

Very anharmonic molecular vibrations*

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Abstract. This is a survey of various types of highly anharmonic molecular vibrations. Its purpose is to be tutorial in nature rather than exhaustive.

Keywords. Anharmonic molecular vibrations; fluorine scrambling.

1. Introduction

Although this paper deals with very anharmonic vibrations, it is useful to give a brief summary of harmonic and slightly anharmonic vibrations for contrast.

1.1 Harmonic vibrations

For most molecular vibrations, a good initial approximation is that they are harmonic. For a diatomic molecule:

$$F = -k \cdot \Delta r \text{ (Hooke's Law),} \quad (1)$$

$$V = k(\Delta r)^2/2 \text{ (A parabola),} \quad (2)$$

$$G = \omega(v + 1/2), \quad (3)$$

where F = restoring force; Δr = displacement from equilibrium bond length (diatomic molecule); k = force constant; V = potential energy; G = vibrational energy in cm^{-1} ; ω = a frequency (in cm^{-1}) characteristic of the oscillator and v = vibrational quantum number 0, 1, 2, 3

Either (1) or (2) defines a harmonic oscillator. For a polyatomic molecule

$$2V = \sum_i^{3N-6} \lambda_i Q_i^2 \quad (4)$$

in the harmonic approximation, where Q_i = a normal coordinate (polyatomic molecule) and $\lambda_i = 4\pi^2\nu_i^2$.

1.2 Slightly anharmonic vibrations

The above equations are not adequate for precise work because molecular vibrations are actually slightly anharmonic. For a diatomic molecule the real potential has the shape of figure 1 rather than of a parabola. A parabola fits quite well near the bottom of

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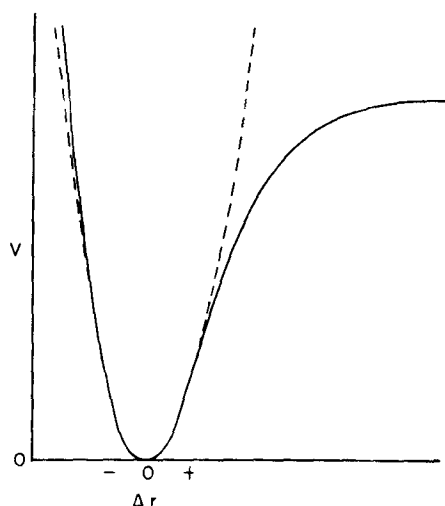


Figure 1. Potential curve for a harmonic oscillator (dashed line) and for a diatomic molecule (solid line).

the real potential well, but deviates as the bond is stretched. For small deviations from a parabola,

$$V = 1/2 k(\Delta r)^2 - l(\Delta r)^3 + m(\Delta r)^4 + \dots, \quad (5)$$

where $k \gg l \gg m \dots$. The energy levels are then given by:

$$G_v = \omega_e(v + 1/2) - (\omega_e x_e)(v + 1/2)^2 + (\omega_e y_e)(v + 1/2)^3 + \dots, \quad (6)$$

where ω_e , $\omega_e x_e$, and $\omega_e y_e$ are constants characteristic of the oscillator, with $\omega_e \gg \omega_e x_e \gg \omega_e y_e \dots$. The result is that the energy levels are no longer equally spaced, but slowly converge as v becomes larger. Hence the first overtone is slightly less than twice the fundamental frequency.

For polyatomic molecules the result is similar but more tedious to write as there are more oscillators, and there are cross terms between them as well as higher powers in each normal coordinate.

The essential point is that for small displacements the anharmonicity is usually small and can be treated by a straightforward modification of the simple harmonic oscillator. The dominant terms in the potential energy are those that are quadratic in the displacements.

1.3 Very anharmonic vibrations

There are some vibrations for which the quadratic terms are not dominant. For them the anharmonicity is not small even for small displacements. These vibrations often (but not necessarily) have two or more potential minima separated by low potential barriers. Very anharmonic vibrations are of interest for several reasons: (i) They often produce low-lying energy levels. These are significant energy sinks, and contribute importantly to the entropy and other thermodynamic properties. (ii) They give unusual spectra. If the energies are low, many states are well populated so

that transitions starting from higher states can have significant intensities. Because the anharmonicity is large, the transitions $v = 0-1, 1-2, 2-3, \dots$ are well separated in frequency, in contrast to the harmonic case where they are superimposed. Also because of the large anharmonicity the usual selection rule $\Delta v = \pm 1$ breaks down, and overtones can be surprisingly intense. These factors often lead to a rich low frequency spectrum which may be difficult to unravel. (iii) They present an intellectual challenge by being different from the usual case.

This paper is a survey of various kinds of highly anharmonic vibrations. It makes no pretense of being exhaustive; it is instead intended to be tutorial in nature. The author's hope is that it will lead the reader to see how a number of different cases fit into a coherent whole. There have been some reviews which cover portions of this subject (Wurrey *et al* 1976; Moeller and Rothschild 1971; Lister *et al* 1978).

2. Inversions. Ammonia and related compounds

We shall start with the inversion of ammonia because it was the first highly anharmonic vibration which was thoroughly studied and understood. Also, much of the background from it can be applied to ring puckering modes and to the bending of quasi-linear molecules. The ammonia inversion is discussed well by Herzberg (1945).

2.1 Potential function (part 1)

Ammonia is a pyramidal molecule which can (and does) invert (figure 2). The inverted form is *not* obtainable by a rotation. The potential function has the form shown in figure 3. If the molecule did not invert, it would be confined to one of the two potential wells of figure 3A, which would be approximately parabolic.

The fact that it does invert means that the two potential wells overlap, so that the resulting potential function has a symmetrical double minimum with a relatively low central barrier (figure 3B). This barrier is tunnelled or surmounted to produce the inversion.

Since the original wells are identical, their energy levels are also identical (figure 3A). Their vibrational wave functions overlap (the tunnelling interaction), and the levels split into two components as shown in figure 3B. Far below the top of the barrier the splitting is very small because there is little overlap of the wavefunctions, but it increases rapidly as the top of the barrier is approached. Far above the barrier the spacings become equal if the outer walls remain parabolic.

The energy levels are marked + or - in figure 3B because the corresponding wave functions are symmetric or antisymmetric to reflection at the origin ($x \rightarrow -x$). The symmetrical function always has the lower energy.

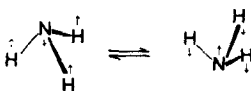


Figure 2. The inversion of ammonia.

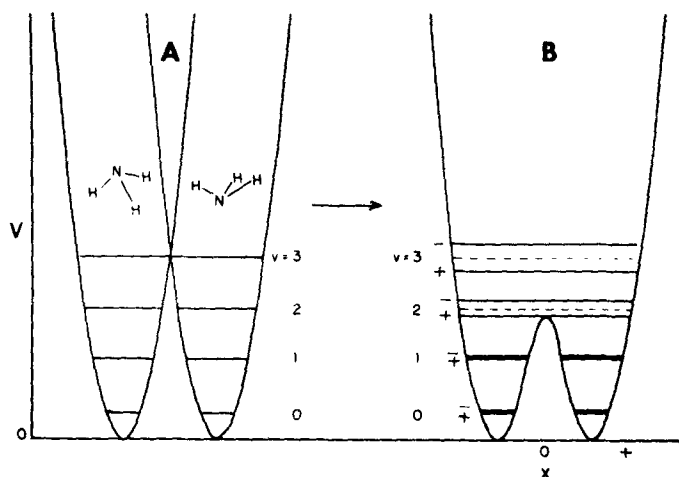


Figure 3. Potential function for the inversion of ammonia. x is the height of the nitrogen atom above the plane of the three hydrogen atoms. The splitting for $v = 0$ has been greatly exaggerated for clarity.

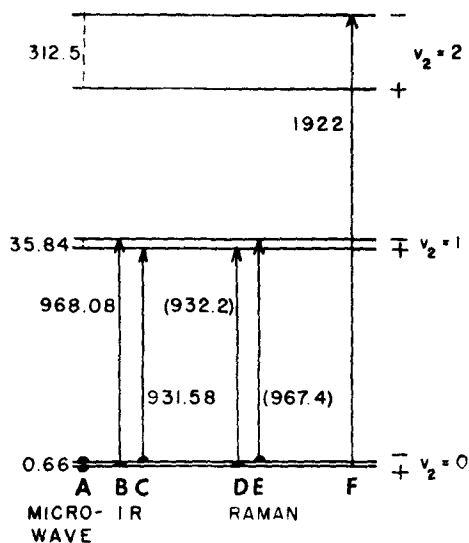


Figure 4. Ammonia. Observed transitions (cm^{-1}) between the inversion-split levels for the symmetric deformation mode ν_2 . The splitting for $v = 0$ is greatly exaggerated. Raman values (in parentheses) are calculated from the observed infrared ones. Measured Raman values are slightly different: 934.0 and 964.3 cm^{-1} (Herzberg 1945).

2.2 Selection rules

The infrared selection rule is $+\leftrightarrow -$, and the Raman one is $+\leftrightarrow +$ and $-\leftrightarrow -$. For both, $\Delta v = 0$ or ± 1 to a fair approximation. These lead to the types of transitions indicated in figure 4.

2.3 IR spectra

None of the vibrations of NH_3 is exactly a motion of the nitrogen against the plane of the three hydrogen atoms. The change of height of the pyramid is greatest for the symmetrical deformation, or umbrella mode, which is designated ν_2 . Therefore the effect of inversion is greater for it than for any of the other three fundamentals. Lines *B* and *C* of figure 4 are at 968.08 and 931.58 cm^{-1} , respectively, a separation of 36.50 cm^{-1} . This is the sum of the splittings for $v = 0$ and $v = 1$.

Cleeton and Williams (1934) performed a famous experiment in 1934 in which they measured the separation of the $v = 0$ levels directly (transition *A* of figure 4) using microwaves of 1 to 4 cm wavelength. There were two brass mirrors 3 feet (~ 91 cm) in diameter, and an echelette grating of corresponding size. One atmosphere of NH_3 was held in a cell of rubberized cloth 90 cm high, 115 cm wide, and 40 cm thick. Intense absorption at 1.25 cm or 0.8 cm^{-1} was observed. This direct observation of inversion doubling was a striking confirmation of a prediction of quantum mechanics applied to molecular structure.

Actually Randall and Wright had already found from measurements in the mid infrared that vibrational levels of NH_3 are split. They deduced that the separation in the ground state is 0.66 cm^{-1} . These and other splittings are given in table 1. The separations increase rapidly as v increases. Vibration ν_1 is the totally symmetric N-H stretch. Although its levels are much higher than those of ν_2 (3337 vs 950 cm^{-1}), they are less split because it produces a smaller change in the height of the pyramid.

2.4 Potential function (part 2)

Several algebraic forms have been suggested for the potential function. One of the best, proposed by Manning (1935), is

$$V = -C \operatorname{sech}^2 r/2\rho + D \operatorname{sech}^4 r/2\rho, \quad (7)$$

where r is the height of the pyramid, and C , D , and ρ are arbitrary constants. Wall and Glockler (1937) suggested a much simpler expression:

$$2V = [|x| - l]^2 \quad (8)$$

where l is the height of the pyramid and x is the displacement. This is considerably less accurate; it gives a barrier which is 50% too high.

By assuming an algebraic form for the potential function, and using the observed energy level separations, one can evaluate the potential constants. With the Manning equation the potential barrier is found to be 2076 cm^{-1} above the minima, so that $2\nu_2$ is

Table 1. Inversion splitting (in cm^{-1}) of vibrational levels for NH_3 and PH_3 .

v	NH_3		PH_3
	$\nu_2 (\sim 950 \text{ cm}^{-1})$	$\nu_1 (\sim 3337 \text{ cm}^{-1})$	$\nu_2 (\sim 991 \text{ cm}^{-1})$
0	0.66 (ground state)	0.66	(1.5×10^{-4}) calc.
1	35.84	0.9	2.4
2	312.6		
3	481		

just below the barrier top. The equilibrium height of the NH_3 pyramid (distance from potential maximum to minimum) is 0.38 Å.

2.5 PH_3

For phosphine the potential barrier is nearly the same as that for NH_3 , and ν_2 is similar (991 cm^{-1}). However, as shown in table 1, the splittings for ν_2 are much smaller.

2.6 Inversions in ammonia derivatives

Aniline, $\text{C}_6\text{H}_5\text{NH}_2$, provides an interesting example. At equilibrium the structure is one in which the NH_2 plane is tilted below (or above) the plane of the phenyl ring by 37.5° (Lister *et al* 1974). Since there are two equivalent structures, it is again a double minimum problem. Three types of potential functions have been used for aniline and its derivatives: (a) a Gaussian barrier in a quadratic well, (b) a quadratic barrier in a quartic well, and (c) a truncated Fourier expansion with cosine terms only, such as is commonly used for torsions (see § 4). All give nearly the same barrier height (Kydd and Kreuger 1980), which for aniline is 526 cm^{-1} (Kydd and Kreuger 1977). The second function, which is the most useful, is

$$V = -Ax^2 + Bx^4 \quad (9)$$

where x is an appropriate inversion coordinate. (This function will be described more fully in the next section.) Kydd and Mah (1982) have studied the inversion in substituted anilines, and give references to earlier work on them.

3. Inversions. Puckering of nearly planar rings

Ring puckering vibrations provide another type of inversion. Z -membered rings have $Z-3$ vibrations perpendicular to the equatorial plane of the ring. Hence 4-membered rings have one such mode, 5-membered rings have two, and so on. Bell (1945) first pointed out that these vibrations should be very anharmonic because their potential function is dominated by a quartic term. Carreira *et al* (1979) have given an excellent review of the subject.

3.1 Cyclobutane

Cyclobutane is the prototype for such molecules. At equilibrium its ring is folded, or puckered, rather than planar (figure 5). This is the result of two competing effects. On

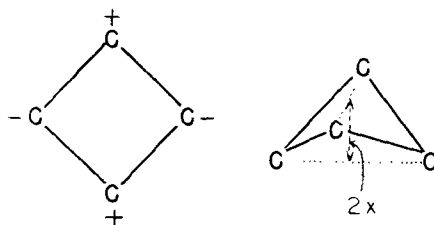


Figure 5. Cyclobutane. Two representations for the inversion, or puckering, of the ring. $2x$ is the vertical distance between the ring diagonals.

the one hand the bond angles of the four-membered ring are considerably strained when the ring is planar, and become more so if it is folded. This tends to keep the ring planar. On the other hand the repulsive interactions between the hydrogen atoms are at a maximum for a planar ring, and this tends to drive the ring into a folded conformation. The equilibrium structure is determined by the balance between these two forces.

Four-membered folded rings have a vibration which varies the extent of the folding, or puckering, of the ring. If its amplitude is large enough, the ring is inverted. The result is a symmetrical double minimum potential function analogous to that for the inversion of NH_3 (figure 6).

For cyclobutane the inversion occurs readily at room temperature. The inversion mode is forbidden in the infrared, but since it is a totally-symmetric vibration it is Raman-active and polarized. It was observed in the gas for both C_4H_8 and C_4D_8 (Stone and Mills 1970; Miller and Capwell 1971). Because of the large anharmonicity, several transitions were observed (figure 7) and were assigned as shown on the right side of figure 6.

Defining the coordinate x as half the distance separating the ring diagonals (figure 5) (x is zero for the planar conformation) a satisfactory expression for the potential function is

$$V = -Ax^2 + Bx^4. \quad (10)$$

Only even terms appear in the power series because of the mirror symmetry of the potential [$V(x) = V(-x)$]. The first term inserts an inverted parabola in the center of the quartic well, thus giving a central barrier and two symmetrical wells. Note that the

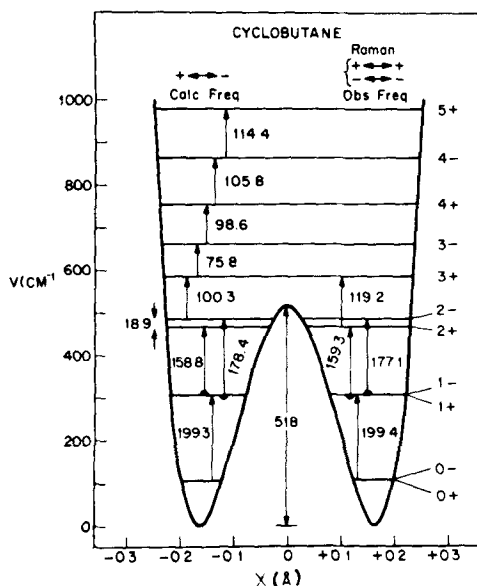


Figure 6. Cyclobutane. Potential curve and energy levels for the ring puckering. Observed Raman transitions are shown on the right, and some calculated infrared ones on the left. (Miller and Capwell 1971).

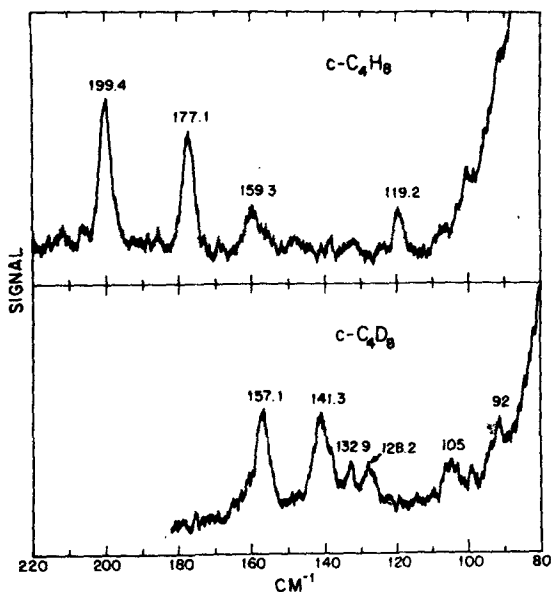


Figure 7. Observed Raman bands for the puckering mode of cyclobutane and cyclobutane- d_8 . Gas, 1000 torr pressure. Slit width 2 cm^{-1} . (Miller and Capwell 1971).

outer walls in this case are quartic and not quadratic, so the separations between the energy levels above the top of the barrier will get steadily larger (figure 6.)

This potential expression is applied in the Schrödinger equation and the energy levels are calculated. Their differences are compared with the observed spectrum, and the parameters A and B are adjusted until the fit is optimized. The largest uncertainty is in the value of the reduced mass, which depends on the assumed form of the normal coordinate. Fortunately the barrier height is independent of the reduced mass.

Some results which Miller and Capwell (1971) obtained for cyclobutane are:

$$V = -3.790 \times 10^4 x^2 + 6.932 \times 10^5 x^4 \quad (11)$$

Barrier height = $518 \pm 5\text{ cm}^{-1}$; Equilibrium dihedral angle = 35° ; Potential minima occur at $x = \pm 0.165A$.

Figure 6 shows the potential function and energy levels. The four observed Raman transitions are shown on the right. Note that the highest is from a level just below the barrier to one just above the barrier. The puckering frequencies are forbidden in the infrared, but they have been deduced from infrared-active combination tones (Miller and Capwell (1971)). In the left-hand well of figure 6 are given some calculated values for $+$ \leftrightarrow $-$ transitions, which compare well with the frequencies deduced from combination tones.

3.2 Other 4-membered ring molecules

The inversions of many of the 4-membered ring molecules studied have been summarized well by Blackwell and Lord (1972) (table 2) and Carreira *et al* (1979). Wurrey *et al* (1976) also reviewed Raman studies of them.

Table 2. Barriers for inversion of some 4-membered rings.
$$\begin{array}{c}
 \text{CH}_2\text{-CH}_2 \\
 | \quad | \\
 \text{CH}_2\text{-X}
 \end{array}$$

X	Barrier (cm ⁻¹)	Equilibrium conformation
CH ₂	510	Puckered
CF ₂	240	Puckered
SiH ₂	440	Puckered
O	15	Planar
S	274	Puckered
Se	373	Puckered
> C=O	5	Planar
> C=CH ₂	160	Puckered

Blackwell and Lord 1972.

If the ground state is above the central potential maximum, the molecule is planar. However the existence of the low barrier makes itself known by its measurable effect on the energy levels. Trimethylene oxide is an example.

So far it has been assumed that the double minimum is symmetrical. This is not true for all four-membered ring molecules. A good example is trimethylene imine (Carreira *et al* 1979; Carreira *et al* 1969). Because inversion moves the N-H between two non-equivalent positions (figure 8), the corresponding potential has an unsymmetrical double minimum (figure 9).

3.3 Five membered rings

These have two out-of-plane modes. However if the ring contains a double bond, as in cyclopentene or 2,5-dihydrofuran, it may be regarded as a pseudo 4-membered ring as far as ring puckering is concerned. The reason is that it is so difficult to twist the double bond that this mode has a much higher frequency and is approximately harmonic.

Cyclopentene has a remarkable far infrared spectrum due to the puckering mode (figure 10). Figure 11 shows that the transitions involve levels far above the potential barrier (Laane and Lord 1967).

The situation in cyclopentane is more complicated. If it had a planar ring, the two

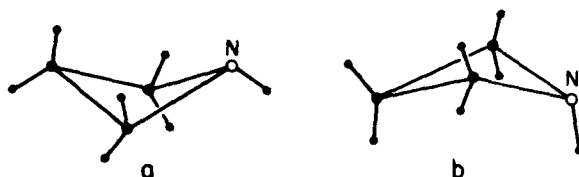


Figure 8. Two non-equivalent conformations for trimethylene imine leading to an asymmetrical ring-puckering potential function. The interconversion of the conformers may also be accomplished *via* the N-H rocking vibration. (Carreira and Lord 1969).

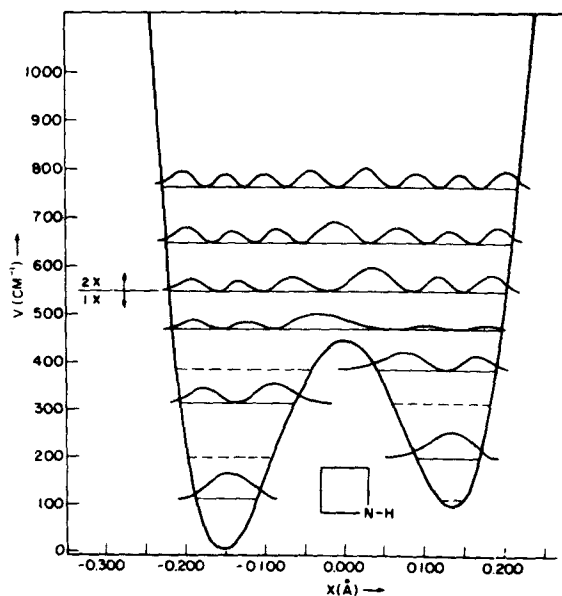


Figure 9. Ring puckering potential function for trimethylene imine. The squared wave functions indicate the definite left well \leftrightarrow right well identifications of the first four levels. (Carreira and Lord 1969).

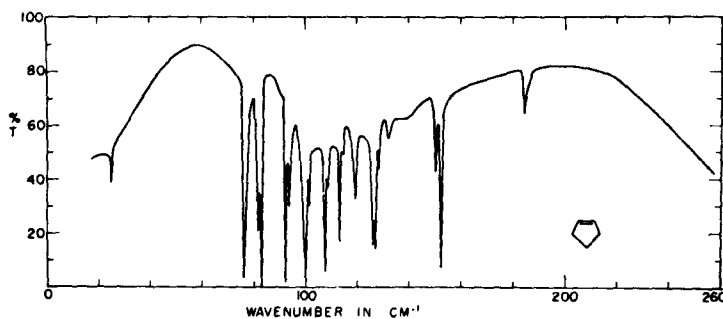


Figure 10. Cyclopentene. Far infrared absorption due to the ring puckering mode. (Laane and Lord 1967).

out-of-plane ring modes would be degenerate. However it is not planar, and a phenomenon termed pseudorotation results. This is a rather complex subject which we shall not consider here (Carreira *et al* 1979 and Laane 1972 may be consulted).

If the 5-membered ring has a heteroatom, as in tetrahydrofuran, the degeneracy is removed, the pseudorotation becomes hindered, and the situation is so complex that the spectrum could not be fully interpreted (Carreira *et al* 1979).

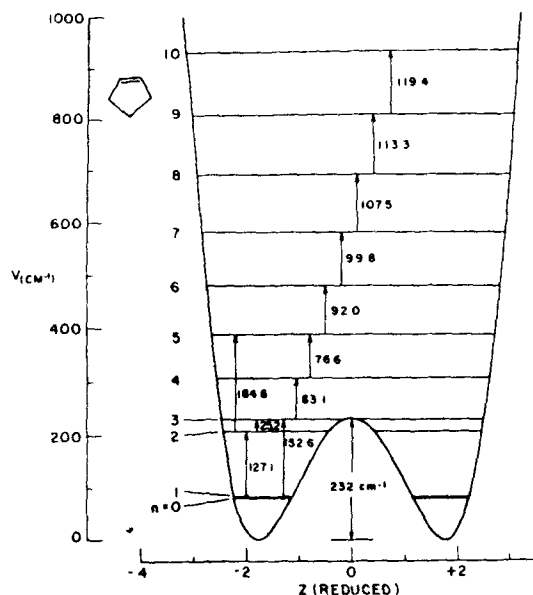


Figure 11. Ring puckering in cyclopentene: potential curve, energy levels, and observed transitions. (Laane and Lord 1967).

4. Torsions or hindered internal rotations

4.1 Introduction

In rotations around single bonds the potential energy almost always changes during the rotation, so there is a potential barrier to be surmounted. The form of the potential function determines the conformation of a molecule. This is important, as is well known for DNA, proteins, and synthetic polymers. The stable conformation of ethane is the staggered form rather than the eclipsed one, that for 1,2-dichloroethane is the *trans* form, and that for acetaldehyde has a hydrogen atom opposed to the oxygen atom (figure 12A). (Would the reader have predicted the last of these? A useful rule, which always works, is to regard the double bond as two bent single bonds, and then assume a staggered conformation [figure 12B]).

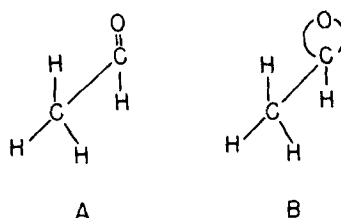


Figure 12. A. Stable conformation of acetaldehyde. B. The banana-bond model for deducing the stable conformation.

4.2 Potential function for torsion

In contrast to inversion, where the outer walls of the potential well rise steeply, the potential function for torsion must be cyclic. By far the most widely used expression is a cosine equation obtained as follows. Let α be the angle of internal rotation, and write $V(\alpha)$ as a Fourier series:

$$V(\alpha) = \frac{a_0}{2} + \sum_{n=1}^{\infty} [a_n \cos n\alpha + b_n \sin n\alpha]. \tag{12}$$

Since $V(-\alpha) = V(\alpha)$, all the $\sin n\alpha$ terms are zero because $\sin(-\alpha) = -\sin \alpha$. Hence

$$V(\alpha) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos n\alpha. \tag{13}$$

This is now modified so that V is always positive and its smallest value is zero:

$$V(\alpha) = \sum_{n=1}^{\infty} V_n(1 - \cos n\alpha)/2. \tag{14}$$

The first few terms written explicitly are:

$$V(\alpha) = V_1(1 - \cos \alpha)/2 + V_2(1 - \cos 2\alpha)/2 + V_3(1 - \cos 3\alpha)/2 + \dots \tag{15}$$

which gives $V = 0$ when $\alpha = 0$.

Figure 13 shows the $n = 1, 2,$ and 3 terms, and their sum, for $V_1 = V_2 = V_3$. Potential functions of various shapes can be obtained by adjusting the values of V_n .

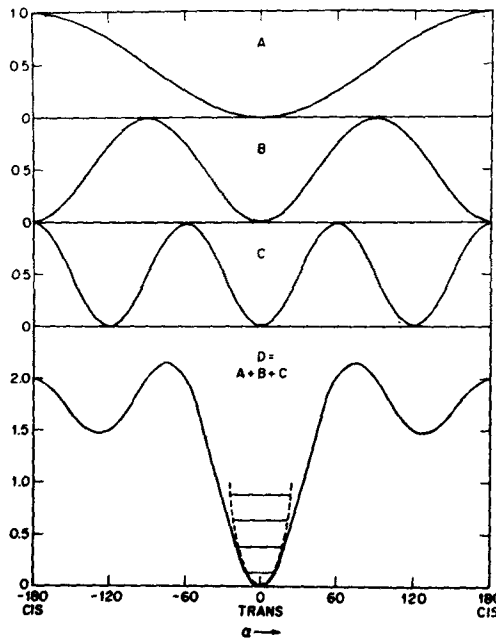


Figure 13. Components of the potential function $V(\alpha) = \sum_{n=1}^{\infty} V_n(1 - \cos n\alpha)/2$. A. $(1 - \cos \alpha)/2$ B. $(1 - \cos 2\alpha)/2$ C. $(1 - \cos 3\alpha)/2$ D. $A + B + C$. (Fateley et al 1965).

If the molecule has symmetry, some of the V_n terms may be zero. Consider acetaldehyde as an example, which has a three-fold rotor rotating relative to a planar frame (figure 12). Because of the symmetry, V must be three-fold symmetric; *i.e.*

$$V(\alpha) = V(\alpha \pm 2\pi/3). \quad (16)$$

Only terms in (14) where n is a multiple of 3 will satisfy this, so the series becomes

$$V(\alpha) = V_3(1 - \cos 3\alpha)/2 + V_6(1 - \cos 6\alpha)/2 + V_9(1 - \cos 9\alpha)/2 + \dots \quad (17)$$

As another example, consider $\text{H}_3\text{C}-\text{BH}_2$. The bonds around the boron atom are planar, so $V(\alpha)$ is now six-fold symmetric. Then n must be a multiple of 6, and the series is

$$V(\alpha) = V_6(1 - \cos 6\alpha)/2 + V_{12}(1 - \cos 12\alpha)/2 + \dots \quad (18)$$

Toluene and nitromethane are other molecules in this category.

4.3 Procedure

The procedure for deducing V_n and the barrier height has been described in detail earlier (Fateley and Miller 1961; 1963). In brief, the analytical expression for $V(\alpha)$ is applied in the Schrödinger equation and the latter is solved for the allowed energies. In doing this, three assumptions are made.

(i) That the V_n s are known. They really are not, and calculations are made with various trial values. (ii) That the reduced mass for the internal rotation is known, and often that it is independent of α . This can be a problem. (iii) That the internal rotation is independent of all other vibrations. In some cases this is a questionable assumption.

The solutions are those for the Mathieu equation, and are tabulated. Once the energy levels have been calculated, differences between them can be taken and compared with the observed spectrum. The V_n parameters are varied until a satisfactory match is obtained.

We shall now consider some specific examples.

4.4 Torsions with two potential minima

4.4a. *Para-fluorophenol*: (Miller 1968). This has a torsion with a two-fold symmetric potential function, *e.g.* with two equivalent minima and maxima (figures 14A, 15). Because of tunnelling, the torsional levels are split into symmetric and antisymmetric components analogous to those for inversion. Three infrared transitions were observed. With the potential function

$$V(\alpha) = V_2(1 - \cos 2\alpha)/2 + V_4(1 - \cos 4\alpha)/2 \quad (19)$$

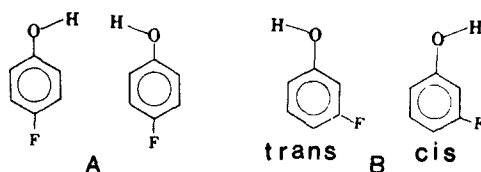


Figure 14. A. The two equivalent stable conformations of *para* fluorophenol. B. The two non-equivalent planar conformations of *meta* fluorophenol.

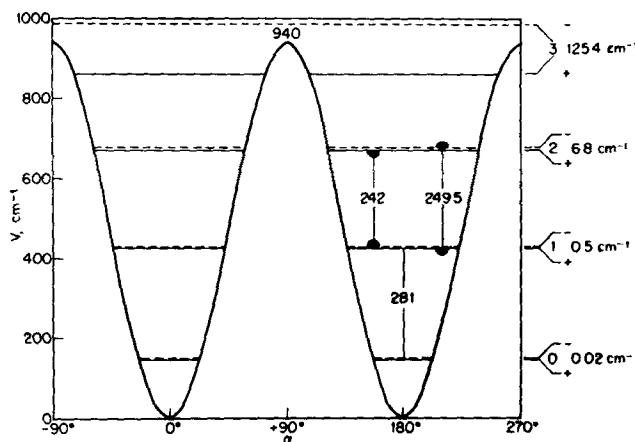


Figure 15. Potential function and energy levels for hindered internal rotation of a symmetrical two-fold rotor. Calculated and drawn to scale for *para*-fluorophenol. $V_2 = 940 \text{ cm}^{-1}$, $V_4 = 0$. (Miller 1968).

they gave $V_2 = 940 \text{ cm}^{-1}$, $V_4 \cong 0$, and calculated + to - splittings as shown in figure 15.

4.4b. *Meta*-fluorophenol: (Manocha *et al* 1973). The far infrared spectrum of this compound contains a striking group of doublets (figure 16). Symmetry indicates that the potential function has two non-equivalent minima and two equal maxima

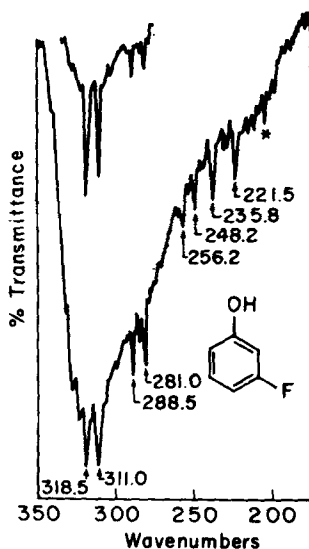


Figure 16. Infrared spectrum of *meta*-fluorophenol in the gas phase. Upper spectrum, 1 m cell at room temperature. Lower spectrum, 1 m cell at 65°C. The weak band at 202 cm^{-1} (marked with an asterisk) is due to a trace of water vapour. (Manocha *et al* 1973).

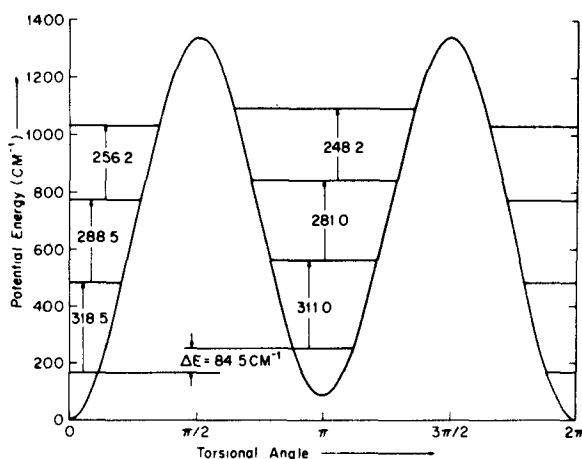


Figure 17. *Meta*-fluorophenol. Calculated potential curve, energy levels, and observed transition frequencies for internal rotation. $\alpha = 0$ for the *cis* form. (Manocha *et al* 1973).

(figures 14B and 17). The torsional energy levels in the two wells are no longer identical, and therefore do not interact significantly. Instead the stacks of levels in the two wells are essentially independent of one another, giving rise to doublets. From the three transitions observed in each well, the potential function in the form of (14) was deduced to have the constants $V_1 = 88.1$, $V_2 = 1282.9$, $V_4 = -12.2$, $V_3 = V_5 = V_6 \approx 0$. For these values V_1 gives the difference in energy between the two potential minima. The IR data do not indicate which rotamer has the lower energy, but a theoretical calculation indicates that it is the *cis* form for this compound (Manocha *et al* 1973).

4.4c. *Hydrogen peroxide*: (Hunt *et al* 1965; Hunt and Leacock 1966). This is the simplest molecule having an internal rotation (figure 18). Here the torsional potential function has two equivalent minima and two different maxima (figure 19). The expression used was

$$V = V_0 + V_1 \cos \alpha + V_2 \cos 2\alpha + V_3 \cos 3\alpha. \quad (20)$$

The purpose of V_0 is to make the potential zero at the minimum. The V_1 term gives the interaction between the two OH dipoles, which has a periodicity of 2π . The V_2 term includes an interaction between the non-bonding p electrons on the oxygen atoms, which has a periodicity of π . The V_3 term is merely a small correction. It was found that $V_0 = 787$, $V_1 = 993$, $V_2 = 636$, and $V_3 = 44 \text{ cm}^{-1}$.

4.4d. *Butadiene* (figure 20): The *trans* form is known to be the stable rotamer, but for some time there was a question whether a metastable rotamer also exists. If so, is it the *cis* form (coplanar) or the *gauche* one (twisted to give either of two equivalent non-planar conformations)? Carreira (1975) seems to have settled the question in favor of the *cis* form. The potential curve and energy levels are shown in figure 21. He observed 7 Raman transitions in the *trans* well and 3 in the *cis* well. The minimum of the *cis* well is 873 cm^{-1} above that of the *trans*, and the barrier for *trans* to *cis* is 2504 cm^{-1} . The potential function was equation 14, with $V_1 = 600 \pm 100$, $V_2 = 2068 \pm 50$, $V_3 = 273 \pm 8$, and $V_4 = -49 \pm 18 \text{ cm}^{-1}$.

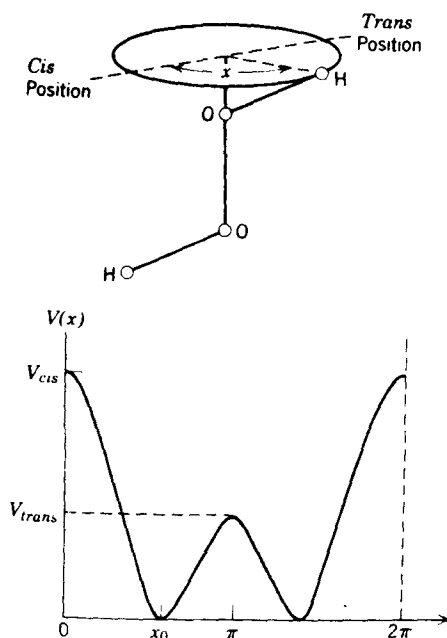


Figure 18. Hydrogen peroxide. Description of the torsion, and form of the hindering potential. (Hunt *et al* 1965).

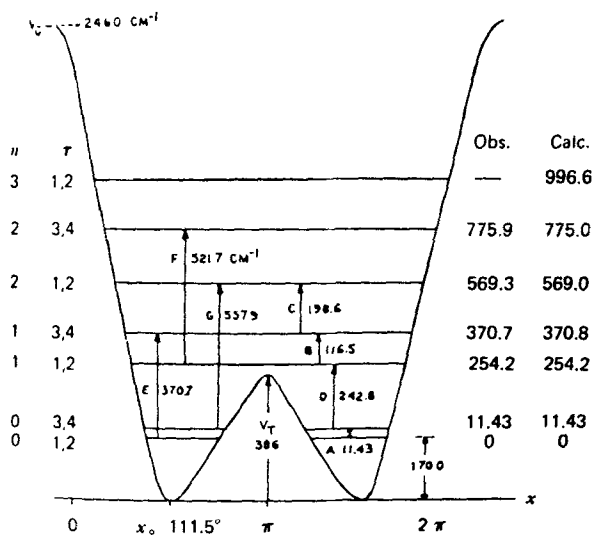


Figure 19. Potential curve and energy levels for the torsion in hydrogen peroxide. (Hunt *et al* 1965).

4.5 Torsions with three potential minima

We now consider the case where the potential function is three-fold symmetric, as for acetaldehyde (figure 22). If there were no interaction between the torsional levels, they

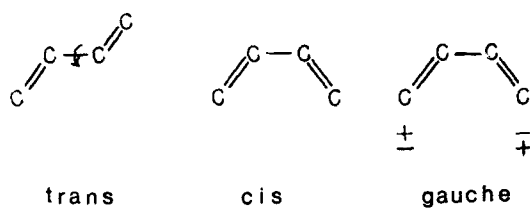


Figure 20. Carbon skeleton of butadiene showing three possible rotamers.

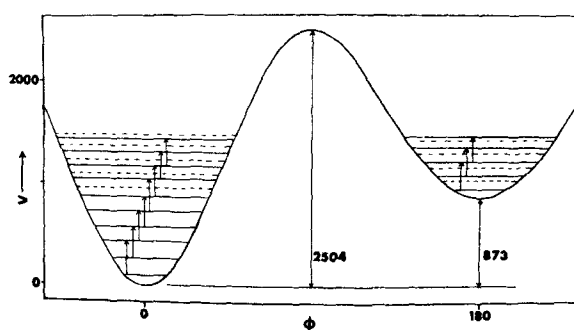


Figure 21. 1,3-butadiene. Potential function, energy levels, and observed transitions for the torsion. Zero degrees corresponds to the *trans* conformation. (Carreira 1975).

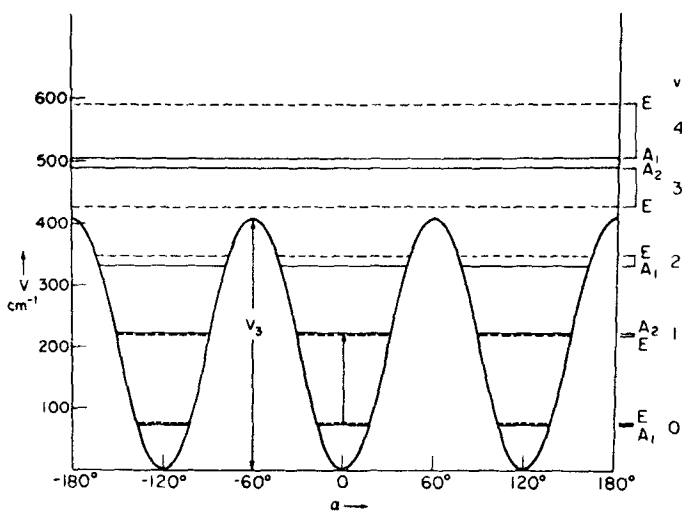


Figure 22. Potential curve and energy levels for hindered internal rotation of a symmetrical three-fold rotor. $V(\alpha) = V_3 (1 - \cos 3\alpha)/2$. Drawn to scale for acetaldehyde, with $V_3 = 413 \text{ cm}^{-1}$. (Fateley and Miller 1961 with slight modification).

would be three-fold degenerate. However the tunneling interaction splits them into a singly degenerate and a doubly degenerate pair. The sequence is A_1-E , $E-A_2$, A_1-E , $E-A_2$, --- (figure 22). The potential function has only V_3 , V_6 , $V_9 \dots$ terms (equation 17).

4.5a. *Ethyl chloride*: The observed infrared torsional bands for ethyl chloride and three of its deuterated derivatives are given in figure 23. Figure 24 shows one of the three potential wells, and five torsional transitions which were observed for the parent compound (Fateley *et al* 1970). The latter sample the well over about two thirds of its depth, and provide an opportunity to see whether the V_6 term is important. The inclusion of a V_6 term does not change the height of the threefold barrier because it makes no contribution at either the potential minimum or maximum. The barrier height is therefore still given by V_3 . What the V_6 term does do is to change the shape of the well, as shown in an exaggerated way in figure 25. A positive V_6 makes the potential well narrower and the barrier broader. It therefore causes the torsional levels for $v = 0, 1, 2 \dots$ to be somewhat more widely separated than they would be if V_6 were zero. A negative V_6 has the opposite effect; the levels are slightly compressed relative to their spacings for $V_6 = 0$. Conversely, if the separations of the levels can be measured, it might be possible to evaluate V_6 .

For ethyl chloride the 0-1, 1-2, 2-3, and 3-4 torsional transitions have been observed (figures 23 and 24). It was found that V_6 is zero. For several other molecules V_6 is non-zero, but always small—less than 3% of V_3 (Fateley and Miller 1963).

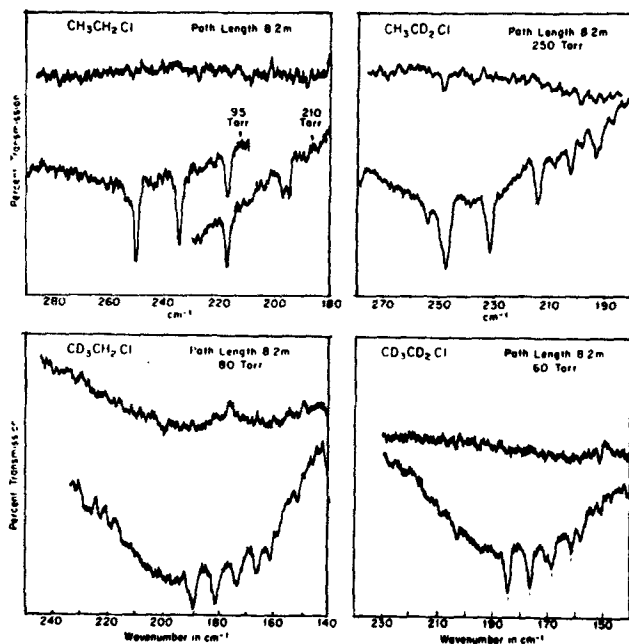


Figure 23. Observed infrared torsional bands for ethyl chloride and three of its deuterated derivatives. The upper curve is the transmission of the evacuated cell. Spectral slit width was $1.3-1.8 \text{ cm}^{-1}$. (Fateley *et al* 1970).

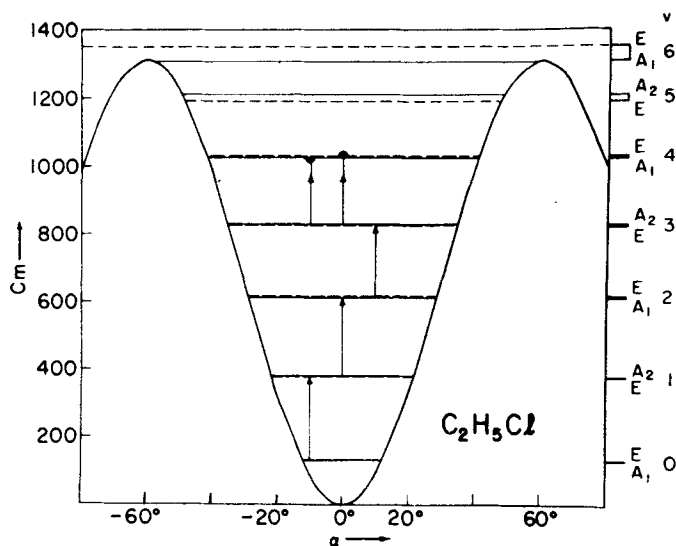


Figure 24. Potential curve and energy levels for the torsion in ethyl chloride. The observed infrared transitions are indicated by vertical lines. (Fateley and Miller 1963).

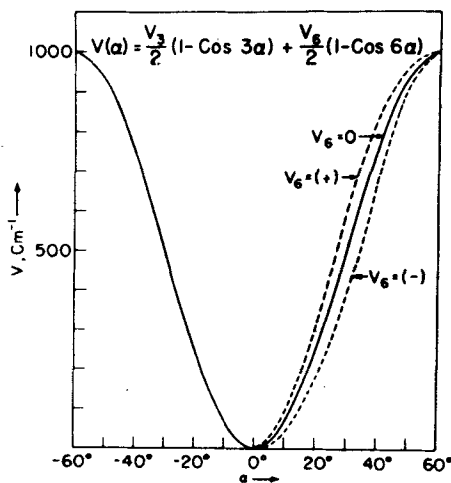


Figure 25. Effect of V_6 on the shape of the potential curve for a symmetrical three-fold rotor. $V_3 = 1000$, $V_6 = 100, 0$, and -100 cm^{-1} . (Fateley and Miller 1963).

4.5b. Ethane: This also has a three-fold symmetric potential function. The torsional transition is forbidden in both the infrared and Raman spectrum, but Weiss and Leroi (1968) observed it in the infrared at high pressure and long path length (6 atm and 10 m). They found the 0–1 transition at 289, 1–2 A_1 and 255, and 1–2 E at 258 cm^{-1} . From these they calculated $V_3 = 1024 \pm 9 \text{ cm}^{-1}$ and $V_6 = 0$.

4.5c. *1,2-dichloroethane*: This molecule can be in either the *trans* or in one of the two equivalent *gauche* forms (figure 26). Since the former is known to be more stable, the potential curve has the form shown in figure 27. Mizushima *et al* (1975) have done a great deal of work on this molecule, and have published a lengthy paper on its vibrations. They observed only one torsional transition, at 125 cm^{-1} in the infrared spectrum of the liquid, which was assigned to both *trans* and *gauche* rotamers. However they *calculated* eight transitions in the *trans* well and four in the *gauche* wells.

Torsions with four- and five-fold barriers have received little study, so we go to the six-fold case.

4.6 Torsions with a six-fold symmetric potential

Toluene, nitromethane, and CH_3BF_2 are examples of this. In each of these cases a C_{3v}

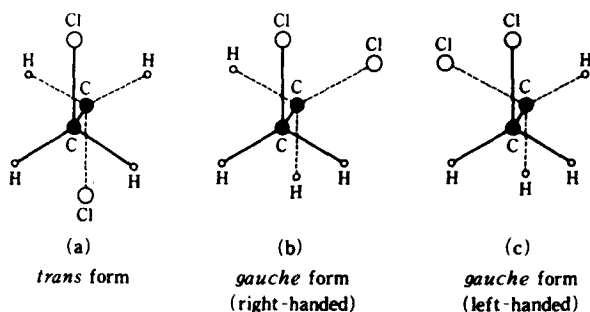


Figure 26. Stable conformations of 1,2-dichloroethane (Mizushima *et al* 1975).

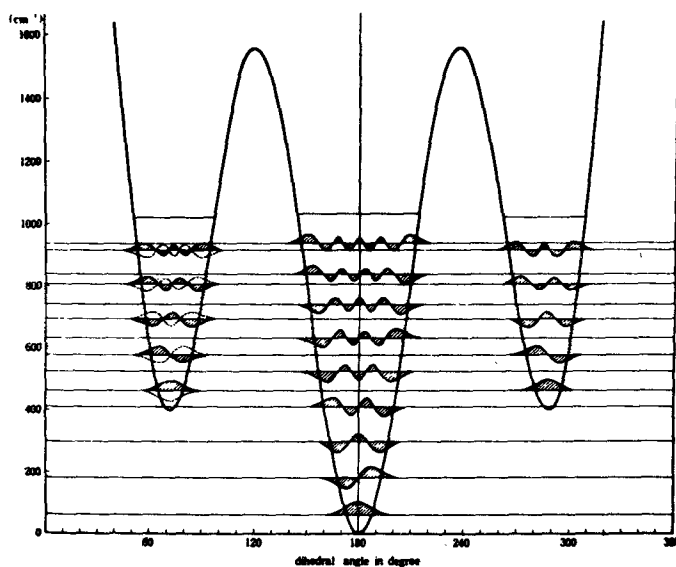


Figure 27. 1,2-dichloroethane. Calculated energy levels and eigenfunctions for the internal rotation (Mizushima *et al* 1975).

top rotates relative to a C_{2v} frame, with the C_3 and C_2 axes co-linear. The potential function is equation (18). The potential barriers are very small: 12.7 cm^{-1} for toluene, 2.11 cm^{-1} for CH_3NO_2 , and 4.82 cm^{-1} for CH_3BF_2 (all from microwave measurements). This can be rationalized qualitatively by noting that $V(\alpha)$ oscillates so frequently during one cycle of rotation that it does not have an opportunity to become large.

4.7 More complex torsions

Many systems have asymmetrical potential functions for torsion. For example $\text{XYZC-CH}_2\text{Cl}$ has three non-equivalent wells. Compton (1981) has reviewed the relatively few asymmetrical potentials which have been studied. Another type of complication which occurs when several rotors are attached to the same atom, as in $(\text{CH}_3)_2\text{O}$, $(\text{CH}_3)_2\text{S}$, and $(\text{CH}_3)_3\text{CX}$, is that they interact ("gear"). This topic has been discussed by Moeller and Rothschild (1971) and by Groner *et al* (1981).

5. Bending modes of quasi-linear molecules

There are several molecules with a linear or nearly linear skeleton which have a very anharmonic bending vibration. They are termed quasi-linear, carbon suboxide, O=C=C=C=O , is the outstanding example. Its vibrational spectrum was a puzzle for a long time, and some details are still not understood. Some of its bands have remarkable fine structure. It is now known that the lowest bending mode, the infrared active ν_7 , is highly anharmonic (Carreira *et al* 1973). It has a double minimum potential with a low barrier of $14 \pm 2 \text{ cm}^{-1}$ at the linear configuration. Since the zero point energy level is at 19.7 cm^{-1} , and above the barrier, the molecule is linear in all vibrational states. The deduced potential function is:

$$V(\text{cm}^{-1}) = -(6.40 \pm 0.36)q^2 + (0.728 \pm 0.010)q^4 \quad (21)$$

where q is a reduced polar coordinate. (Note that this has the familiar form $V = -Ax^2 + Bx^4$.) The potential curve is shown in figure 28, together with some energy levels.

It is surprising that C_3O_2 has this potential function and barrier, and that the bending mode is so low. One would expect the system of cumulated double bonds to be relatively rigid. A theoretical explanation has been offered by Olsen and Burnelle (1969) *via* some molecular orbital calculations. The other two bending modes are conventional.

Another well-studied example is disiloxane, $\text{H}_3\text{Si-O-SiH}_3$. Durig *et al* (1977) obtained the Raman spectra of the gaseous parent compound and its perdeuterated derivative, and have reviewed other work. They conclude that the molecule at equilibrium is bent, with an Si-O-Si angle of $149 \pm 2^\circ$. The barrier to linearity is 112 cm^{-1} . At room temperature many of the molecules are above the barrier, so the assembly behaves in some respects as though the molecules were linear. The potential function is

$$V(\text{cm}^{-1}) = -21.9q^2 + 1.07q^4 \quad (22)$$

where q is a reduced polar coordinate.

Other molecules showing quasi-linear behavior are carbon sub-sulfide (S=C=C=C

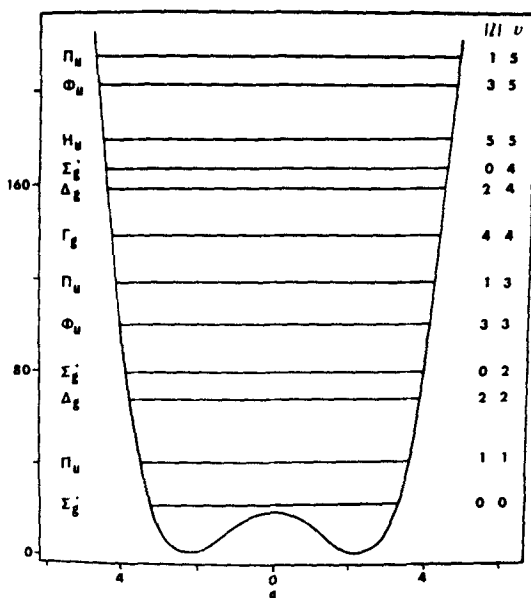


Figure 28. Carbon suboxide. A cross-sectional slice of the potential surface for the v_7 bending mode. The energy levels are labelled according to the v and $|l|$ quantum numbers and their respective symmetries (Carreira *et al* 1973).

$=S$), C_3 , and some compounds, containing the groups $-\dot{S}iNCO$, $-\dot{S}iNCS$, or $-\dot{S}iN_3$ (Wurrey *et al* 1976).

6. Fluorine scrambling in PF_5

Phosphorus pentafluoride is a trigonal bipyramid, with the two axial fluorines distinctly different from the three equatorial ones. For example the bond length of $P-F$ (axial) is 1.577 Å, and for $P-F$ (equatorial) is 1.534 Å. Nonetheless NMR spectroscopy gives only one fluorine resonance in both gas and liquid. In the liquid this is true down to $-140^\circ C$. Therefore there is some mechanism which scrambles the axial and equatorial fluorines rapidly relative to the NMR time scale. It operates for isolated molecules of gas. What is it?

Berry (1960) suggested that the interchange occurs *via* the doubly degenerate axial bending vibration (figure 29). This mode, designated v_7 , is Raman active and is the lowest fundamental, at 175 cm^{-1} . The interchange has a barrier corresponding to a C_{4v} structure. If the barrier is low, the corresponding vibration should be very anharmonic. Bernstein, *et al* (1975) looked for anharmonicity in the form of hot bands around 175 cm^{-1} , and found eight transitions in the Raman spectrum of the gas (figure 30). They interpreted these with a potential function

$$V(\rho, \phi) = 1/2 a\rho^2 - b \cos(3\phi)\rho^3 + c\rho^4 \quad (23)$$

where ρ and ϕ are polar displacement coordinates. The barrier for C_{4v} geometry is 1371 cm^{-1} .

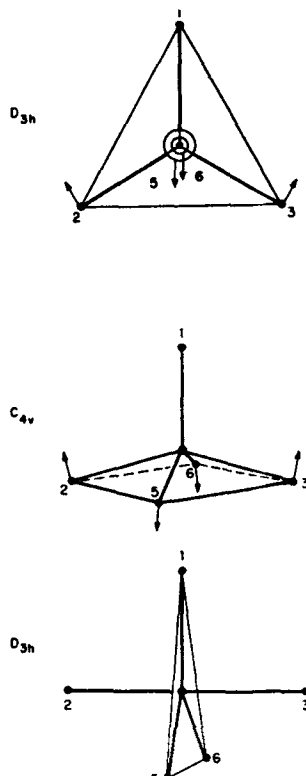


Figure 29. Possible mechanism for the fluorine scrambling in PF_5 (Hoskins and Lord 1967).

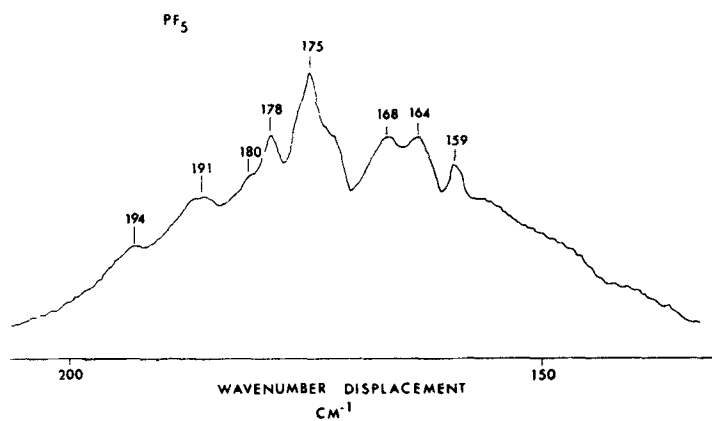


Figure 30. PF_5 . Gas phase Raman spectrum of the ν_7 mode at about 1 cm^{-1} resolution (Bernstein *et al* 1975).

Similar results should apply to molecules such as AsF_5 , VF_5 , TaF_5 , and NbF_5 , but results are not yet available.

7. Conclusions

Five types of very anharmonic vibrations have been considered for which the potential energy term that is quadratic in the displacement coordinate is not the major one, in contrast to harmonic modes.

Inversions, ring puckerings, and certain bending modes of quasi-linear molecules have double minima potentials which can usually be represented by an inverted parabola centered in a quartic well. For torsions the potential curves are cyclic so there are no walls rising indefinitely. Their curves can have any of a large variety of shapes with 2, 3, 4, 5, 6 . . . wells which may or may not be identical.

In conclusion, it is worth mentioning that these low-frequency, large amplitude vibrations are often very sensitive to the physical state, sometimes *increasing* in frequency by as much as 20% on going from gas to liquid (benzaldehyde) (Fateley *et al* 1964). One should therefore be cautious about using condensed state values to deduce potential functions and barriers, especially because the square of the frequency is involved.

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