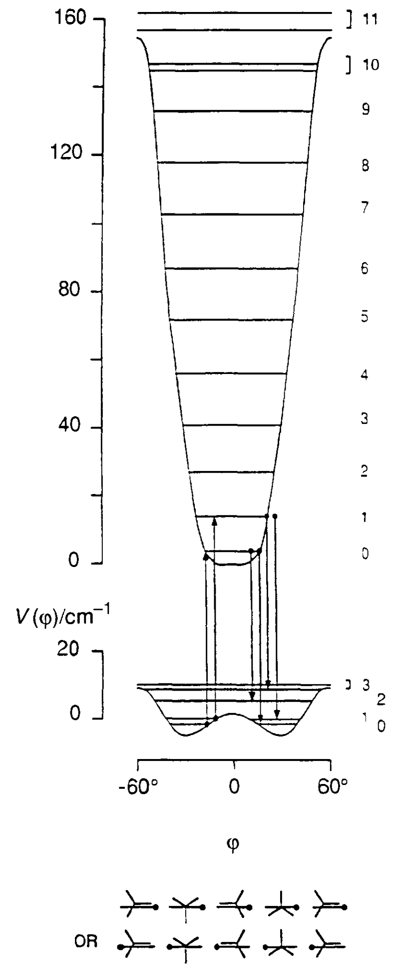

Figure 11 CF_3-torsional potentials and energy levels for 3-aminobenzotrifluoride in S_1 (upper) and S_0 (lower) electronic states
(Reproduced by permission from *Chem Phys Lett* 1991 **183** 377)

A rather different type of molecule with an interesting CF_3 torsional problem is trifluoronitrosomethane (20) Microwave spectroscopy and electron diffraction studies have shown that the equilibrium configuration in S_0 is eclipsed The S_1–S_0 electronic transition involves a π^*–n promotion which results in a staggered equilibrium configuration [22] There is barrier of 238 4 cm^{-1} (2 851 kJ mol^{-1}) in S_0, for which $V_3 = 238$ 4 cm^{-1} and $V_6 = -5$ 8 cm^{-1}, and a barrier of 601 5 cm^{-1} (7 194 kJ mol^{-1}) in S_1, for which $V_3 = 601$ 5 cm^{-1} and $V_6 = -1$ 0 cm^{-1}

Unusual cases of toluene substituted in the ring are the 2-, 3-, and 4-methylbenzyl radicals generated by laser photolysis of the appropriate α-chloroxylene followed by cooling in a supersonic jet [23] FE and SVLF spectra were obtained and interpreted to give methyl torsional potentials in the D_0 and D_1 states (these are doublet states) The highest barriers were found in 2-methylbenzyl (21) for which $V_3 = 754$ cm^{-1} (9 02 kJ mol^{-1}) in D_0 and 362 cm^{-1} (4 33 kJ mol^{-1}) in D_1

When there is monosubstitution in the methyl group of toluene the torsional energy barrier is considerably increased For example, in benzyl alcohol (22) the parameters in the torsional potential are[24] $V_2 = 140$ cm^{-1} in S_0 and $V_2 = 330$ cm^{-1}, $V_4 = 3$ cm^{-1} in S_1, the barrier height being 140 cm^{-1} (1 67 kJ mol^{-1}) in S_0 and 330 cm^{-1} (3 95 kJ mol^{-1})

The question of the planarity of styrene (3) was long-standing and unsolved until the use of laser fluorescence techniques So far as the geometry is concerned, there are two competing effects Planarity is favoured because it results in maximum π-electron conjugation between the ring and the substituent, whereas this configuration results in maximum steric hindrance.

The first proof of the planarity of (3) came from SVLF spectra obtained in the gas phase under low-pressure, collision-free conditions.[25] As many energy levels as possible of the C(1)−C(α) torsional vibration, ν_{42}, are required to obtain the parameters in the torsional potential of equation 4. Observations up to $\nu_{42} = 4$, together with some $\Delta v = 2$ transitions observed in the gas phase Raman spectrum, which accessed higher levels resulted in $V_2 = 1145$ cm^{-1} and $V_4 = -278$ cm^{-1}. This potential is plotted in Figure 12 which also shows, in the upper curve, the effect of putting $V_4 = 0$. The comparison illustrates the drastic effect of the large, negative value of V_4. It pulls down the potential, making it very flat-bottomed. The molecule is planar, because the minimum is at $\phi = 0°$, but it takes only 4.8 kJ mol^{-1} of energy to twist the vinyl group 50° out-of-plane. The effect of V_4 on the lower energy levels is to close them up so that, for example, the $v = 1$–0 separation is only 38 cm^{-1}, and to cause them to **diverge** up to about $v = 9$. This very unusual behaviour can be attributed to the effect of π-electron conjugation winning the fight against steric hindrance, but only just.

With slightly improved data[26] the values of $V_2 = 1070$ cm^{-1} and $V_4 = -275$ cm^{-1} have been obtained. The energy barrier in going to the perpendicular configuration is 1070 cm^{-1} (12.80 kJ mol^{-1}).

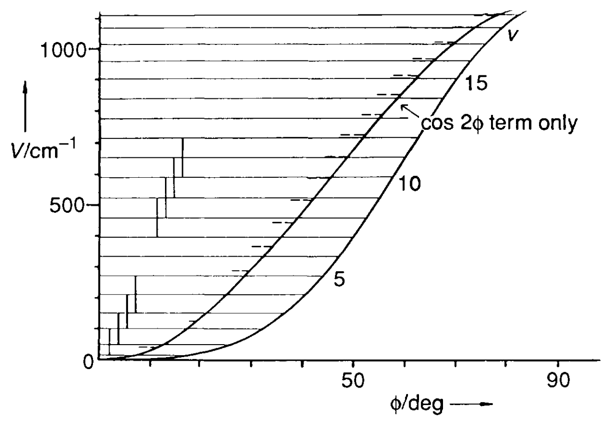

Figure 12 Torsional potential and energy levels for styrene in S_0. The upper curve with the dashed energy levels is plotted for $V_4 = 0$ to illustrate the effect of the large negative value of V_4 in the potential in the lower curve.
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In the S_1 state of (3) the evidence points to planarity with a more purely V_2 potential resulting in the lower torsional vibrational levels being almost harmonic. However, there is an unusually strong Duschinsky effect resulting in the normal coordinates which describe C(1)−C(α) torsion and out-of-plane bend about C(1) in S_0 being heavily mixed in S_1. The fact that torsional motion is distributed between two vibrations in S_1 means that it is not possible to determine the torsional barrier in S_1 but it almost certainly considerably higher than in S_0. The more rigid planarity in S_1 is consistent with the simple valence picture in which the π-electron conjugation between C(1) and C(α) is increased compared to S_0.

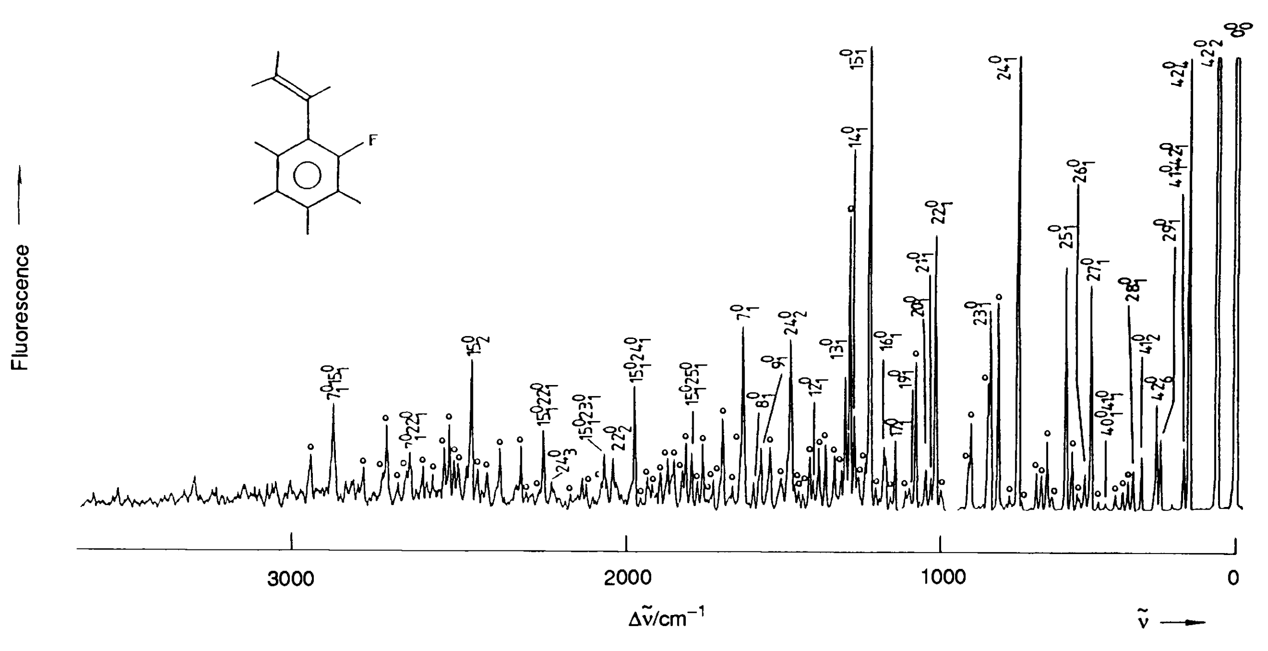
When a fluorine atom is substituted in the 2-position, as in 2-fluorostyrene (23), there is a possibility of two planar rotational isomers (rotamers). In fact only the *trans* rotamer (23) is known, presumably because steric hindrance destabilizes the *cis* rotamer. Figure 13 shows the SVLF spectrum of (23) in a supersonic jet with excitation in the 0^0_0 band.[27] The high intensity of the progression in the C(1)−C(α) torsional vibration, ν_{42}, compared to that observed for styrene is due to a larger change in the shape of the torsional potential from S_0 to S_1. In S_0, $V_2 = 895$ cm^{-1} and $V_4 = -333$ cm^{-1} resulting in a small barrier to planarity of 15 cm^{-1} (0.18 kJ mol^{-1}) at $\phi = 0°$. This barrier is below the zero-point level and the molecule is said to be quasiplanar. Although this level is above the barrier, the $v = 0$ wavefunction is concentrated above the minima, rather than at $\phi = 0°$, so that the molecule spends more time out-of-plane when in the $v = 0$ state that it would if there were no barrier. In fact it can be shown that there is a barrier at $\phi = 0°$ if

$$4|V_4| > V_2 \qquad (5)$$

When a methyl group is substituted in the 2-position, in 2-methylstyrene (24), once again only the *trans* rotamer is found. SVLF spectra in a supersonic jet show even longer progressions in the C(1)−C(α) torsional vibration.[28] The S_0 torsional potential, with $V_2 = 670$ cm^{-1} and $V_4 = -420$ cm^{-1}, is illustrated in Figure 14 and shows that the vinyl group is now rigidly about 33° out-of-plane. The barrier to planarity is 151 cm^{-1} (1.81 kJ mol^{-1}).

The effect of increasing non-planarity when a methyl group is

Figure 13 The 0^0_0 SVLF spectrum of *trans*-2-fluorostyrene.
(Reproduced by permission from *Chem. Phys. Lett.* 1989, **154**, 14.)



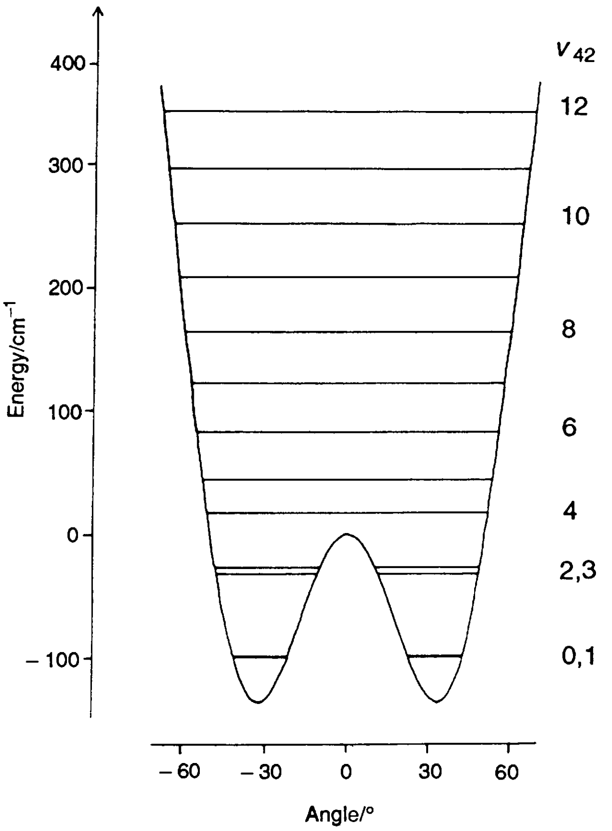


Figure 14 The C(1)–C(α) torsional potential for the S_0 state of *trans*-2-methylstyrene
(Reproduced by permission from *J. Chem. Soc. Faraday Trans.*, 1991, **87**, 3335.)

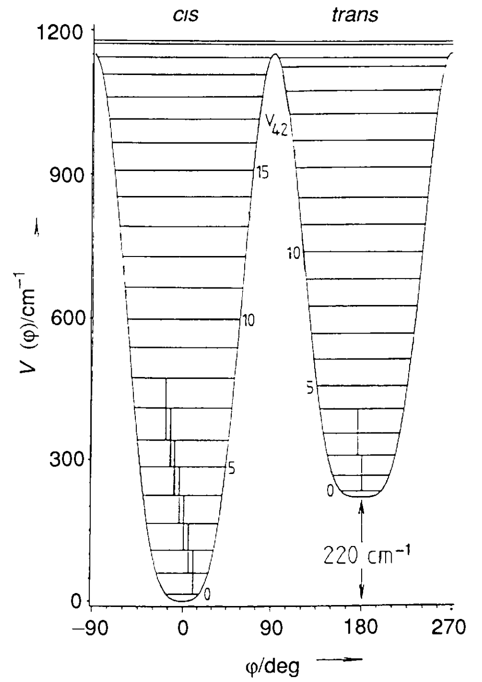


Figure 15 The C(1)–C(α) torsional potential for the S_0 state of *cis*- and *trans*-3-fluorostyrene
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substituted in the 2-position in styrene, to give the *trans* rotamer, appears to be due to an increasing steric hindrance between the substituent and the hydrogen atom in the α-position. A similar effect results when a methyl group is substituted on the α-carbon atom to give α-methylstyrene (25). A REMPI spectrum of this molecule[29] shows a very long progression in the C(1)–C(α) torsional vibration due to a W-shaped potential in S_0 in which the substituted vinyl group is twisted out-of-plane by 45°. This group is coplanar with the benzene ring in S_1.

Substitution in the 3-position in styrene is more likely to result in similar amounts of two rotamers. The FE spectrum of 3-fluorostyrene shows two 0^0_0 bands,[30] 275 cm^{-1} apart, which are attributed to the *cis*-(26) and *trans*-(27) rotamers. SVLF spectra, obtained with excitation into these and other bands, have allowed the observation of C(1)–C(α) torsional levels up to $v = 8$ in the *cis* and $v = 4$ in the *trans* rotamers. These levels were fitted to a single torsional potential for S_0, with $V_1 = 220$ cm^{-1}, $V_2 = 1040$ cm^{-1}, and $V_4 = -247$ cm^{-1}, which is shown in Figure 15.

The values of V_2 and V_4 are similar to those for styrene and result in the characteristic flat-bottomed minima for each rotamer. The value of 220 cm^{-1} for V_1 corresponds to the energy difference (2.63 kJ mol^{-1}) between the two rotamers. These results agree with those of a microwave investigation[31] in that the *cis*-rotamer is the more stable but V_1 was estimated[31] to be 26 cm^{-1} with a large uncertainty of 46 cm^{-1}. Reasons for the discrepancy include the assumptions that, in the electronic spectrum, the transition probabilities for the two 0^0_0 transitions are equal and that, in the microwave spectrum, the two permanent dipole moments are equal.

The *trans*-stilbene molecule (28) presents an interesting torsional and structural problem which is closely related to that in styrene (3). One difference, however, is that, since there are two phenyl groups, there are two torsional vibrations. The supersonic jet SVLF spectra, with excitation in the 0^0_0 and other bands, show[32] progressions, with Δv even, in the a_u torsional vibration ν_{37}. Torsional levels up to $\nu_{37} = 9$ were observed and fitted to a potential for S_0 with $V_2 = 305$ cm^{-1} and $V_4 = -85$ cm^{-1}. Because of the large, negative value of V_4 the potential is qualitatively similar to that for the torsional vibration of styrene.[26] The potential is very flat-bottomed, and may even show a small energy barrier to the planar configuration. The molecule is planar, or possibly quasiplanar, but is very easily twisted, even more so than styrene: for example, an energy equivalent to only 100 cm^{-1} (1.2 kJ mol^{-1}) twists it through a torsional angle of about 50° and the barrier height in going to the 90° configuration is only 305 cm^{-1} (3.65 kJ mol^{-1}).

The configuration of the biphenyl molecule (29) is interesting because of the possible effect of steric hindrance between hydrogen atoms on either side of the bond joining the two benzene rings. The effect may be sufficiently large to cause the equilibrium configuration to be twisted about the central bond.

Unlike the case of *trans*-stilbene (28), biphenyl has only one torsional vibration, with a_u symmetry, involving one ring twisting relative to the other. The motion analogous to the other torsional vibration in stilbene becomes an overall rotational motion. In the REMPI spectra[33] of (29) in a supersonic jet there are long progressions in the torsional vibration indicating a large change of torsional angle from S_0 to S_1. Fitting levels up to $v = 13$ in S_1 resulted in values of $V_2 = 1195$ cm^{-1}, $V_4 = -190$ cm^{-1}, and $V_6 = 18$ cm^{-1} corresponding to a single minimum and a planar configuration. In S_0, the potential was obtained from only one torsional vibrational interval and the intensity distribution in the progressions in the REMPI spectra. The values of $V_2 = 50$ cm^{-1} and $V_4 = -148$ cm^{-1} for S_0 are not, therefore, very reliable. They correspond to a W-shaped potential with an equilibrium torsional angle of about 44° and a barrier to planarity of about 125 cm^{-1} (1.50 kJ mol^{-1}). Whatever the uncertainty regarding the S_0 state potential, it is clear that, because the molecule is planar in S_1 and the torsional progressions are very long, there must be appreciable non-planarity in S_0.

Tolane (30) is a planar molecule which contains two benzene rings and, like biphenyl, has only one torsional vibration and this has a_u symmetry. Several SVLF spectra[34] of 30 are shown in

Figure 16 These spectra were obtained with excitation into the $\nu_T = 0$, 1 2 3, and 4 levels of the torsional vibration, ν_T, of an excited electronic state This excited state may be S_3, the highest of three predicted low-lying singlet states Because the torsional transitions must obey the Δv even selection rule, the odd-quantum levels could only be accessed by excitation into the T_1^1 and T_1^3 bands [The $\nu_T = 1$ level in S_0 is sufficiently low-lying (17 cm^{-1}) to be appreciably populated in the supersonic jet] The spectra in Figure 16 show that torsional levels up to $\nu_T = 14$ were observed and these were fitted to a pure V_2 potential with $V_2 = 202$ cm^{-1} (2 42 kJ mol^{-1}) and shown in Figure 17

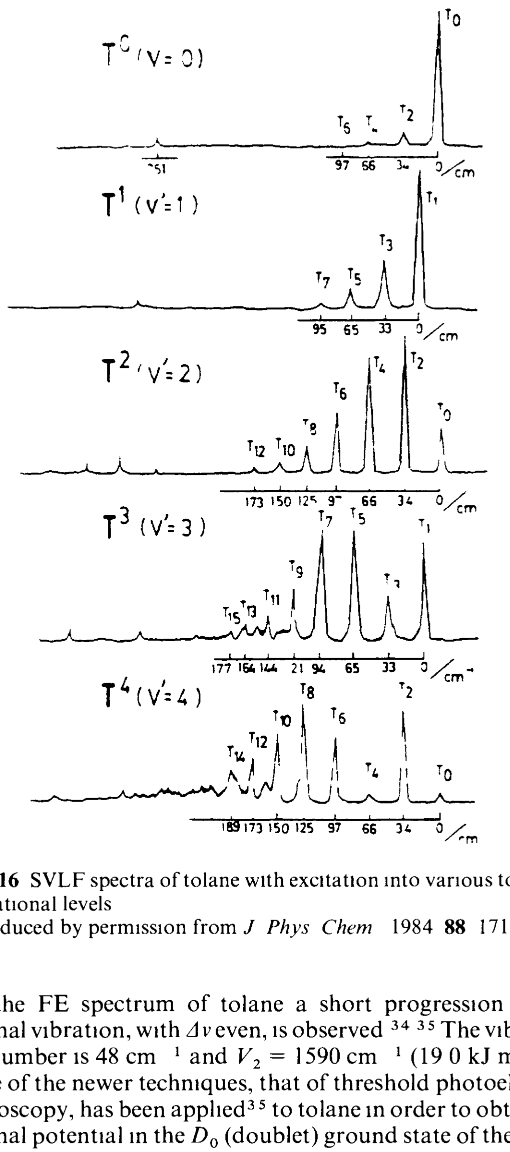

Figure 16 SVLF spectra of tolane with excitation into various torsional vibrational levels
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In the FE spectrum of tolane a short progression in the torsional vibration, with Δv even, is observed[34 35] The vibration wavenumber is 48 cm^{-1} and $V_2 = 1590$ cm^{-1} (19 0 kJ mol^{-1})

One of the newer techniques, that of threshold photoelectron spectroscopy, has been applied[35] to tolane in order to obtain the torsional potential in the D_0 (doublet) ground state of the singly charged positive ion This technique involves multiphoton ionization of tolane in which one photon takes it to a vibronic level of S_3 and a second photon, of a different colour (wavelength) from the first and tunable, ionizes the molecule to produce the ion in the D_0 state Tuning the second photon through the ionization band system takes the ion to various vibrational levels of D_0 Unlike ordinary photoelectron spectroscopy, in threshold photoelectron spectroscopy the ions are produced under field-free conditions and extracted with a pulsed electric field, in this case of 1 V cm^{-1}

A torsional vibration wavenumber of 54 cm^{-1} and a value of $V_2 = 1980$ cm^{-1} were obtained for the D_0 state The torsional progression in the threshold photoelectron spectrum is only short This is a consequence of the torsional potentials in the S_3 state of the molecule and the D_0 state of the ion being similar, leading to small Franck–Condon factors

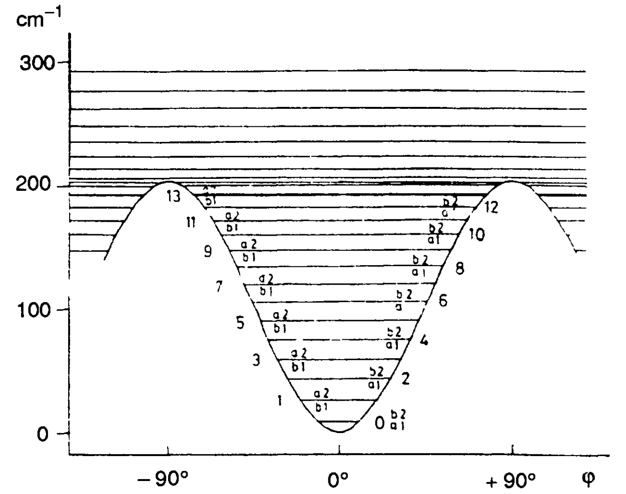

Figure 17 The torsional potential and energy levels in the S_0 state of tolane
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4 Conclusions

Low wavenumber vibrations have large amplitudes and this property makes them of particular interest from the point of view of molecular structure and conformation Because they have large amplitudes they are very susceptible, and therefore the corresponding molecular structural parameter is very susceptible, to changes in the immediate molecular environment

One important effect of the environment concerns the phase of the molecular sample For example, it is a well-known but not always well-remembered fact that low wavenumber vibrations, below about 300 cm^{-1}, have wavenumbers which are of the order of 10 cm^{-1} higher in the liquid than in the gas phase An example of this is the out-of-plane, boat-form vibration of the oxygen atoms in *p*-benzoquinone (31) which has a wavenumber of 108 cm^{-1} in the liquid and 87 cm^{-1} in the gas phase The reason for an increase in wavenumber in the liquid is that the large amplitude motions of the atoms are much more restricted by neighbouring molecules, resulting in a reduction of the amplitude, than are motions of smaller amplitude

For similar reasons the structure of a molecule in a crystal or, perhaps, adsorbed onto a surface is likely to be affected in those parts of the molecule where vibration has a large amplitude Even if the equilibrium structure remains the same the shape of the potential for the large amplitude motion may be changed

In small molecules it is extremely unusual for a vibration to have a wavenumber less than 100 cm^{-1} In this review we have seen that this is not the case for larger molecules The smallest vibration wavenumbers in the molecules discussed here are 7 cm^{-1} in the S_1 state of 3-aminobenzotrifluoride (5) and 8 cm^{-1} in the S_0 state of *trans*-stilbene (28) Clearly some larger molecules can be very floppy indeed

The importance of supersonic jet electronic spectroscopy in the determination of molecular conformation or structure cannot be overemphasized Two of the more traditional methods have been *X*-ray crystallography and electron diffraction The problem with *X*-ray crystallography is that it relates to molecular structure in the pure crystal which may be different from that in the free molecule, particularly when the molecule has large amplitude motions Electron diffraction gives a vibrationally averaged structure and, in larger molecules of fairly low symmetry, there are likely to be too many overlapping peaks in the radial distribution function for small structural differences to be distinguishable Far infrared spectroscopy can be useful for observing low wavenumber vibrations but very long absorption pathlengths are often necessary and the resulting spectra can be extremely complex making assignments difficult Microwave spectroscopy is a very powerful tool in distinguishing possible gross molecular structures, such as *cis*- and *trans*-isomers and in determining whether a molecule is planar This technique can also give information relating to potential functions for large amplitude vibrations from the determination of rotational constants in excited states of these vibrations

The study of electronic spectra of molecules seeded into a supersonic jet started almost twenty years ago and it is now one of the most powerful techniques for investigation of molecular structure In a supersonic jet the molecules are so rotationally and vibrationally cold that their electronic spectra are dramatically simplified to such an extent that vibrational progressions stand out with great clarity By contrast, in the gas phase at ambient temperatures, they are often overlaid by rotational and vibrational structure caused by appreciable population of rotational and vibrational levels which are drastically depopulated in the jet However, we still have to rely on the Franck–Condon factors to inject intensity into these progressions But, because large amplitude motions are particularly sensitive to changes in the immediate molecular environment, the promotion of an electron to a higher orbital in going to an excited electronic state is very often sufficient to cause such a change and produce a progression Then the fitting of the observed vibrational levels of the large amplitude vibration to a model potential provides accurate structural information, and magnitudes of energy barriers to changes in that structure This information is not confined to the ground electronic state but is extended to low-lying excited electronic states and, more recently, to states of the positive ion

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