

2.5 THE QUARTIC-QUADRATIC OSCILLATOR

The oxygen atom of the water molecule possesses two lone electron pairs. Together with the two O-H bonds, these are arranged in a tetrahedral configuration wrt. the oxygen. To form a hydrogen bonded complex the HF molecule can approach either of the two pairs giving rise to two equivalent tetrahedral complex geometries. The conversion from one tetrahedral form to the other can be achieved by inversion through the planar configuration, which is normally expected to involve overcoming an energy barrier. A one-dimensional section through the molecular potential energy hyper-surface corresponding to the inversion vibration would therefore be of symmetric double minimum type and would no longer be described even approximately by the harmonic oscillator.

(i) The potential

The most successful analytical form for a double minimum potential is the quartic-quadratic oscillator:

$$V = ax^4 + bx^2 \quad 2.97$$

where x is a linear displacement along the vibrational coordinate and a and b are constants. The quartic-quadratic oscillator has been widely used for treating low frequency vibrations in small ring molecules.²⁶ It has also been used as an inversion potential for ammonia²⁷ and for cyanamide (NH_2CN),²⁸ which has a structure similar to that of $\text{H}_2\text{O}\cdots\text{HF}$.

The Hamiltonian for a one-dimensional quartic-quadratic oscillator is:

$$H = -\frac{\hbar^2}{2\mu} p_x^2 + V \quad 2.98$$

where: $p_x = -i\hbar/dx$

μ is the reduced mass for the vibration

V is given by eq. 2.97

If we change to a new dimensionless coordinate z defined by:

$$z = (2\mu/\hbar^2)^{1/6} a^{1/6} x \quad 2.99$$

and also let:

$$A = (\hbar^2/2\mu)^{2/3} a^{1/3} \quad 2.100$$

$$B = (2\mu/\hbar^2)^{1/3} a^{-2/3} b \quad 2.101$$

the Hamiltonian 2.98 transforms to:

$$\begin{aligned} H &= A(p_z^2 + z^4 + Bz^2) \\ &= AH_z \end{aligned} \quad 2.102$$

The new Hamiltonian corresponds to the reduced potential:

$$V = A(z^4 + Bz^2) \quad 2.103$$

with:

$$V_0 = AB^2/4 \quad 2.104$$

$$z_{\min}^2 = -B/2 \quad 2.105$$

where V_0 is the height of the central barrier and z_{\min} are the z coordinates of the two minima.

The Hamiltonian 2.102 does not have solutions that are in closed analytical form and the problem is solved using approximate methods. The anharmonic eigenfunctions are expressed as linear combinations of some other functions ϕ_v where:

$$\psi_{\text{ah}}^i = \sum_v c_v^i \phi_v \quad 2.106$$

The energy matrix is set up in the ϕ_v basis set and then diagonalized. The resulting eigenvalues and the eigenvectors give the anharmonic energy levels and the coefficients c_v^i respectively. It is possible, by making use of the form of 2.102, to determine the vibrational energy levels by, first, solving the dimensionless Hamiltonian H_z (with $V = z^4 + Bz^2$), then scaling up the solutions with the constant A . A useful tabulation of the solutions to H_z , for a range of values of B , is given in ref.27. The harmonic oscillator basis set is normally used for the functions ϕ_v and the non-zero matrix elements necessary for setting up H_z are listed in Table 2.3. Since the energy matrix is infinite in v , the number of basis functions used in the calculation has to be in excess of the number of the required energies. The first fifty harmonic oscillator functions are regarded as being sufficient to determine the first ten quartic-quadratic levels accurately. The summation in 2.106 should therefore be for v ranging from 0 to 49.

Once the eigenfunctions ψ_{ah} are available, the expectation values of the various powers of the z coordinate can be evaluated. Thus:

$$\langle z \rangle_{ii} = \langle z^3 \rangle_{ii} = 0 \quad 2.107$$

$$\begin{aligned} \langle z^2 \rangle_{ii} &= \frac{1}{2} \sum_{v=0}^{49} (c_v^i)^2 (2v+1) + \frac{1}{2} \sum_{v=0}^{47} c_v^i c_{v+2}^i \{(v+1)(v+2)\}^{\frac{1}{2}} \\ &+ \frac{1}{2} \sum_{v=2}^{49} c_v^i c_{v-2}^i \{v(v-1)\}^{\frac{1}{2}} \end{aligned} \quad 2.108$$

$$\begin{aligned} \langle z^4 \rangle_{ii} &= \frac{3}{4} \sum_{v=0}^{49} (c_v^i)^2 (2v^2 + 2v + 1) + \frac{1}{2} \sum_{v=0}^{47} c_v^i c_{v+2}^i \\ &\quad (2v+3)\{(v+1)(v+2)\}^{\frac{1}{2}} \\ &+ \frac{1}{2} \sum_{v=2}^{49} c_v^i c_{v-2}^i (2v-1)\{(v-1)v\}^{\frac{1}{2}} \\ &+ \frac{1}{4} \sum_{v=0}^{45} c_v^i c_{v+4}^i \{(v+1)(v+2)(v+3)(v+4)\}^{\frac{1}{2}} \\ &+ \frac{1}{4} \sum_{v=4}^{49} c_v^i c_{v-4}^i \{v(v-1)(v-2)(v-3)\}^{\frac{1}{2}} \end{aligned} \quad 2.109$$

(ii) Treatment of rotational constants

The expectation values 2.107 - 2.109 can be used to treat the effect of a double minimum potential on the observed rotational constants. If there are no

Coriolis effects, the vibration-rotation interaction is thought to be the result of quantum mechanical averaging of the molecular structure over the vibration. The instantaneous rotational constant B_{gg} (A, B or C) can be expressed as a Taylor series in the normal coordinates²⁹:

$$B_{gg} = B_{gg}^0 + \sum_k^{3N-6} b_k^{gg} Q_k + \sum_{kl}^{3N-6} b_{kl}^{gg} Q_k Q_l + \sum_{klm}^{3N-6} b_{klm}^{gg} Q_k Q_l Q_m + \dots \quad 2.110$$

where:

$$b_k^{gg} = \partial(B_{gg})/\partial Q_k, \quad b_{kl}^{gg} = \partial^2(B_{gg})/\partial Q_k \partial Q_l \text{ etc} \quad 2.111$$

The time averaged value of the rotational constant is obtained by replacing the coordinates Q_k with the appropriate quantum mechanical averages. Since we are interested in rotational constants when only the inversion vibration (Q_1 say) is populated, expression 2.110 can be rearranged to give, for i quanta of the inversion:

$$\begin{aligned} \langle B_{gg} \rangle_{ii} &= \{ B_{gg}^0 + \sum_k' b_k^{gg} \langle Q_k \rangle_{oo} + \sum_{kl}' b_{kl}^{gg} \langle Q_k Q_l \rangle_{oo} + \dots \} \\ &+ \{ b_1^{gg} + \sum_k' b_{kl}^{gg} \langle Q_k \rangle_{oo} + \sum_{kl}' b_{kl1}^{gg} \langle Q_k Q_l \rangle_{oo} + \dots \} \langle Q_1 \rangle_{ii} \\ &+ \{ b_{11}^{gg} + \sum_k' b_{k11}^{gg} \langle Q_k \rangle_{oo} + \sum_{kl}' b_{kl11}^{gg} \langle Q_k Q_l \rangle_{oo} + \dots \} \\ &\quad \langle Q_1^2 \rangle_{ii} + \dots \\ &= B_{gg}^0 + \beta_1' \langle Q_1 \rangle_{ii} + \beta_2' \langle Q_1^2 \rangle_{ii} + \dots \quad 2.112 \end{aligned}$$

Σ' designates a summation where terms involving Q_1 are omitted. The symmetry of the quartic-quadratic oscillator requires the expectation values of the odd powers of the coordinate to be zero. The expansion 2.112 converges sufficiently quickly for terms higher than the quartic to be ignored, hence, in terms of the reduced coordinate z , we have:

$$B_v = B^0 + \beta_2 \langle z^2 \rangle_{vv} + \beta_4 \langle z^4 \rangle_{vv} \quad 2.113$$

The coefficients B^0 , β_2 and β_4 are normally treated as empirical parameters and are obtained from a least squares fit to the observed rotational constants where $\langle z^2 \rangle_{vv}$ and $\langle z^4 \rangle_{vv}$ are calculated from a known function. If the dynamics of the double minimum vibration are known and contributions from the other modes can be ignored, it is possible to estimate the three coefficients from structural considerations,³⁰ since, from 2.112 and 2.111, $\beta'_2 \approx \partial^2 B / \partial Q^2$ etc. The conversion relationships between the normal and the reduced coordinates now become important as the dynamics calculations will usually be carried out in the former. If A has the units of cm^{-1} , B and z are dimensionless, a is in $\text{cm}^{-1} \text{ \AA}^{-4}$, b is in $\text{cm}^{-1} \text{ \AA}^{-2}$ and x is in \AA , then the factor $(2\mu/\hbar^2)$ in equations 2.99 - 2.101 can be replaced by $0.059304 \cdot \mu$, where μ is in amu. Hence:

TABLE 2.3

Matrix elements, in the harmonic oscillator basis set, necessary for evaluating the reduced Hamiltonian for a one dimensional quartic-quadratic oscillator

$$\langle v | p_z^2 | v-2 \rangle = -\frac{1}{2} \{v(v-1)\}^{\frac{1}{2}}$$

$$\langle v | p_z^2 | v \rangle = \frac{1}{2} (2v+1)$$

$$\langle v | p_z^2 | v+2 \rangle = -\frac{1}{2} \{(v+1)(v+2)\}^{\frac{1}{2}}$$

$$\langle v | z^2 | v-2 \rangle = \frac{1}{2} \{v(v-1)\}^{\frac{1}{2}}$$

$$\langle v | z^2 | v \rangle = \frac{1}{2} (2v+1)$$

$$\langle v | z^2 | v+2 \rangle = \frac{1}{2} \{(v+1)(v+2)\}^{\frac{1}{2}}$$

$$\langle v | z^4 | v-4 \rangle = \frac{1}{4} \{v(v-1)(v-2)(v-3)\}^{\frac{1}{2}}$$

$$\langle v | z^4 | v-2 \rangle = \frac{1}{2} (2v-1) \{v(v-1)\}^{\frac{1}{2}}$$

$$\langle v | z^4 | v \rangle = \frac{3}{4} (2v^2 + 2v + 1)$$

$$\langle v | z^4 | v+2 \rangle = \frac{1}{2} (2v+3) \{(v+1)(v+2)\}^{\frac{1}{2}}$$

$$\langle v | z^4 | v+4 \rangle = \frac{1}{4} \{(v+1)(v+2)(v+3)(v+4)\}^{\frac{1}{2}}$$

$$z = (0.059304 \mu)^{1/6} a^{1/6} x$$

$$A = (0.059304 \mu)^{-2/3} a^{1/3}$$

$$B = (0.059304 \mu)^{1/3} a^{-2/3} b \quad 2.114$$

and the corresponding reverse relations are:

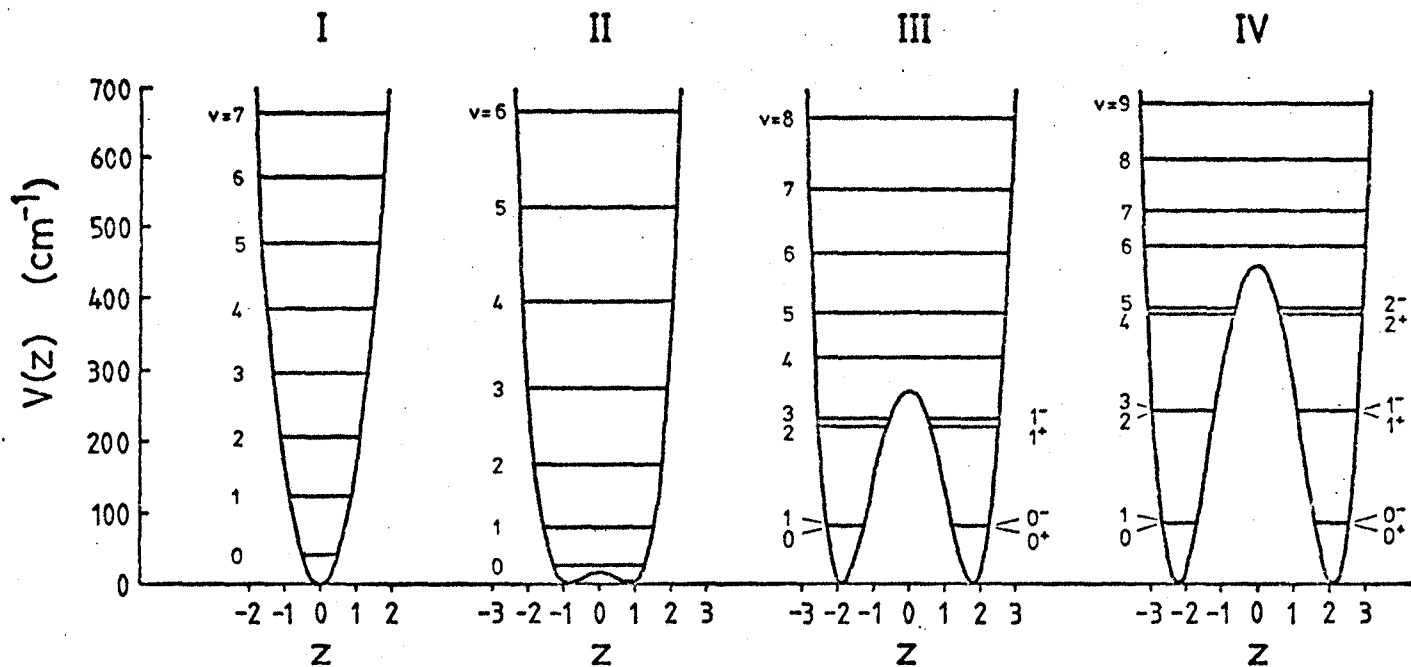
$$x = (0.059304 \mu)^{-1/6} A^{-1/2} z$$

$$a = A^3 (0.059304 \mu)^2$$

$$b = A^2 B (0.059304 \mu) \quad 2.115$$

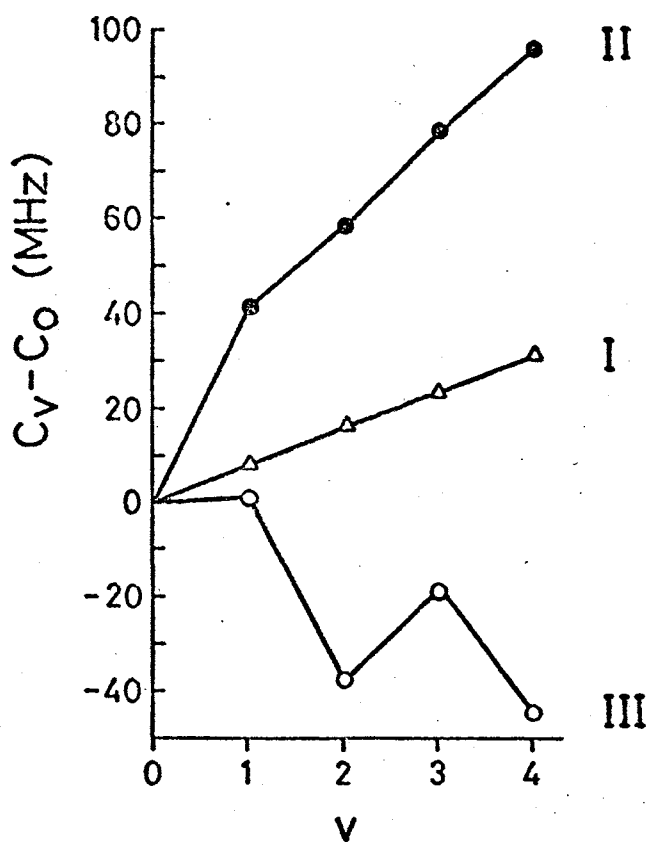
(iii) Effect on rotational spectra

The shape of the reduced quartic-quadratic potential (eq.2.103) is governed by B while A acts merely as a scaling factor. Positive values of B lead to a single minimum potential. Negative values of B introduce a quadratic hump at the centre of the quartic well which gives rise to a double minimum. Figure 2.3 gives a few examples illustrating the range of potentials encountered in practice. The appearance of the central barrier is seen to push the levels 0 and 1, 2 and 3 etc. together, resulting, at the high barrier limit, in degenerate pairs of levels (hence the notation $0^+ - 0^{-1}$, $1^+ - 1^- \dots$). The microwave spectrum would reflect such behaviour in relative intensities of satellites belonging to the satellite series for the vibration in question. If measurements on the first two excited states are available



I - cyclopent. 3. enone	$V = 11.31(z^4 + 12.56 z^2)$	ref. 31
II - oxetane	$V = 28.15(z^4 - 1.474 z^2)$	ref. 32
III - thietane	$V = 23.33(z^4 - 6.827 z^2)$	ref. 33
IV - silacyclobutane	$V = 20.53(z^4 - 9.335 z^2)$	ref. 34

FIGURE 2.3 Four experimentally determined quartic-quadratic potentials illustrating the effect of the quadratic term on the shape of the potential and the positions of the energy levels.



- I - cyclopent-3-enone ref.35
 II - oxetane ref.36
 III - thietane ref.37

FIGURE 2.4 Variation of the C rotational constant with the ring bending quantum number for the potentials of fig.2.3 .

then the ratio of the first two energy level spacings ($2 \leftarrow 1/1 \leftarrow 0$) gives an indication of the nature of the potential. The ratio should be equal to 1 for a pure quadratic oscillator, 1.335 for a pure quartic oscillator and should be greater than 1.335 for a quartic-quadratic oscillator possessing a double minimum.

The quartic-quadratic potential also manifests itself in characteristic behaviour of rotational constants with the quantum number for the vibration (figure 2.4). Single minimum potentials exhibit smooth changes in the rotational constants, while double minimum potentials introduce irregularities, that are dependent on the reduced mass for the vibration and the height of the central barrier. In some cases,³⁹ the rotational constants can be such that, on the frequency scale, one of the vibrational satellites lies to one side of the ground state, while the remaining satellites in the progression are on the opposite side. At the high barrier limit, as in silacyclobutane,³⁸ the changes in the rotational constants are described by a step function, as constants for the near degenerate vibrational pairs converge. Coriolis interaction between vibration and rotation becomes important in such cases, and it is necessary to eliminate the resulting contributions to the rotational constants^{37b,38} if an expansion like 2.113 is to be employed.

Chapter 2 (cont.)

21. J.C.Decius, *J.Chem.Phys.* 16, 1025 (1948)
22. E.B.Wilson Jr., *J.Chem.Phys.* 9, 76 (1941)
23. D.Kivelson and E.B.Wilson Jr., *J.Chem.Phys.* 21, 1229 (1953)
24. J.L.Duncan, *Chemical Society Special Periodical Reports: Molecular Spectroscopy*, 3, 104 (1975)
25. J.H.Meal and S.R.Polo, *J.Chem.Phys.* 24, 1119 (1956); *ibid.* 24, 1126 (1956)
26. recent reviews: C.A.Carreira, R.C.Lord and T.B.Malloy Jr., *Topics in Current Chemistry: 82, Large Amplitude Motion in Molecules II*, Springer Verlag (1979); A.C.Legon, to be published, *Chem.Rev.* (1980)
27. J.Laane, *Appl.Spectrosc.* 24, 73 (1970)
28. T.R.Jones and N.Sheppard, *J.Chem.Soc.Chem.Comm.* 1970, 715
29. S.I.Chan, J.Zinn, J.Fernandez and W.D.Gwinn, *J.Chem.Phys.* 33, 1643 (1960)
30. S.I.Chan, J.Zinn and W.D.Gwinn, *J.Chem.Phys.* 34, 1319 (1961)
31. J.W.Bevan and A.C.Legon, *J.Chem.Soc.Faraday Trans.II* 69, 916 (1973); J.D.Lewis and J.Laane, *J.Mol.Spectrosc.* 53, 417 (1974)
32. S.I.Chan, T.R.Borgers, J.W.Russell, H.L.Strauss and W.D.Gwinn, *J.Chem.Phys.* 44, 1103 (1966)
33. H.Wieser, J.A.Duckett and R.A.Kydd, *J.Mol.Spectrosc.* 51, 115 (1974)
34. J.Laane and R.C.Lord, *J.Chem.Phys.* 48, 1508 (1968)
35. J.W.Bevan and A.C.Legon, *J.Chem.Soc.Faraday Trans.II* 69, 902 (1973)
36. S.I.Chan, J.Zinn, J.Fernandez and W.D.Gwinn, *J.Chem.Phys.* 33, 1643 (1960)
37. D.O.Harris, H.W.Harrington, A.C.Luntz and W.D.Gwinn, *J.Chem.Phys.* 44, 3467 (1966); L.H.Scharpen, *J.Chem.Phys.* 48, 3552 (1968)
38. W.C.Pringle Jr., *J.Chem.Phys.* 54, 4979 (1971)
39. E.Hirota, *J.Mol.Spectrosc.* 38, 367 (1971)

Chapter 3

1. S.C.Rogers, *PhD Thesis*, University of London (1978)
2. A.S.Georgiou, *PhD Thesis*, University of London (1979)