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EFFECTS OF ANHARMONICITY OF MOLECULAR VIBRATIONS ON THE DIFFRACTION OF ELECTRONS

Part V. Tetrahedral molecules

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ABSTRACT

Unless the skewing of radial distribution peaks is properly taken into account, diffraction analyses of gas molecules may lead to geometrically inconsistent arrays of internuclear distances. It is shown how to derive the required nonbonded skew parameter $\hat{a}$ for a tetrahedral AX_4 molecule from its potential constants in the case of an ensemble distributed among too many vibrational states to make the standard perturbation or variation methods feasible. Elements of the transformation tensor relating curvilinear coordinates $\mathcal{S}_i$ to rectilinear coordinates S_i are found and applied in a treatment using the "effective potential energy" approach of Miller. Illustrative calculations are carried out for hot CF_4 and SiF_4 molecules. It is verified that the contributions to $\hat{a}$ from nonlinear transformations and from Morse stretching deduced by a simple model in Part III of this series are in reasonably good agreement with the more rigorous contributions calculated in this research. It is shown, however, that certain other contributions are larger.

INTRODUCTION

Electron diffraction studies of hot molecules [1] have revealed unexpectedly large asymmetries in the radial distribution functions of the geminal nonbonded distances. The pronounced skewing, opposite in sense to that naturally associated with the curvilinear bending trajectories, was traced to a strong contribution by bend—bend—bend cubic constants, a source of anharmonicity not easily characterized by spectroscopy [2]. What is most significant about this is the appealingly simple pattern of behavior of molecules that was discovered when potential surfaces for bending deformations were examined [3]. Because insufficient spectroscopic information had been available to test our hypothesis about the origin of the skewness, a mechanical model of repelling points-on-a-sphere (POS) [3—6] based on the valence-shell-electron-pair-repulsion (VSEPR) theory [7] was introduced to estimate magnitudes. When it proved reasonably successful in accounting for the diffraction observations [6] its implications were compared with those of molecular orbital theory. A remarkable parallel was found [3]. The

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insight to be gained by pursuing this lead warrants the development of a practical analysis relating the potential energy surfaces of molecules to their electron diffraction patterns. Therefore this problem is addressed in the following.

Prior treatments connecting molecular force fields to electron diffraction intensities have been of two kinds: (a) variational [8] and perturbation [9—11] calculations applicable to individual vibrational states and (b) calculations [6] based on a Boltzmann distribution in potential energy. Treatment (a) works excellently in cases where thermal populations require averages only over a small number of states. It is prohibitive in studies of molecules sufficiently hot to manifest the bending anharmonicity conspicuously. Treatment (b) is dubious unless the temperature is high enough to make $kT \gg h\nu$. Such severe conditions suggest rapid thermal decomposition and amplitudes of vibration so large that the anharmonic potential energy may no longer be a small perturbation. A promising approach, retaining the simplicity of (b) but substantially improving its accuracy is to carry out averages over a Boltzmann distribution in an effective potential energy V_{eff} suggested by Miller [12] and already applied to one dimensional anharmonic cases in electron diffraction by Spiridonov et al. [13, 14]. Effects of the nonlinear transformation from curvilinear to normal coordinates, treated somewhat crudely in prior work [15], can readily be incorporated in the V_{eff} treatment. Details of the treatment, as they apply to AX_4 molecules of T_d symmetry, are outlined in the following.

Because the characterization of AX bond distributions and their contributions to diffraction intensities has received extensive and quite successful treatment in existing literature [11, 15—18] we will focus our attention upon asymmetry in geminal nonbond distributions. Such skewing has led to heretofore poorly understood "anharmonic shrinkage effects" [6, 19] but contains valuable information about bending anharmonicity.

TREATMENT

Cubic force field

Following an earlier convention [20] in which plain symbols correspond to rectilinear coordinates and decoration by a tilde implies that an internal or symmetry coordinate is a curvilinear coordinate, we write the potential energy in its most natural form [21] as

$$V = 1/2 \sum_i \sum_j f_{ij} \tilde{S}_i \tilde{S}_j + 1/6 \sum_i \sum_j \sum_k \tilde{f}_{ijk} \tilde{S}_i \tilde{S}_j \tilde{S}_k + \cdots \qquad (1)$$

Plausible values of the cubic constants $\tilde{f}_{ijk}$ can be derived with the aid of the KBFF model [9, 18] (or, for bending, the POS model [3]) from molecular orbital calculations [3, 22] or, occasionally, from experiment. For the vibrational calculations needed subsequently it is far simpler to work in terms of rectilinear symmetry and normal coordinates S_i and Q_i for which

$$V = 1/2 \sum_i \sum_j f_{ij} S_i S_j + 1/6 \sum_i \sum_j \sum_k f_{ijk} S_i S_j S_k + \cdots \tag{2a}$$

$$= 1/2 \sum \phi_{ii} Q_i^2 + 1/6 \sum_i \sum_j \sum_k \phi_{ijk} Q_i Q_j Q_k + \cdots \tag{2b}$$

where **Q** and **S** are related by the linear transformation

$$\mathbf{S} = \mathbf{L}\,\mathbf{Q} \tag{3}$$

while $\tilde{\mathbf{S}}$ and **S** are connected nonlinearly by

$$\tilde{S}_i = S_i + 1/2 \sum_j \sum_k T_i^{jk} S_j S_k + \cdots \tag{4}$$

From eqns. (3) and (4) follow the required transformations [20]

$$f_{ijk} = \tilde{f}_{ijk} + \sum_r \left(f_{ri} T_r^{jk} + f_{rj} T_r^{ik} + f_{rk} T_r^{ij}\right) \tag{5}$$

$$\equiv \tilde{f}_{ijk} + f_{ijk}^{tr}$$

and [21]

$$\phi_{ijk} = \sum_l \sum_m \sum_n f_{lmn} L_{li} L_{mj} L_{nk} \tag{6}$$

Elements of the T tensor of eqns. (4) and (5), derived for tetrahedral AX_4 molecules from considerations of geometry, are listed in Table 1. Cubic force constants for these molecules corresponding to the KBFF recipe, including the stretch—stretch—stretch, stretch—stretch—bend, and stretch—bend—bend interactions needed in the present calculations [23, 24], are

$$\tilde{f}_{111} = -3aK/2 + 2F_3/r_e \tag{7}$$

$$\tilde{f}_{133} = -3aK/2 + 2(-F' + F + F_3)/3r_e \tag{8}$$

$$\tilde{f}_{134} = (2F + F_3)/3r_e \tag{9}$$

$$\tilde{f}_{233} = (5F' + 7F/2 + 2F_3)/54^{1/2} r_e \tag{10}$$

$$\tilde{f}_{122} = (-F' + F + F_3)/6r_e \tag{11}$$

TABLE 1

Non-zero elements T_i^{jk} of transformation tensor[a] of eqns. (4) and (5) with i, j, k representing symmetry coordinates 1, $2a$, $3z$, or $4z$ for the AX_4 molecule with T_d symmetry

i	Elements			
1	$T_1^{22} = 1/6R$	$T_1^{44} = 1/4R$		
$2a$	$T_2^{12} = -1/2R$	$T_2^{22} = -6^{1/2}/24R$	$T_2^{34} = -6^{1/2}/4R$	$T_2^{44} = 6^{1/2}/8R$
$3z$	$T_3^{24} = 6^{1/2}/12R$			
$4z$	$T_4^{14} = -1/2R$	$T_4^{23} = -6^{1/2}/6R$		

[a] Symmetry coordinate convention of ref. 25. R is the AX bond length.

$$\bar{f}_{144} = (-5F' - 3F + F_3)/6r_e \tag{12}$$

$$\bar{f}_{234} = (-8^{1/2}F' + F_3)/108^{1/2}r_e \tag{13}$$

in the notation of ref. 9. For the present purposes we use molecular orbital results for the bend—bend—bend constants $\bar{f}_{222}$ and $\bar{f}_{244}$. It should be noted that sign conventions in the above equations conform to those of Shimanouchi [25] and ref. 9, rather than those of Cyvin [26] and Pulay et al. [22].

Probability density and effective potential energy

Miller [12] has shown how to obtain a "better than classical" approximation for the Boltzmann density matrix by a path integral technique. From an effective potential energy V_{eff}, given explicitly for a one-dimensional problem (eqn. (22) of ref. 12), can be calculated a probability density

$$\rho = N \exp(-V_{eff}/kT) \tag{14}$$

that is exact if V is quadratic and which quite accurately reflects the first three moments of a Morse oscillator distribution at temperatures above $h\nu/2k$. Extension to the multidimensional case of eqn. (2b) can be accomplished with tolerable accuracy by modifying the quadratic and cubic constants to

$$\phi^e_{ii} = \phi_{ii}W_i \tag{15}$$

$$\phi^e_{iii} = \phi_{iii}(1 + 3W_{ii}/2) \tag{16}$$

$$\phi^e_{ijj} = \phi_{ijj}(W_iW_j + W_{jj}/2) \quad , (i \neq j) \tag{17}$$

$$\phi^e_{ijk} = \phi_{ijk}\, W_iW_jW_k \quad , (i \neq j \neq k) \tag{18}$$

where

$$W_i = (\tanh v_i)/v_i \tag{19}$$

$$W_{ii} = \mathrm{sech}^2 v_i - W_i \tag{20}$$

and

$$v_i = h\nu_i/2kT \tag{21}$$

To simplify the problem further, we separate V_{eff} into its harmonic and anharmonic components V_h^{eff} and V_a^{eff} and write

$$\begin{aligned}\rho &= N \exp(-V_h^{eff}/kT)\cdot\exp(-V_a^{eff}/kT)\\ &\approx N \exp(-V_h^{eff}/kT)\cdot(1 - V_a^{eff}/kT)\end{aligned} \tag{22}$$

treating V_a^{eff}/kT as a perturbation. It is readily shown that

$$\exp(-V_h^{eff}/kT) = \Pi_i \exp(-Q_i^2/2\langle Q_i^2\rangle) \tag{23}$$

where

$$\langle Q_i^2 \rangle = (h\nu_i/2\phi_{ii}) \coth (h\nu_i/2\,kT) \tag{24}$$

is the exact mean square amplitude for a quantum harmonic oscillator whatever the temperature.

Moments and skew parameter

As outlined elsewhere [6], the radial distribution function of an internuclear distance is specified, adequately enough to characterize its contribution to a diffraction pattern, by its first three moments. Let q, q_e, and x represent the instantaneous X$\cdots$X distance, the equilibrium distance, and the displacement from equilibrium, respectively, in AX_4. From the moments

$$\langle x^n \rangle = \int x^n \rho(Q_1, Q_2, \cdots)\, dQ_1 dQ_2 \tag{25}$$

can be found the mean internuclear distance

$$q_g = q_e + \langle x \rangle \tag{26}$$

the mean-square displacement from the mean

$$l_g^2 = \langle x^2 \rangle - \langle x \rangle^2 \tag{27}$$

and the skew parameter [6] herein sought

$$\begin{aligned} \hat{a} &= \langle (x - \langle x \rangle)^3 \rangle / l_g^4 \\ &= (\langle x^3 \rangle - 3\langle x^2 \rangle \langle x \rangle + 2\langle x \rangle^3)/l_g^4 \end{aligned} \tag{28}$$

In order to evaluate the integrals of eqn. (25), x for the $X_1 \cdots X_2$ distance is expanded in the Taylor series [9]

$$\begin{aligned} x &= (2/3)^{1/2} (L_{11}Q_1 + \sigma Q_{3z} + \tau Q_{4z}) + L_{22}Q_{2a}/3 + \cdots \\ &\equiv \gamma_1 Q_1 + \gamma_2 Q_{2a} + \gamma_3 Q_{3z} + \gamma_4 Q_{4z} + \cdots \end{aligned} \tag{29}$$

where $\sigma = L_{33} + L_{43}/2$ and $\tau = L_{34} + L_{44}/2$. When this result, together with eqn. (22), is inserted into eqn. (25), integration is straightforward. If V_a^{eff} in eqn. (22) is retained only through cubic terms, and corrections in moments, through mean square amplitudes cubed, then the second moment is [9]

$$\begin{aligned} \langle x^2 \rangle &= \gamma_1{}^2 \langle Q_1{}^2 \rangle + \gamma_2{}^2 \langle Q_2{}^2 \rangle + \gamma_3{}^2 \langle Q_3{}^2 \rangle + \gamma_4{}^2 \langle Q_4{}^2 \rangle \\ &\quad + (L_{11} \langle Q_1 \rangle / r_e) [(L_{22})^2 \langle Q_2{}^2 \rangle /3 + \sigma^2 \langle Q_3{}^2 \rangle + \tau^2 \langle Q_4{}^2 \rangle] \end{aligned} \tag{30}$$

where

$$\langle Q_1 \rangle = -\frac{\langle Q_1{}^2 \rangle}{2\ kT} (\phi_{111}^e \langle Q_1{}^2 \rangle + 2\phi_{122}^e \langle Q_2{}^2 \rangle + 3\phi_{133}^e \langle Q_3{}^2 \rangle + 3\phi_{144}^e \langle Q_4{}^2 \rangle) \tag{31}$$

First and third moments can be expressed as

$$\langle x \rangle = \sum_{i \leqslant j \leqslant k} \sum \sum - \lambda_{ijk}\ (\phi_{ijk}^e / kT) \gamma_i \langle Q_i^2 \rangle \langle Q_j^2 \rangle \tag{32}$$

and

$$\langle x^3 \rangle = \sum_{i<j<k} \sum \sum -\eta_{ijk} (\phi^e_{ijk}/kT) \gamma_i \langle Q_i^2 \rangle \langle Q_j^2 \rangle$$
$$\times (\zeta_1 \langle Q_1^2 \rangle + \zeta_2 \langle Q_2^2 \rangle + \zeta_3 \langle Q_3^2 \rangle + \zeta_4 \langle Q_4^2 \rangle \qquad (33)$$

where coefficients γ_i are identified in eqn. (29) and λ_{ijk}, η_{ijk}, and ζ_l^{jkl} are listed in Table 2. From the above moments can be calculated the desired distribution function parameters of eqns. (26)—(28). These are related to diffraction intensities as illustrated in ref. 6.

Explicit expressions for the effect of the interactions of greatest interest, the purely bending cubic constants $\bar{f}_{222}$ and $\bar{f}_{244}$, can be written simply if the conversion from V to V_{eff} is not made in the anharmonic potential energy. Correcting inconsistencies in ref. 6, we write for the bending contributions to the asymmetry constants

$$\bar{a}_{222} = -\bar{f}_{222} \langle S_2^2 \rangle^3 / (27 l_g^4 kT) \qquad (34)$$

and

$$\bar{a}_{244} = -\bar{f}_{244} \langle S_2^2 \rangle (\langle S_4^2 \rangle + 2\langle S_3 S_4 \rangle)^2 / (6 l_g^4 kT) \qquad (35)$$

For bending modes of hot molecules the corrections to V_{eff} are less crucial than to stretching modes. If corrections are made, as seems desirable routinely, it is no longer attractive to work in terms of symmetry coordinates and expressions (29)—(33) are more appropriate.

ILLUSTRATIVE CALCULATIONS

Computations were carried out for illustrative purposes using the force fields of Clark and Rippon [27] for CF_4 and SiF_4 as if they were bona fide quadratic components of an anharmonic force field. Cubic constants for stretch—stretch—stretch, stretch—stretch—bend, and stretch—bend—bend

TABLE 2

Coefficients for calculating moments of eqns. (32) and (33)[a]

ijk	λ_{ijk}	η_{ijk}	ζ_1	ζ_2	ζ_3	ζ_4
111	1/2	3/2	$5\gamma_1^2/3$	γ_2^2	γ_3^2	γ_4^2
122	1	3	γ_1^2	$2\gamma_2^2$	γ_3^2	γ_4^2
133	3/2	9/2	γ_1^2	γ_2^2	$5\gamma_3^2/3$	γ_4^2
134	0	6	0	0	0	$\gamma_3\gamma_4$
144	3/2	9/2	γ_1^2	γ_2^2	γ_3^2	$5\gamma_4^2/3$
222	0	1	0	0	γ_3^2	0
233	0	3	0	0	γ_3^2	0
234	0	6	0	0	0	$\gamma_3\gamma_4$
244	0	3	0	0	0	γ_4^2

[a] Coefficients γ_i are defined in eqn. (29).

were KBFF values based on Set II and Set I potential constants and reference bond lengths taken from ref. 18. Pure bend—bend—bend constants $\bar{f}_{222}$ and $\bar{f}_{244}$ (aJ Å^{-3}) of —0.628 and —1.287, respectively, for CF_4, —0.250 and —0.473 for SiF_4 are from semiempirical molecular orbital calculations later closely checked for CF_4 by ab initio calculations [3]. Differences between Set II and Set I may give a rough idea of uncertainties associated with force fields. Alternatively, a comparison between our anharmonic constants and those of Suzuki and Overend [28], derived for CF_4 with a somewhat similar model, can be made in Table 3.

Listed in Table 4 are mean displacements of nonbonded distances from equilibrium (including ordinary "shrinkage" [26], namely the foreshortening encountered via the nonlinear transformations [20]). Also in Table 4 are some of the more important contributions to the asymmetry parameter $\hat{a}$ including the substantial effect of the pure bend—bend—bend components from $\bar{f}_{222}$ and $\bar{f}_{244}$. Although these cubic constants are modest in comparison with some of the others such as $\bar{f}_{111}$, their influence is amplified by the large amplitudes of the bending modes. Morse and transformation contributions to $\hat{a}$ were supposed to have been derivable, approximately, also by the simplified "predictive model" of ref. 15. Numerical calculations [18] made prior to the present work do agree approximately with those of the present more rigorous approach, as shown in Table 4.

As forecast in ref. 6, the skew parameter $\hat{a}$ is not strongly dependent upon temperature once a molecule is hot enough for the present treatment to be valid. This is illustrated in Table 5. If the standard coefficient of skewness [6]

$$A_3 = \hat{a}l_g$$

TABLE 3

Model cubic constants C_{ijk} (in cm^{-1}) for dimensionless normal coordinates[a] of CF_4: subset required for calculation of $\hat{a}_{FF}$

ijk	Set I[b]	Set II[c]	S&O[a]
111	—18.2	—21.4	—27.0
122	0.8	—7.3	—20.5
133	—69.1	—57.3	—41.7
134	—58.3	—46.5	—47.5
144	—8.9	—20.4	—36.7
222	—9.0	—9.0	—9.9
233	—37.1	—35.3	—10.7
234	34.8	21.0	—11.7
244	—22.7	—26.2	—32.4

[a] Ref. 28. Because the present research uses Shimanuchi's sign conventions (ref. 25) the signs of the Suzuki and Overend constants were changed for C_{134} and C_{234}. [b] KBFF Set I of ref. 18 for all but bend—bend—bend curvilinear constants where MO values of ref. 3 were adopted. [c] As for footnote b except that Set II constants of ref. 18 replace Set I constants. In ref. 18 Set II was preferred.

TABLE 4

Selected results[a] of computations, x in A, $\hat{a}$ in A^{-1}, for nonbonded distributions of CF_4 at 1700 K (top of table) and SiF_4 at 900 K (bottom)

Cubic const.	$10^3\langle x\rangle$	$10^4\langle x^2\rangle$	$\hat{a}^{b}_{Morse}$	$\hat{a}^{c}_{trans}$	$\hat{a}^{d}_{bbb}$	$\hat{a}_{tot}$
CF_4						
Set II	17.5	106.2	0.32	−0.65	1.33	2.15
Set II Boltz[e]			0.36	−0.68	1.38	2.29
Set I	13.8		0.32	−0.65	1.33	1.55
f^{tr}_{ijk} only	−5.9		0	−0.65	0	−0.65
Model, ref. 15			0.58	−0.59		
SiF_4						
Set II	5.8	125.5	0.18	−1.26	2.01	1.27
Set II Boltz[e]			0.24	−1.45	2.11	1.31
Set I	3.7		0.18	−1.26	2.01	1.06
f^{tr}_{ijk} only	−8.9		0	−1.26	0	−1.26
Model, ref. 15			0.14	−1.13		

[a] See footnote b and c of Table 3 for meanings of Sets I and II. [b] Contribution from $\bar{f}_{111}$ and $\bar{f}_{122}$. [c] Contribution from nonlinear transformation from $\bar{S}_i$ to S_i. [d] Contribution of pure bend—bend—bend curvilinear MO constants. [e] Simple Boltzmann average over V (anharmonic) instead of using V_a^{eff}. Correct harmonic probability density adopted.

TABLE 5

Selected results of computation for nonbonded distribution of CF_4, Set II[a], x in A, $\hat{a}$ in A^{-1}, at various temperatures

Parameter	Temperature (K)		
	1300	1500	1700
$\hat{a}_{tot}$	2.113	2.135	2.153
$10^4\langle(x-\langle x\rangle)^2\rangle$	70.5	94.2	106.2
$10^3\langle x\rangle$	14.29	15.84	17.46

[a] See footnotes, Table 3.

or the frequency modulation parameter κ for scattering intensities, namely

$$\kappa = \hat{a}l_g^4/6$$

had been tabulated instead, a larger temperature dependence would have been seen. That is one reason for choosing $\hat{a}$ to characterize asymmetry, although it is well established that, for Morse diatomic oscillators, $\hat{a}$ is appreciably lower when $kT \ll h\nu$ than at higher temperatures where it levels off [6, 16].

DISCUSSION

It is fair to ask whether the present considerations are fundamentally different from the "curvilinear effects" treated more simply by Gershikov et al. [29] and whether diffractionists should be concerned about the asymmetry parameter, $\hat{a}$, in practical structure analyses. After all, few molecules can be as well characterized as the simple T_d molecules treated in the foregoing and the treatment looks bothersome. General treatments of more complex molecules would need even more intricate computations and some source of information on the relevant anharmonic potential constants. A few comments on the latter problem of feasibility are appropriate before addressing the first questions.

For simple molecules (e.g. AX_4, AX_6) a brief program for a microcomputer quickly carries out the necessary calculations. For more general molecules a modest extension of a program built around the L tensor of Hoy et al. [21] should suffice. Plausible cubic parameters are readily guessed from quadratic force constants if the POS model [5, 6] is invoked for bends and the KBFF model [9, 18] for most of the remainder. Meanwhile, the present illustrative calculations offer an indication of magnitudes involved.

The kinematic treatment of curvilinear effects for bending motions by Gershikov et al. [29] is supposed to interrelate, approximately, the r_α and r_g parameters for the bonds of linear AB_2 and planar AB_3 molecules, despite its neglect of potential energy considerations. Now, bending in linear AB_2 and out-of-plane bending in AB_3 contribute nothing, in first approximation, to $\hat{a}$(BB) either by nonlinear transformation or by pure bend cubic constants (zero by symmetry in these special cases). In-plane bends of AB_3 do, of course, contribute to $\hat{a}$(BB) but are not addressed by the kinematic treatment [29]. Because an extension of this treatment to more general cases could not account for the major part of the skew parameters so far observed, the kinematic treatment cannot be considered an alternative approach to the present problem.

Effects of the skewing of geminal nonbond distributions, if not taken into account, may distort least squares refinements by over 0.01 Å for hot, fairly rigid molecules [1] and up to 0.1 Å for certain pseudorotating molecules [30], by virtue of large bending amplitudes. Not only may the internuclear distances be influenced by neglect of asymmetry. Even amplitudes of vibration of neighboring peaks have been found, in practice, to be altered. In the case of hot AX_4 and AX_6 molecules, temperatures inferred from AX and XX mean-square amplitudes failed to agree with each other until suitable $\hat{a}$ values were adopted [31]. Rational analyses extracting the full information implicit in diffraction intensities require appropriate asymmetry parameters.

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