Mixed Quartic-Harmonic Oscillators: A Study of the Ring Puckering Vibration of a Cyclic Amino Acid Dimer

Robert Withnall[a], David L. Andrews[b], Andrew P. Mendham[a] and Babur Z. Chowdhry[a]

[a] School of Chemical and Life Sciences, University of Greenwich, Wellington Street, Woolwich, London SE18 6PF, UK.
[b] School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, UK

ABSTRACT

A band at ca. 150 cm^{-1} in the far infrared spectrum of diketopiperazine (DKP) is assigned to a ring puckering vibration. The multiplet structure reported for this band in the low temperature (77 K) far IR spectrum can be interpreted if the vibration is assumed to have quartic character. By means of Rayleigh-Schrödinger perturbation theory, a new vibrational selection rule, $\Delta n = \pm 1, \pm 3$, has been derived for mixed quartic-quadratic vibrations in the near harmonic region for the case of zero electrical anharmonicity. Assignments of the multiplet components have been made in the light of this vibrational selection rule. A two-parameter potential energy function of the ring puckering coordinate has been derived for the DKP molecule. This has enabled a value of ca. 355 cm^{-1} to be estimated for the energy barrier to interconversion of enantiomeric boat forms of DKP. The 0-1 transition has been estimated to have a wavenumber value of 0.033 cm^{-1} (1 GHz) in excellent agreement with the value of ~1 GHz obtained from a gas phase microwave spectroscopic study.

Keywords: vibrational spectroscopy, quartic oscillator

1. INTRODUCTION

As part of a programme of work on the vibrational properties of cyclic dipeptides, we have examined the unsubstituted molecule, diketopiperazine (DKP), see Figure 1. The crystal structure of DKP suggests that the 6-membered ring has a planar conformation,[1] unlike other cyclic dipeptides for which boat and twisted boat conformations have been reported.[2] The ^{1}H NMR spectrum of DKP in aqueous solution has also been interpreted to indicate that the ring has a planar conformation.[3]
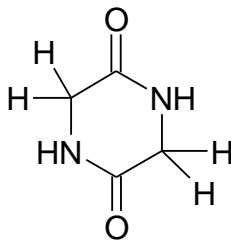

Figure 1: Schematic representation of the DKP molecule.

The planar ring conformation of DKP, determined by the aforementioned experiments, has not been predicted for the isolated molecule by *ab initio* calculations.[4,5] An *ab initio* calculation of the molecular structure of DKP involving correlation-corrected basis functions [MP2/cc-pVDZ] predicted that a structure having a boat conformation of the ring (of C$_2$ symmetry) is lower in energy by 441 cm^{-1} than a structure with a planar ring (of C$_{2h}$ symmetry) (4). Thus at room temperature (kT ~209 cm^{-1}) some interconversion can be expected to take place between the two forms. Although the *ab initio* calculations have been carried

out for the isolated molecule, it is possible that such an interconversion could also occur in the condensed phase. In the solid extensive intermolecular H-bonding takes place between the C=O and N-H functional groups, and in aqueous solution H-bonding will occur with the water molecules of the aqueous solvent. In spite of the H-bonding in the condensed phase, the non-rigid ring of DKP may still exhibit a conformational interconversion. This would not necessarily be detected in the X-ray and NMR experiments which would provide only ensemble or time-averaged structures. Vibrational spectroscopy provides another means of investigating structure and dynamics, so it is of interest to examine the possibility of DKP ring conformational interconversion using IR and Raman spectroscopy.

The possibility of ring conformational interconversion was mentioned above in connection with DKP at room temperature. However even at low temperature, when the thermal energy is substantially less than that of the energy barrier, an interconversion may still occur by a quantum tunneling mechanism. Such a mechanism is known to occur, for example, in the ammonia molecule which has two enantiomeric pyramidal geometries. These can interconvert by tunneling through a higher energy planar geometry. The conformational change occurs along the vibrational coordinate that connects the two geometries, *i.e.* the ν_2 symmetric deformation of the NH_3 molecule. The potential energy surface has a symmetric double well minimum along this vibrational coordinate. This is due to a mixed quartic-quadratic dependence of the potential energy, $V(x)$, on the displacement, x, according to:

$$V(x) = ax^4 + bx^2 \qquad (1)$$

where a and b are constants, which may be of like or opposite sign (see later).

In the case of the DKP molecule, the two enantiomeric boat conformations are connected along the ring puckering vibrational coordinate. Recent microwave spectroscopic results indicate that the boat forms of gas phase DKP are located at the minima of a double-well potential energy surface, and that the ring puckering vibration has mixed quartic-quadratic character.[5] Thus its potential energy may also be described by equation 1 (see above).

The $\Delta n = \pm 1$ selection rule of the harmonic oscillator does not hold rigorously when a term due to quartic anharmonicity appears in the potential energy function. Although it is widely appreciated that the selection rule becomes modified,[6,7] a derivation of the modified rule for a mixed quartic-quadratic oscillator has not been given in the literature, as far as we are aware. Consequently a vibrational selection rule for the mixed quartic-quadratic oscillator will be derived in this work (see section 4, later).

2. THE FAR INFRARED SPECTRUM OF DKP

The infrared and Raman spectra of DKP have been interpreted on the basis of a planar ring geometry, the isolated molecule belonging to the C_{2h} molecular point group.[8] As the C_{2h} DKP molecule possesses a center of symmetry, its vibrational spectrum is governed by the rule of mutual exclusion. There are three ring torsional modes; of these two are infrared active and have A_u symmetry and one is Raman active and has B_g symmetry.

The room temperature far infrared spectrum of DKP exhibits two bands in the 100-400 cm^{-1} region, at 148 and 177 cm^{-1}, which have been assigned to a lattice mode and one of the infrared active ring torsional modes, respectively.[8] The assignment of the 148 cm^{-1} band to a lattice mode disagreed with a previous assignment of this band to the other infrared active ring torsional mode.[9] The re-assignment was based on the report of a band at 285 cm^{-1} in the inelastic neutron scattering spectrum.[10] This was believed to be due to one of the infrared active ring torsional modes, which was presumed to have an intensity too low to be observed in the infrared spectrum. However a recent inelastic neutron scattering spectroscopic study of DKP[11] has revealed that there is no band at 285 cm^{-1}. Consequently we favour the original assignment of both the 148 and 177 cm^{-1} far infrared bands to the ring torsional modes of A_u symmetry.

It is interesting that a mysterious multiplet structure was reported for the band at *ca.*148 cm^{-1} when the DKP sample was at liquid nitrogen temperature.[8] Components at 148, 155 and 158 cm^{-1} were

apparently observed, the first being a shoulder on the neighboring component and the last two being of medium intensity. A possible explanation for the occurrence of this multiplet can be proposed in the light of the re-assignment of the *ca.* 148 cm^{-1} band to a ring torsional mode. This is because the vibration that gives rise to this band is now believed to be the ring puckering vibration, which would have some quartic character. Thus a quartic-quadratic vibrational selection rule would apply to this mode, and more than one vibrational transition could result (see later).

It is noteworthy that, shortly after suggesting that this vibrational mode of DKP could have quartic character,[12] confirmatory evidence was reported from the results of a gas phase rotation-inversion spectroscopic study of DKP.[5]

3. EXAMPLES OF QUARTIC-QUADRATIC OSCILLATORS

The potential energy, $V(x)$, of a pure quartic oscillator would show a fourth power dependence of the displacement, x *i.e.* $V(x) = kx^4$, where k is a constant of proportionality. Clearly any notional harmonic force constant, obtained in the normal way from the radius of curvature at the bottom of the potential well, would not be a constant for such a vibration as it does not relate to a quadratic potential energy function. Such a treatment is consequently inadequate for this type of vibration, as the quartic behaviour needs to be properly accounted for.

It is worthwhile to consider what type of vibration might exhibit quartic behaviour. Over fifty years ago Bell[13] predicted that the ring puckering vibration of a 4-membered ring such as cyclobutane, C_4H_8, would be one such example; this prediction was later proved correct.[14,15] It was reasoned that a first order infinitesimal displacement (x) in the ring atoms, perpendicular to the plane of the ring, would result in only a second order change in the angles between any pair of bonds attached to the same atom or in the distances between any pair of atoms. Since the changes in the bond distances and bond angles vary with the square of the displacement (x^2), the change in potential energy is proportional to the fourth power of the displacement, *i.e.* $V(x) = kx^4$ as above. Newton's equation of motion for this oscillator is:

$$m\ddot{x} + \lambda x^3 = 0 \qquad (2)$$

where λ is a constant. It can be shown that the classical frequency, obtained by determination of the vibrational time period, depends on the total energy of the oscillator.[13] This contrasts with the classical frequency of a harmonic oscillator, which is independent of its total energy.

It should be mentioned that, in considering the quartic ring strain potential of cyclobutane, the assumption was made that there is free rotation about the C-C bonds. This is not the case because there will always be some torsional (or twisting) forces of ring bonds, which will have quadratic character. For this reason, it is unlikely that any molecular vibration will exhibit pure quartic behaviour, although the ring puckering vibration of trimethylene oxide apparently comes very close.[16] Furthermore, the sign of the quadratic coefficient, b in Equation (1), may be the same as the quartic coefficient a, or it may be opposite. In the former case, the ring strain and torsional forces act in the same direction and reinforce each other, whereas in the latter they are opposed. These two cases give rise to single minimum and double minimum potential energy wells, respectively.

The out of plane bending vibration of planar tetratomic molecules with the general formula XY_3 might also be expected to show quartic character, based on similar arguments to those given above. However a rehybridisation of the s and p orbitals can account for a first order change in the bond angles for small atomic displacements. Clearly there will also be a first order change for the symmetric bending vibration of pyramidal XY_3 molecules, such as ammonia. Planar XY_3 molecules will have a single minimum potential energy well, whereas pyramidal XY_3 species will have a double minimum. The potential energy function of the former has a and b coefficients (see Equation 1) of the same sign, whereas these coefficients have opposite signs for the latter. However the relevant bending vibrations of both types of XY_3 molecule are likely to have a great deal of quadratic character, unlike the puckering vibration of cyclobutane. In the following discussion, quartic-quadratic oscillators having large percentages of either

quartic or quadratic character will be taken to belong to the 'near quartic' and 'near harmonic' regimes, respectively. The near harmonic regime has previously been regarded as where the energy levels differ from harmonic ones by less than 10%, and the near quartic regime as the regime in which energy levels differ from pure quartic ones by less than 10%.[17] It has also been reported that the percentage of quartic or quadratic character depends not only on the values of a and b in Equation (1), but also on the degree of vibrational excitation, *i.e.* on the vibrational quantum number; the higher the vibrational quantum number, the greater the degree of quartic anharmonicity.[17]

4. SELECTION RULE FOR A MIXED QUARTIC-QUADRATIC OSCILLATOR

The selection rule can be derived using perturbation theory within the framework of the simple harmonic oscillator (S.H.O.) model, recognising that this treatment applies strictly within the near harmonic regime. For IR transitions the dipole moment operator, μ, needs to be considered, and this can be expanded in a Taylor series of the vibrational coordinate, x;

$$\mu = \mu_o + \sum_i \left(\frac{\partial \mu}{\partial x_i}\right)_{x=0} x_i + \frac{1}{2}\sum_{ij}\left(\frac{\partial^2 \mu}{\partial x_i \partial x_j}\right)_{x=0} x_i x_j + ... \tag{3}$$

The first term in Equation (3) is the permanent dipole moment which plays no role in the absorption of radiation for a vibrational transition. If the third term is very small and can be neglected, the dipole moment can be assumed to vary linearly with the vibrational coordinate and the vibration is regarded as 'electrically harmonic'. In the case of Raman transitions, the polarisability can be treated in an analogous way to the dipole moment. Thus for both IR and Raman, the $m' \rightarrow n'$ transition between (S.H.O. modified) levels involves a transition moment proportional to $\langle n'|x|m'\rangle$.

For a quartic perturbation, βx^4, the modified S.H.O. levels given by Rayleigh-Schrödinger perturbation theory[18,19] are represented by;

$$|m'\rangle = |m\rangle + \sum_{s \neq m}|s\rangle \frac{\langle s|\beta x^4|m\rangle}{E_m - E_s} + ... \quad ,$$

and the resultant transition amplitudes are;

$$S \equiv \langle n'|x|m'\rangle = \langle n|x|m\rangle + \beta\left[\sum_{s \neq m}\frac{\langle n|x|s\rangle\langle s|x^4|m\rangle}{E_m - E_s} + \sum_{s \neq n}\frac{\langle n|x^4|s\rangle\langle s|x|m\rangle}{E_n - E_s}\right] + ... \quad , \tag{4}$$

neglecting terms of higher order. Now writing x in terms of the lowering operator a and raising operator a^+ for harmonic wavefunctions,[20] we have $x = i\lambda(a - a^+)$ where $\lambda = (\hbar/2\mu\omega)^{1/2}$ for a vibration of circular frequency $\omega = v/2\pi$ and effective mass μ (note: λ is *not* a small parameter) and

$$S = i\lambda\langle n|(a - a^+)|m\rangle$$
$$+ i\beta\lambda^5\left[\sum_{s \neq m}\frac{\langle n|(a-a^+)|s\rangle\langle s|(a-a^+)^4|m\rangle}{E_m - E_s} + \sum_{s \neq n}\frac{\langle n|(a-a^+)^4|s\rangle\langle s|(a-a^+)|m\rangle}{E_n - E_s}\right] + ...$$

$$\tag{5}$$

Then since $a|m\rangle = m^{1/2}|m-1\rangle; a^+|m\rangle = (m+1)^{1/2}|m+1\rangle$, each a lowers the quantum number by one and each a^+ raises it by one. Hence the first term is non-zero (it has a non-vanishing result) only for $n = m+1$ or $n = m-1$, *i.e.* $\Delta n = \pm 1$, as is usual.

Considering the numerator of the second term in Equation (5), the second (x^4) Dirac bracket will be non-zero only for $s = m$, $m\pm2$, $m\pm4$, and so when it multiplies the other Dirac bracket, requiring $n = s\pm1$, we can end up with non-zero contributions only for $n = m\pm1$, $m\pm3$, $m\pm5$. It works similarly with the third term. The energy levels of a pure quartic oscillator diverge with increasing quantum number,[17] showing a $(n+\frac{1}{2})^{4/3}$ dependence for large quantum numbers, n. However, since we are working within the near harmonic regime, the energy levels can be regarded as equally spaced in energy, to a first approximation; this has intuitive advantages and is consistent with the adoption of Rayleigh-Schrödinger perturbation theory. Specifically, performing calculations with proper regard for the orderings of a and a^+ since they do not commute, we obtain:

$\underline{\Delta n = 0}$ (*i.e. n = m*); $S = 0$

$\underline{\Delta n = +1}$ (*n = m+1*); $S = -i\lambda\sqrt{(m+1)} + 6i(\hbar\omega)^{-1}\beta\lambda^5\sqrt{(m+1)^3}$

$\underline{\Delta n = +2}$ (*n = m+2*); $S = 0$

$\underline{\Delta n = +3}$ (*n = m+3*); $S = i(\hbar\omega)^{-1}\beta\lambda^5\sqrt{(m+1)(m+2)(m+3)}$

$\underline{\Delta n = +4}$ (*n = m+4*); $S = 0$

$\underline{\Delta n = +5}$ (*n = m+5*); $S = 0$

$\underline{\Delta n = -1}$ (*n = m-1*); $S = i\lambda\sqrt{m} - 6i(\hbar\omega)^{-1}\beta\lambda^5\sqrt{m^3}$

$\underline{\Delta n = -2}$ (*n = m-2*); $S = 0$

$\underline{\Delta n = -3}$ (*n = m-3*); $S = -i(\hbar\omega)^{-1}\beta\lambda^5\sqrt{m(m-1)(m-2)}$

$\underline{\Delta n = -4}$ (*n = m-4*); $S = 0$

$\underline{\Delta n = -5}$ (*n = m-5*); $S = 0$

As mentioned above, it can be seen from the form of Equation (5) that non-zero contributions will be restricted to $n = m\pm1$, $m\pm3$, $m\pm5$. However it transpires that, for either of the cases $\Delta n = \pm5$, the two different contributions, *i.e.* the second and third terms in Equation (5), cancel exactly in Rayleigh-Schrödinger perturbation theory. This is because they have the same numerator but equal and opposite energy denominators. Cases of still larger Δn values all give zero unless we go to yet higher orders of perturbation theory.

The above analysis has provided the selection rule $\Delta n = \pm1$, ±3 for a mixed quartic-quadratic oscillator in the near harmonic regime. It can be seen that the $\Delta n = \pm1$ selection rule of an S.H.O. has become modified, as second overtone transitons ($\Delta n = \pm3$) are now allowed. Furthermore it is satisfying that the degree of 'allowedness' increases with the percentage of quartic character (defined by the value of β), as it can be seen that the transition amplitudes (*S* values) are proportional to β for the $\Delta n = \pm3$ transitions (see above). Moreover, this treatment indicates that first overtone transitions ($\Delta n = \pm2$) are forbidden for mixed quartic-quadratic oscillators in the near harmonic regime, if electrical harmonicity is assumed – see Equation (3) above. This same assumption is also made, of course, in the derivation of the S.H.O. selection rule ($\Delta n = \pm1$). The selection rule of $\Delta n = \pm1$, ±3 for a mixed quartic-quadratic oscillator appears to contradict the empirical selection rule of $\Delta n = \pm1$ (for IR) and $\Delta n = \pm2$ (for Raman), which is given in a standard textbook on Raman spectroscopy.[21] Presumably, it has been possible to observe features associated with $\Delta n = \pm2$ transitions in Raman spectra of mixed quartic-quadratic oscillators, on account of an appreciable degree of electrical anharmonicity, *i.e.* a non-negligible third term in Equation (3).

5. INTERPRETATION OF THE DKP FAR INFRARED SPECTRUM

As previously mentioned, molecules having 4-membered rings (e.g. cyclobutane) are expected to have a ring puckering vibration exhibiting a large percentage of quartic character. In addition, molecules with larger rings and rigid, double bonds can also have such a vibration. In these molecules, any two atoms joined by a double bond can be considered to play the role of a single atom. Thus, cyclopentene and 1,4-cyclohexadiene can both be regarded as molecules with pseudo 4-membered rings. DKP comes into this category because the C-N bonds of the two peptide linkages are rigid (see Figure 1, above). Furthermore, as for the ammonia molecule, DKP has a double minimum potential well and consequently exhibits inversion doubling of vibrational levels. Thus 0,1 are close and so are 2,3 and 4,5 etc., with the energy spacing of the inversion doublets increasing with vibrational quantum number. The $v = 0$ and $v = 1$ levels have a small energy separation, coming in the microwave region, because they are the components of the lowest energy doublet. At a temperature of 77 K these two levels will be populated more than any others according to a Maxwell-Boltzmann distribution (in thermal equilibrium). Consequently, features are expected in the far infrared region at *ca.* 150 cm^{-1} due to 1-2 and 0-3 transitions, in view of the selection rule derived above for mixed quartic-quadratic oscillators. Admittedly, the DKP ring puckering vibration is outside the near harmonic region, so we make the assumption that our selection rule is still valid when extrapolating beyond this region.

The eigenvalues for mixed quartic-quadratic potential functions in reduced (*i.e.* dimensionless) form have been tabulated by Laane[6] for varying degrees of quartic and quadratic character. In order to facilitate the computation, the physically dimensioned potential of Equation (1) was transformed to the reduced potential given by:

$$V = A\,(Z^4 + BZ^2) \tag{6}$$

where

$$Z = \left(\frac{2\mu}{\hbar^2}\right)^{\frac{1}{6}} a^{\frac{1}{6}} x; \qquad B = \left(\frac{2\mu}{\hbar^2}\right)^{\frac{1}{3}} a^{-\frac{2}{3}} b; \qquad A = \left(\frac{\hbar^2}{2\mu}\right)^{\frac{2}{3}} a^{\frac{1}{3}}.$$

Here the magnitude of B determines the degree of quartic and quadratic character of the oscillator. If $B = 0$, the levels are those of a pure quartic oscillator, and when $B = \pm\infty$, the levels are those of an S.H.O. When B is negative, the potential is of the double minimum type with an energy barrier of height $B^2/4$. The parameter A scales the eigenvalues to the wavenumbers.

If the components at 155 and 158 cm^{-1} of the DKP far IR multiplet are assigned to the 1-2 and 0-3 transitions, respectively, Laane's tables[6] can be used to obtain a B value of -8.0 and an A value of 22.2 cm^{-1}. These come quite close to the B and A values, respectively, of -6.18 and 24.3 cm^{-1} for cyclopentene (also having a pseudo 4-membered ring) and -6.80 and 23.7 cm^{-1} for silacyclobutane.[6] This determination of the two parameter potential function of DKP provides an estimate of 355 cm^{-1} for the energy barrier, and a wavenumber value of 0.033 cm^{-1} (*i.e.* 1 GHz) for the 0-1 transition. This latter result is in excellent agreement with the value of ~1 GHz obtained from a recent gas phase microwave spectroscopic study.[5]

6. CONCLUSIONS

The band at *ca.* 150 cm^{-1} in the far IR spectrum of DKP has been re-assigned to a ring torsional vibration. The reported multiplet structure of this band at low temperature has been interpreted on the basis that this mode has a substantial quartic character. This interpretation is in agreement with the conclusions of a recent microwave spectroscopic study.[5]

A new vibrational selection rule of $\Delta n = \pm 1, \pm 3$ has been derived for a mixed quartic-quadratic oscillator in the near harmonic regime using Rayleigh-Schrödinger perturbation theory, assuming no electrical anharmonicity.

The components of the far IR multiplet at ca. 150 cm^{-1} have been assigned to 1-2 and 0-3 transitions of the ring puckering (torsional) vibration, both of which are allowed according to the selection rule derived in this work. These assignments have been used to obtain a two-parameter, double minimum potential energy function by making use of eigenvalues tabulated in the literature.[6] This has provided an estimate of 355 cm^{-1} for the energy barrier to interconversion of the enantiomeric boat conformers of DKP. It has also provided an estimate of 0.033 cm^{-1} (1 GHz) for the wavenumber of the 0-1 transition, in excellent agreement with the value obtained from gas phase spectroscopy.[5]

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