EFFECTS OF ANHARMONICITY OF MOLECULAR VIBRATIONS ON THE DIFFRACTION OF ELECTRONS

Part III. Predictive models

L. S. BARTELL

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109 (U.S.A.)

(Received 2 August 1979)

ABSTRACT

It has long been known how to relate anharmonic vibrational distribution functions to scattered electron intensities when deriving molecular parameters from gas-phase electron diffraction patterns. What has been lacking is a convenient procedure for estimating the characteristic asymmetry parameters of radial distribution functions for polyatomic molecules, particularly in the case of non-bonded internuclear distances. In the present work alternative models of bond distribution functions are discussed briefly and a plausible model is proposed for geminal non-bonded distances. Numerical examples are worked out for the ground-states of CO_2, CS_2, H_2O, and D_2O. Variations of the asymmetry parameters of SO_2 and SF_6 with temperature are examined. It is shown that the effect of asymmetry can become quite large at elevated temperatures.

INTRODUCTION

Molecular vibrations complicate determinations of molecular structure, whether spectroscopic or diffraction, and substantially interfere with the accuracy of determining physically meaningful structural parameters. Many years ago [1], preliminary attempts were made to treat the effects of vibrational anharmonicity in gas-phase electron diffraction. Subsequent studies [2—13] substantially broadened the scope of the treatment. Diatomic molecules were successfully characterized. Covalent bonds in polyatomic molecules were treated, for the most part, as one-dimensional Morse-like oscillators. That this may not always be a good approximation was indicated by a recent study [14] showing that the conventional Morse parameter accounts for only half the observed vibrational displacement of bonds from their equilibrium lengths in the case of SF_6. Non-bonded distances present an even more difficult problem.

Several workers [2—5, 8] have shown, in principle, how to calculate the necessary asymmetry parameters for individual molecules. Such calculations were carried out for methane [6] and a few triatomic molecules [3, 5, 8, 10] to obtain ground-state anharmonic distributions for both bonded and non-bonded distances. While these treatments serve as valuable illustrations, they are much too complex for routine use in electron diffraction.

Prior analyses [4] have established how to interpret diffraction patterns once the asymmetry of each peak in the distribution function $P(r)$ is known. What is lacking is a practical scheme for estimating asymmetry parameters, particularly for non-bonded distances. In special cases the effect upon the diffraction pattern is so conspicuous that the parameter can be refined directly from experiment. More often it turns out that the effect is close to the noise level. Although it is unprofitable in such cases to try to establish the asymmetry parameter from experiment, it is equally unwise to neglect it, because such neglect may degrade the determination of internuclear distances by several thousandths of an Ångstrom unit.

A rigorous derivation of asymmetry parameters requires, (a) a knowledge of the anharmonic force field, and (b) an average over a thermal distribution of molecules whose ground and excited vibrational wavefunctions have been calculated from the anharmonic force field. Since these requirements are rarely met for polyatomic molecules it is necessary to resort to rather severe approximations in order to estimate the magnitude of the parameters needed. A provisional investigation in this direction is described in the following sections, after a brief review of the effects of anharmonicity upon electron-diffraction patterns.

ANHARMONICITY AND DIFFRACTED INTENSITY

Throughout the present treatment we shall assume, as in earlier treatments, that the component of molecular diffracted intensity associated with a particular internuclear distance is given by Debye's relation [15]

$$M(s) = c \int_0^\infty P(r) \frac{\sin sr}{sr} \, dr \tag{1}$$

where $M(s)$ is the usual reduced intensity function. Failures of the Born approximation and other factors not taken into account in eqn. (1) can be incorporated in the usual way. It is convenient to express the internuclear probability distribution function as

$$P(y) = A(2\pi l^2)^{-1/2} \left(1 + \sum_{n=1}^\infty c_n y^n\right) \exp\left(-y^2/2l^2\right) \tag{2}$$

where $y = r - r_R$ and r_R is an arbitrary reference internuclear distance parameter. In ref. 4 the propagation of the parameters c_n into the $M(s)$ function was treated in detail, along with the conversions between the various types of parameters r_g, r_e, l_g, l_m, l_e, etc., representing distances and amplitudes of vibration. Explicit formulae were given for the particular case of the Morse oscillator in its ground state when r_R is taken as r_e and l represents the amplitude for the fictional harmonic oscillator with the same quadratic force constant. In the present rough treatment where, at most, only the first three

moments of the distribution function are likely to be known, it is more practical to take r_R as r_g (so that $\langle y \rangle = 0$) and l^2 as $l_g^2 \equiv \langle y^2 \rangle$. If, further, the potential function is not radically different from that of a Morse oscillator, the above conversion makes $c_1 \approx -3l^2c_3$ and makes c_2 small enough to be unimportant; terms higher than cubic are of significance only at quite high temperature or in individual excited states. Accordingly, the three parameters r_g, l, and c_3 characterize the distribution, the latter giving rise to the skewness we seek to examine.

The effect of the asymmetry, or skewness, of $P(y)$ is to introduce a phase modulation into the molecular oscillations of $M(s)$ according to the expression

$$sr_aM(s) \approx Ac \exp(-l^2s^2/2) \sin[s(r_a - \kappa s^2 + \cdots)] \tag{3}$$

where $r_a \equiv r_g(1) \approx r_g - (l^2/r_g)$, and where the coefficient of the leading term in the phase correction is [1, 4]

$$\kappa \approx (c_3 - r_s^{-1}c_2)l^6 \tag{4}$$

In eqn. (4), c_2 normally plays a minor role, even if it is non-zero by the convention adopted for r_R and l, and we shall henceforth disregard it. As can be seen from eqn. (3) the effective value of the internuclear distance implied by the electron interference fringes in the vicinity of $s = s_n$ is $(r_a - \kappa s_n^2)$. If neither the magnitude nor the sign of κ is known, the derivation of the desired average r_a is impaired. In the remainder of the paper we shall consider ways to estimate c_3 and, hence, κ, from information currently available.

ASYMMETRY OF BOND DISTRIBUTION

Because no general, quantitatively predictive representation of polyatomic force fields (short of Schrödinger's equation) has yet been formulated, we can draw only tentative conclusions. We shall briefly compare the implications of two reasonably successful model fields, the Morse valence force field (MVFF) and an anharmonic Urey—Bradley force field (KBFF) formulated two decades ago [5]. In the MVFF it is assumed that bond stretches are represented by Morse-like potentials, the parameters of which are given to sufficient accuracy by Badger's rules [16] or the tables of Herschbach and Laurie [17] or Kuchitsu and Morino [10]. In the KBFF, Morse parameters contribute the predominant anharmonic effects but geminal non-bonded interactions may significantly influence anharmonicity. Evidence of the superiority of the KBFF has been discussed in several references [10, 14, 18—20].

Let us first compare the implications of the two force fields at modest temperatures where bond stretches are still in their ground states. As shown elsewhere [1, 4]

$$c_3 \approx a/6l^2 \tag{5}$$

where a is the Morse parameter which can be derived from the Herschbach—Laurie derivatives [17] as $(-V'''/3V'')$, or from Kuchitsu and Morino's tables [10]. A rigorous derivation of c_3 from the KBFF cannot be carried

out without first calculating the anharmonic vibrational wavefunctions corresponding to the field. Nevertheless, a crude assessment can be made by displacing one bond along its z (stretch) coordinate while holding all others constant. This bond (bond i) then experiences the potential function [5, 13]

$$V(\Delta z_i) = K_i' r_R \Delta z_i + \tfrac{1}{2} K_i (\Delta z_i)^2 - \tfrac{1}{2} K_i a (\Delta z_i)^3 + \sum_j [F_{ij}' (q_R)_{ij} \Delta q_{ij}$$

$$+ \tfrac{1}{2} F_{ij} (\Delta q_{ij})^2 + (F_3/6q_R)_{ij} (\Delta q_{ij})^3] \tag{6}$$

where K', K, F', and F are the usual UB force constants, a is the Morse parameter, and $(F_3/q_R)_{ij}$ is the third derivative of the non-bonded potential, with r_R and q_R being the bond and non-bonded distances in the reference structure. Resolving forces for a symmetric AX_n molecule, (see ref. 13 for relevant details), we find

$$V(\Delta z_i) = \tfrac{1}{2} [K + m(c^2 F' + s^2 F)] (\Delta z_i)^2$$

$$- \tfrac{1}{2} K \{a + (m/6Kr_R) [3c^2 (F' - F) - s^2 F_3]\} (\Delta z_i)^3 \tag{7}$$

where m is the number of geminal non-bonded distances, s and c represent $\sin (\alpha_{ij}/2)$ and $\cos (\alpha_{ij}/2)$, respectively, and the quadratic force constant $[K + m(c^2 F' + s^2 F)]$ is simply the UB representation of the valence stretch constant k_r. According to eqn. (7), the effective "Morse" parameter $a_{KB} \equiv (-V'''/3V'')$ in the KBFF is

$$a_{KB} = \{Ka + (m/6r_R) [3c^2 (F' - F) - s^2 F_3]\}/k_r \tag{8}$$

A dynamic average over vibrations would modify the factor somewhat.

In order to determine whether a and a_{KB} are significantly different, it is instructive to examine the case of SF_6, where six fluorines are tightly packed around the central sulfur atom. For this example, there are prior estimates [14] of the relevent force constants. These estimates yield the values 1.8 $Å^{-1}$ and 1.6 $Å^{-1}$, respectively, for a and a_{KB}. A roughly comparable difference in the case of CH_4 can be inferred from results tabulated by Kuchitsu [12], where vibrational averaging was carried out [6]. Since the differences are not large compared with uncertainties in the input parameters, and since the differences would often be smaller (with smaller m or F_3, or larger q_R), there is small incentive, at this stage, to go beyond the simple Morse model.

Here it is appropriate to comment on the commonly encountered assumption that, for a covalent bond in a polyatomic molecule, the mean vibrational displacement $\langle \Delta r \rangle$ from equilibrium is given by the diatomic formula $3a_f l^2/2$, where a_f is an effective Morse asymmetry parameter. If this were true, calculated $\langle \Delta r \rangle$ values for CH_4 [6] and SF_6 [14], based on the KBFF, as well as experimental $\langle \Delta r \rangle$ values in the latter case, would imply an a_f value substantially greater than the diatomic Morse parameter. However, the reported skew of the bonded C—H distribution [12] and the above a_{KB} value for SF_6 are smaller than predicted by the diatomic model. It may be inferred, then, that significant contributions to the displacement $\langle \Delta r \rangle$ are made by bending as well as stretching modes, and that anharmonic vibrations

do not skew the distribution function of polyatomic molecules as much as they do those of diatomic molecules, per unit mean displacement. One source which can be easily visualized leading to displacement (namely, Δ_b in the notation of ref. 13), while contributing little skew, is discussed elsewhere [13].

At temperatures high enough to excite stretching modes it is, of course, no longer appropriate to use eqn. (5) to estimate the skew parameter c_3. Several treatments have appeared, the most useful one of simple form, perhaps, being the diatomic formula

$$c_3 \approx a[1 + 8\chi(1 + \chi)^{-2}]/6l^2 \tag{9}$$

proposed by Kuchitsu [21], where $\chi = \exp(-h\nu/kt)$. It is of interest to examine the diatomic high temperature limiting form of $P(y, T)$ applying when $kT \gg h\nu$, namely $N \exp[-V(y)/RT]$. For example, if the potential energy of a Morse oscillator is expanded about $r_R = r_e$, with $x = r - r_e$, the result is

$$P(x, T) \approx N_T [1 + (a/2l^2)x^3 - (7a^2/24l^2)x^4 + \cdots] \times \exp(-x^2/2l^2) \tag{10}$$

making

$$c_3 \approx a/2l^2 \tag{11}$$

where the temperature-dependent mean-square amplitude l^2 is very nearly kT/k_r, with k_r representing the stretching force constant. It is evident that eqn. (9) successfully reproduces eqns. (5) and (11) at the appropriate limiting temperatures.

GEMINAL NON-BONDED DISTRIBUTIONS

If details of bond distributions are not yet fully resolved, details of non-bonded distributions are even less well understood. We propose the following models, then, not because they are rigorous but because they are tractable, and one of them yields fairly satisfactory results in those few cases for which more rigorous results exist. Let us consider the $X_i \cdots X_j$ non-bonded distance q in the fragment $X_i - A - X_j$, whose vibrational displacements from mean (not equilibrium) positions are specified in terms of the internal coordinates Δr_i, Δr_j, and $\Delta \alpha$. We assume that the displacement Δq can be written as

$$\Delta q = \Delta q_i + \Delta q_j + \Delta q_b \tag{12}$$

where the three components arise from the stretching of bonds i and j, and from bending, respectively. If cross-terms are neglected, the components in eqn. (12) are simply related to the diagonal terms in the Taylor series expansion given by Shimanouchi [22] as

$$\Delta q_i = s_{ij}\Delta r_i + \cdots \tag{13}$$

$$(\Delta q)_j = s_{ji}\Delta r_j + \cdots \tag{14}$$

and

$$(\Delta q)_b = D_1 \Delta \alpha + D_2(\Delta \alpha)^2 + \cdots + \delta \tag{15}$$

where $s_{ij} = (r_i - r_j \cos \alpha)/q_{ij}$, $D_1 = (t_{ij} t_{ji} r_i r_j)^{1/2}$, $t_{ii} = r_j \sin \alpha/q$, $D_2 = -s_{ij} s_{ji} r_i r_j/2q$ and where δ is a shrinkage parameter defined to make $\langle \Delta q \rangle_b = 0$.

It is assumed that the bending and two stretching vibrations act independently in shaping the distribution $P(\Delta q)$. It will emerge that considerations of dynamic bending trajectories require a significant correlation between $\Delta \alpha$ and Δr_i, Δr_j in bending modes, but this correlation will be absorbed into the component $(\Delta q)_b$. While it is possible to develop explicit expressions for the distributions $p_s(\Delta q_i)$, $p_s(\Delta q_j)$, and $p_b(\Delta q_b)$ and, further, to reduce them to the desired one-dimensional distributions $P(\Delta q)$ as outlined elsewhere [23], a more compact presentation can be made using a method of moments. We identify the moment $\langle (\Delta q)^n \rangle$, where n is an integer, with the quantity $\langle (\Delta q_i + \Delta q_j + \Delta q_b)^n \rangle$. According to our assumptions of independence in the foregoing, averages of the type $\langle (\Delta q_i)^r (\Delta q_j)^s (\Delta q_b)^t \rangle$ simplify to the product $\langle (\Delta q_i)^r \rangle \langle (\Delta q_j)^s \rangle \langle (\Delta q_b)^t \rangle$. The function we seek is

$$P(\Delta q) = N\{1 + c_3 [-3l^2 \Delta q + (\Delta q)^3] + \cdots\} \exp[-(\Delta q)^2/2l_M^2] \qquad (16)$$

for which $\langle \Delta q \rangle = 0$, $\langle (\Delta q)^2 \rangle = l_M^2$, and the moment

$$\langle (\Delta q)^3 \rangle = 6c_3 l_M^6 + \cdots \qquad (17)$$

isolates the skew parameter c_3 we need for the diffraction κ constant. According to our assumptions, the mean-square amplitude l_{UM}^2 of our uncorrelated model would be

$$l_{UM}^2 = \langle \sum_k (\Delta q_k)^2 + 2 \sum_{k>l} (\Delta q_k)(\Delta q_l) \rangle$$

$$= \sum_k \langle (\Delta q_k)^2 \rangle + 2 \sum_{k>l} \sum \langle \Delta q_k \rangle \langle \Delta q_l \rangle$$

$$= \langle (\Delta q_i)^2 \rangle + \langle (\Delta q_j)^2 \rangle + \langle (\Delta q_b)^2 \rangle$$

$$\approx s_{ij}^2 \langle (\Delta r_i)^2 \rangle + s_{ji}^2 \langle (\Delta r_j)^2 \rangle + D_1^2 \langle (\Delta \alpha)^2 \rangle \qquad (18)$$

since all $\langle \Delta q_k \rangle = 0$. Whether it is advisable to substitute the model amplitude l_{UM} for the actual distribution breadth l_M will be discussed later. For similar reasons the third moment reduces to

$$\langle (\Delta q)^3 \rangle = \langle (\Delta q_i)^3 \rangle + \langle (\Delta q_j)^3 \rangle + \langle (\Delta q_b)^3 \rangle \qquad (19)$$

making the skewing contributions additive, so that the non-bonded skew parameter is the sum of a stretch and bend component, or

$$c_3 = c_{3s} + c_{3b} \qquad (20)$$

Our task, then, is to find distributions giving plausible stretching and bending skews. Following the previous section, we adopt for stretches

$$p(\Delta r_k) = N'\{1 + c_{3k}[-3l_k^2(\Delta r_k) + (\Delta r_k)^3]\} \exp[-(\Delta r_k)^2/2l_k^2] \qquad (21)$$

which, via eqns. (13) and (14) yields, for example,

$$p_s(\Delta q_i)\,dq_i = p(\Delta r_i)\,dr_i$$

$$= N'\;\{1 + c_{3i}\;[-3l_i^2\,(\Delta q_i/s_{ij}) + (\Delta q_i/s_{ij})^3]\}$$

$$\times\;\exp\,[-(\Delta q_i)^2/2\langle(\Delta q)_i^2\rangle]\;d\,(\Delta q_i/s_{ij}) \tag{22}$$

Moments implied by eqn. (22) are $\langle\Delta q_i\rangle = 0$, $\langle(\Delta q_i)^2\rangle = s_{ij}^2\,l_i^2$ and

$$\langle(\Delta q_i)^3\rangle = 6c_{3i}s_{ij}^3\,l_i^6 \tag{23}$$

where c_{3i} is the skew parameter presumed to be known for bond i. This yields for the stretching skew parameter

$$c_{3s} = (c_{3i}\,s_{ij}^3\,l_i^6 + c_{3j}\,s_{ji}^3\,l_j^6)/l_M^6\;c \tag{24}$$

What to do about bending is less obvious. We seek the simplest distribution giving realistic results. The most obvious simple model, the circular arc model, incorporates a bending distribution

$$p_b(\Delta\alpha) = N''\,\exp\,[-(\Delta\alpha)^2/2\sigma_\alpha^2] \tag{25}$$

with mean-square bending amplitude σ_α^2, from which, in the notation of eqn. (15), the moments are

$$\langle(\Delta q_b)^n\rangle = \left\langle\left(\sum_m\;D_m\;(\Delta\alpha)^m + \delta\right)^n\right\rangle \tag{26}$$

Accordingly, the shrinkage δ is established as

$$\delta = -D_2\sigma_\alpha^2 - 3D_4\sigma_\alpha^4 + \cdots \tag{27}$$

from the condition that $\langle\Delta q_b\rangle = 0$, whence

$$\langle(\Delta q_b)^2\rangle = D_1^2\sigma_\alpha^2 + \cdots \tag{28}$$

and

$$\langle(\Delta q_b)^3\rangle = 6D_1^2\,D_2\,\sigma_\alpha^4 + \cdots$$

$$\approx 6c_{3b}\,l_M^6 \tag{29}$$

Unfortunately, this is too crude. Equation (29) yields a value of c_{3b} which is negative, as expected intuitively, but which may be far too large in magnitude. That such a model yields an excessive correction might have been anticipated from probability distributions plotted by Morino and Iijima [8].

It is improper to use a distribution of the form $\exp[-V(\Delta r_i, \Delta r_j, \Delta\alpha)/kT]$, analogous to eqn. (11), even for high temperatures, because such a distribution, valid in a one-dimensional problem, fails to take into account kinetic effects coupling Δr_i, Δr_j and $\Delta\alpha$ in bending trajectories.

A greatly simplified "triatomic bender" model was carried through to a form requiring only mean amplitudes, stretch and bend force constants, and stretch and bend frequencies as input. Since it gave promising results it is provisionally adopted and will now be described. The model consists of a symmetric X—A—X fragment whose potential function is purely quadratic

in terms of the curvilinear internal coordinates, or

$$2V(\Delta r_i, \Delta r_j, \Delta\alpha) = k_r[(\Delta r_i)^2 + (\Delta r_j)^2] + 2k_{rr}\Delta r_i\Delta r_j + H(R\Delta\alpha)^2 \qquad (30a)$$

where $R = r_i = r_j$. Since it is essential in deducing a realistic quantum trajectory for the bending motion to allow a stretching correlated in phase with bending, it is necessary to include stretching as well as bending force constants. Since, however, we seek to model the Morse-like anharmonicity separately, via eqn. (24), we include no cubic stretching terms in eqn. (30). Nevertheless, because the internal coordinates are curvilinear, not rectilinear, the potential function is that of an anharmonic oscillator, and the anharmonicity has a crucial influence on the bending trajectory. Consistent with our goal of developing a universal function of great simplicity, we reduce the problem to two dimensions, the symmetric stretch and the bend. Only the symmetric stretch yields the stretch—bend correlation we need, and we disregard the remainder, recasting eqn. (30a) into

$$2V = F\bar{S}_1^2 + H(R\Delta\alpha)^2 + \cdots \qquad (30b)$$

where $\bar{S}_1 = (\Delta r_i + \Delta r_j)/2^{\frac{1}{2}}$ is the desired symmetry coordinate for stretch and F is the associated force constant (to which the final result is sufficiently insensitive that the valence stretch k_r can be used in its place with little loss in accuracy).

Coordinates are then transformed to rectilinear stretch and bend coordinates [24], $S_1 = (\Delta z_i + \Delta z_j)/2^{\frac{1}{2}}$ and $S_2 = (\Delta x_i + \Delta x_j)$ with $\Delta x_i = \Delta x_j$, whence

$$V(S_1, S_2) = V^{\circ} + V' \qquad (31a)$$

with

$$2V^{\circ} = FS_1^2 + HS_2^2 \qquad (31b)$$

representing the harmonic potential and

$$V' = 2^{\frac{1}{2}}F[1 - (4H/F)]S_1S_2^2/8R + \cdots \qquad (31c)$$

expressing the anharmonic coupling. The two-dimensional quantum problem was solved to obtain a first-order wavefunction for arbitrary quantum numbers $m(S_1)$ and $n(S_2)$. In terms of S_1 and S_2, Δq_b of eqn. (15) becomes

$$\Delta q_b = 2^{\frac{1}{2}}sS_1 + cS_2 + \cdots + \delta \qquad (32)$$

where $s = \sin(\alpha/2)$, $c = \cos(\alpha/2)$, and terms quadratic in S_1, S_2 vanish identically. The shrinkage parameter δ, evaluated from a thermal-average distribution by setting $\langle(\Delta q_b)\rangle = 0$, is

$$\delta \approx (s^2/2q_R)[1 - (4H/F)]R^2\sigma_\alpha^2 \qquad (33)$$

where σ_α^2 is the mean-square amplitude of bending (assuming $\sigma_\alpha^2 \approx \langle S_2^2\rangle/R^2$) and q_R is the reference non-bonded distance. For each quantum state (m, n) the moment $\langle(\Delta q_b)^3\rangle$ was calculated incorporating the thermal average value of δ, and then the average of $\langle(\Delta q_b)^3\rangle$ over a Boltzmann distribution was

determined [25]. From this, via eqn. (17), an expression for the bending skew parameter c_{3b} was found to be

$$c_{3b}(T) = \frac{-s^2 c^2 [1 - (4H/F)] G(T) R^4 \sigma_\alpha^4}{2q_R (1 + S) l_M^6} \tag{34}$$

where σ_α and l_M are evaluated at the temperature of interest, $S = (2\nu_b/\nu_s)$ in which ν_b and ν_s are mean bending and stretching frequencies, and

$$G(T) = \left[1 - \frac{(1 - \chi_b)(1 + \chi_s)S}{(1 + \chi_b)(1 - \chi_s)} - \frac{2\chi_b S^2}{(1 + \chi_b)^2} \right] /(1 - S) \tag{35}$$

with $\chi_s = \exp(-h\nu_s/kT)$ and $\chi_b = \exp(-h\nu_b/kT)$. Note that $G(T)$ approaches unity as T approaches zero.

It is worthwhile comparing the result of eqn. (34) with that of the circular arc model of eqn. (29) which, for the present case with $r_i = r_j$, reduces to

$$c_{3b} \text{ (circular arc)} = -(s^2 c^2 / 2q_R l_M^6) R^4 \sigma_\alpha^4 \tag{36}$$

Presumably, the more difficult it is to stretch or compress the bonds, the more nearly should an actual oscillator yield trajectories with circular arcs. That this is the case is shown by taking the stretching force constant in eqn. (34) to be huge, hence also making $\nu_s \gg \nu_b$. With these conditions imposed, eqn. (34) can be seen to approach the circular arc limit at low temperature. For typical molecular cases, however, the disparity between eqns. (34) and (36) can be considerable.

For non-bonded distances in cases where $r_i \neq r_j$, it would be possible to solve a related but appreciably more complicated problem. At this juncture, perhaps, it might suffice in order of magnitude to alter eqn. (34) by averaging force constants and frequencies for the two bonds and replacing the coefficient $(-s^2 c^2 R^4 / 2q_R)$ by $D_1^2 D_2$, in the notation of eqn. (15).

Before presenting numerical results it is necessary to propose a compromise for the simplified model to compensate partly for the errors associated with the assumption of independent internal coordinates. This assumption, among other things, tends to make the model mean-square amplitude l_{UM}^2 of eqn. (18) somewhat too large (as can be seen in the tabulations of the next section). On the other hand, it tends to exaggerate the effects of l_i, l_j, and σ_α in the individual skew contributions of eqns. (24) and (29). Because the amplitudes are present to a high power (4 or 6), errors are amplified. A practical compromise, useful in the examples worked to date, is to use for l_M of eqns. (24), (29), (34) and (36) the geometric mean of the uncorrelated l_{UM} of eqn. (18), and the actual normal coordinate amplitude l_{NC} for the non-bonded distance. This mean has been used in all of the results tabulated in the next section.

NUMERICAL ILLUSTRATIONS

Molecular systems for which reasonably rigorous calculations are available for comparison include CO_2, CS_2, SO_2, H_2O, D_2O, CH_4 and CD_4. In the following we present results for the foregoing triatomic molecules and for SF_6. Methane, being very similar to water on the basis considered here, is deleted for brevity. For CO_2, CS_2, H_2O and D_2O, input amplitudes for the present model are taken from the references cited by Kuchitsu [12]. In the cases of SO_2 and SF_6 for which we illustrate the effect of temperature, the necessary amplitudes were calculated from the quadratic force fields published elsewhere [26, 14]. For the present purposes the differences between amplitudes calculated from a quadratic field and an anharmonic field are unimportant. In all cases but SF_6, skew parameters c_3 for bonds were taken from Kuchitsu's tabulations of moments [12] to permit comparisons of κ values. For SF_6, c_3 values were based on an estimated [17] Morse parameter of 1.8 $Å^{-1}$.

Table 1 shows the stretching and bending components of the non-bonded skew parameter c_3 calculated according to the present model. Because the circular arc model bending contributions are much too negative, net values for c_3 incorporate the results of the triatomic bender model. Although the present model does not reproduce exactly the Kuchitsu values for the moments, the magnitudes are considerably closer to the more rigorous values than are those based on Kuchitsu's diatomic approximation [10, 12]. Even in the case of SO_2, where the present model appears to be much too small at 0 K, two facts should be noted. Firstly, the important thing is that both c_3 values are small (even the rigorous value is an order of magnitude less than the diatomic value) and, hence, neither contributes a serious skew which could distort the determination of a bond length. Secondly, the effect

TABLE 1

Skew parameter for non-bonded distance distribution at 0 K derived by various approximations ($Å^{-3}$)

Molecule	Present model				Kuchitsu	
	c_{3s}^a	c_{3b}^b	c_{3b}^c	c_3^d	c_3 (mom.)^e	c_3(approx)^f
CO_2	136	0	0	136	129	344
H_2O	3.30	−13.98	−4.81	−1.51	−0.90	28.1
D_2O	5.07	−20.66	−7.09	−2.02	−3.41	40.1
SO_2	24.1	−56.6	−21.2	2.9	26.5	207

[a]Stretching contribution from eqn. (24). [b]Bending contribution according to circular arc model, eqn. (36). [c]Bending contribution according to symmetric bender model, eqn. (34). [d]Total, eqn. (24) plus eqn. (34). [e]Method of moments from first-order wavefunction, ref. 12. [f]Diatomic approximation, ref. 12.

TABLE 2

Vibrational parameters calculated for molecules at various temperatures

Molecule	Distance	T (K)	l_{UM}[a] (Å)	l_{NC}[b] (Å)	a_{eff}[c] (Å^{-1})	$10^6\kappa$[d] (Å^3)	$10^6\kappa_{KK}$[e]	$10^3\kappa s_1^2$[f] (Å)
CO_2	OO	0	0.0489	0.0395	1.27	0.52	0.49	0.63
CS_2	SS	0	0.0547	0.0412	1.08	0.52	0.49	0.58
H_2O	HH	0	0.1180	0.1147	−0.05	−1.5	−1.9	−0.29
D_2O	DD	0	0.1009	0.0963	−1.12	−1.6	−2.6	−0.56
SO_2	OO	0	0.0594	0.0523	0.05	0.06	0.73	0.41
	OO	300	0.0617	0.0551	−0.10	−0.10		
SF_6	SF	0		0.0410	(1.8)	0.85		1.0
	SF	300		0.0419	2.1	1.08		1.2
	SF	1000		0.0565	4.4	7.5		4.7
	FF$_c$	0	0.0649	0.0553	0.04	0.07		0.05
	FF$_c$	300	0.0694	0.0602	−0.02	−0.03		−0.02
	FF$_c$	1000	0.1021	0.0915	−0.12	−2.1		−0.41
	FF$_t$	0	0.0580	0.0511	1.0	1.2		0.9
	FF$_t$	300	0.0593	0.0531	1.2	1.6		1.1
	FF$_t$	1000	0.0799	0.0761	2.3	13		4.5

[a]Mean amplitude according to eqn. (18). [b]Mean amplitude according to normal coordinate theory. [c]Effective Morse parameter of $P_0(x)$ according to eqn. (37). [d]Phase modulation parameter, present calculation. [e]Phase modulation parameter from ref. 12. [f]Anharmonic distance correction at $s_1 = 2^{1/2}/l_{NC}$ (see text); entries for SF_6 from κ values of present model, others from Kuchitsu values, ref. 12.

of temperature is to make c_3 tend rapidly toward negative values, and the rigorous value, which is appropriate at 0 K, may be appreciably too large at room temperature.

The discrepancy between amplitudes l_{UM} calculated according to the uncorrelated model of eqn. (18) and the normal coordinate amplitudes l_{NC} can be seen in Table 2. In future work it would be desirable to formulate a less crude model. For the benefit of those who base their skew in diffraction analyses upon the ground state Morse distribution $P_0(x)$ discussed at length in ref. 2, we also tabulate the effective Morse parameter

$$a_{eff} = 6c_3 l_{NC}{}^2 \tag{37}$$

which imparts the requisite skew into $P_0(x)$. Phase modulation parameters κ are compared with Kuchitsu's values, where available. Finally, to give a more concrete illustration of the practical effect of the skew on a structure determination, we tabulate $10^3 \kappa s_1^2$, the shift (in thousandths of an Angstrom unit) in the effective bond length $(r_a - \kappa s_1^2)$. This is the length inferred from an electron interference fringe at the scattering angle at which the damping envelope $\exp(-l^2 s_1^2/2)$ has dropped to e^{-1}.

It is prudent to emphasize once more the crudeness of the foregoing treatment. It is to be hoped that a better approximation will be forthcoming. As can be seen, particularly in the SF_6 results of Table 2, the effect of skewing increases rapidly with temperature and can far exceed experimental error. Therefore, in view of the increasing interest in the dependence of structure on temperature [14, 27], it is imperative that the effects of anharmonicity be taken into account. While the present treatment is not guaranteed to give precise results, it seems to be less risky than a blind guess or complete neglect of the problem.

Note added in proof: it has been shown by W. H. Miller [28] how to derive an "effective potential" $V_e(x)$, such that the expression, $N \exp [-V_e(x)/kT]$, gives a reasonably faithful distribution function $P(x,T)$ at all temperatures (see eqn. (10) in text, which is only valid at high values of T, and refs. 29 and 30).

REFERENCES

1 L. S. Bartell, J. Chem. Phys., 23 (1955) 1219.
2 A. Reitan Det. Kgl. Nor. Vidensk. Selskabs. Skr., 2 (1958).
3 A. Reitan, Acta Chem. Scand., 12 (1958) 785.
4 K. Kuchitsu and L. S. Bartell, J. Chem. Phys., 35 (1961) 1945.
5 K. Kuchitsu and L. S. Bartell, J. Chem. Phys., 36 (1962) 2460.
6 K. Kuchitsu and L. S. Bartell, J. Chem. Phys., 36 (1962) 2470.
7 N. G. Rambidi, Zh. Strukt. Khim., 4 (1963) 167.
8 Y. Morino and T. Iijima, Bull. Chem. Soc. Jpn., 36 (1963) 412.
9 R. A. Bonham and J. L. Peacher, J. Chem. Phys., 38 (1963) 2319.
10 K. Kuchitsu and Y. Morino, Bull. Chem. Soc. Jpn., 38 (1965) 805, 814.
11 K. Kuchitsu, Bull. Chem. Soc. Jpn., 40 (1967) 498.
12 K. Kuchitsu, Bull. Chem. Soc. Jpn., 40 (1967) 505.
13 L. S. Bartell, J. Chem. Phys., 70 (1979) 4581.

14 L. S. Bartell, S. K. Doun and S. R. Goates, J. Chem. Phys., 70 (1979) 4585.

15 P. Debye, J. Chem. Phys., 9 (1941) 55.

16 R. M. Badger, J. Chem. Phys., 2 (1934) 128.

17 D. R. Herschbach and V. M. Laurie, J. Chem. Phys., 35 (1961) 458.

18 K. Kuchitsu and Y. Morino, Spectrochim Acta, 22 (1966) 33; Y. Morino, Pure Appl. Chem., 18 (1969) 323.

19 L. S. Bartell, S. Fitzwater and W. J. Hehre, J. Chem. Phys., 63 (1975) 3042.

20 L. S. Bartell and K. Kuchitsu, J. Chem. Phys., 68 (1978) 1213.

21 Equations (65) and (66) of K. Kuchitsu, Bull. Chem. Soc. Jpn., 40 (1967) 498.

22 T. Shimanouchi, J. Chem. Phys., 17 (1949) 245.

23 M. A. Kacner and L. S. Bartell, J. Chem. Phys., 71 (1979) 192.

24 See K. Kuchitsu and L. S. Bartell, J. Chem. Phys., 36 (1962) 2460, for conventions used.

25 In Boltzmann averaging, the effect of anharmonicity on energy levels was neglected. Then the identities $(\Sigma\, m e^{-mu}/\Sigma\, e^{-mu}) = \chi/(1 - \chi)$ and $(\Sigma\, m^2 e^{-mu}/\Sigma\, e^{-mu}) = \chi(1 + \chi)/(1 - \chi)^2$, where $\chi = e^{-u}$, with $u = h\upsilon/kT$, made thermal averaging comparatively simple.

26 Y. Morino, Y. Kikuchi, S. Saito and E. Hirota, J. Mol. Spectrosc., 13 (1964) 95.

27 M. Kelley and M. Fink, to be published.

28 W. H. Miller, J. Chem. Phys., 55 (1971) 3146.

29 V. S. Iorish and V. Yu. Zisserman, Chem. Phys. Lett., 34 (1975) 378.

30 V. P. Spiridonov, A. G. Gershikov and B. S. Butayev, J. Mol. Struct., 52 (1979) 53.