

Bond lengths of vibrationally hot AX_n molecules. A simple treatment

L. S. Bartell

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109
(Received 31 January 1979)

Given the form of an anharmonic, modified Urey-Bradley molecular force field for AX_n molecules, it is shown how to express the mean vibrational displacements of bond lengths from equilibrium lengths r_e simply in terms of elementary quantities. The dominant terms isolated are due to Morse stretching anharmonicity, nonbonded interactions, and the centrifugal stretching of bonds encountered as the atoms swing over arced trajectories in bending vibrations. Illustrative calculations are presented for CH₄ and CD₄.

INTRODUCTION

There is an increasing emphasis on the study of vibrationally excited molecules. For many years, particularly in the Soviet Union,¹ molecules issuing from high temperature nozzles have been studied by electron diffraction. More recently, molecules irradiated by infrared lasers have been investigated by a variety of techniques.² In the course of a structure study of sulfur hexafluoride³ we observed that the bond length increases markedly faster with temperature than would be expected according to the frequently invoked diatomic formula⁴

$$r_e - r_e \equiv \langle \Delta r \rangle = 3a \langle (\Delta r)^2 \rangle / 2. \quad (1)$$

After a little reflection it was found to be possible to account very well for the increase with existing information by adopting a model anharmonic force field postulated two decades ago.^{5,6} It also turned out to be possible for certain AX_n molecules to simplify the treatment of $\langle \Delta r \rangle$ considerably from the original perturbation treatment^{5,6} and to express the final results in an elementary form requiring only a modest amount of information as input. The approach is outlined in the following.

THEORETICAL TREATMENT

Molecules to which treatment applies

Although the method of approach sketched below can be generalized to molecules of arbitrary complexity, our aim in the present paper is to derive simple, explicit formulas applicable to AX_n molecules with all bonds equivalent and all bond angles determined by the symmetry of the point group. This restriction excludes $n=5$ and 7 , for example, though AX₅ and AX₇ would be only somewhat more complicated. While AX₆ and molecules with higher coordination qualify, we shall treat only interactions between adjacent bonds and neglect more remote interactions.

Model force field

In principle, if the force field of a molecule were known in detail, it would be possible to carry out a rigorous treatment of vibrational effects as outlined by several authors.⁵⁻⁹ In practice, cubic and higher order force constants are known reliably for only a handful of

molecules. Therefore it is useful to express the force field in a form for which the necessary parameters are available in the literature, can be readily calculated by quantum chemical techniques, or can be guessed closely enough to give a reasonable result. Such a field is the anharmonic, modified Urey-Bradley field first proposed for water⁵ and methane⁶ and later applied to a series of triatomic molecules¹⁰ and to ethane.¹¹ This field will hereafter be referred to as the KB field. Recent *ab initio* molecular orbital calculations have confirmed the essential correctness of the cubic constants predicted for methane^{12,13} and ethane,¹¹ and spectroscopic studies¹⁰ have tested the validity in the case of the triatomic molecules. Systematic deficiencies have been characterized¹⁰⁻¹³ but these do not have a serious influence on the results we seek herein. The KB field is simply the sum of a conventional Urey-Bradley field V_{UB} expanded out to cubic terms, or

$$V_{UB} = \sum [K' r_e (\Delta r_i) + \frac{1}{2} K (\Delta r_i)^2 - \frac{1}{2} a K (\Delta r_i)^3 + \dots] + \sum_{i < j} [H' r_e^2 (\Delta \alpha_{ij}) + \frac{1}{2} H r_e^2 (\Delta \alpha_{ij})^2 + (\frac{1}{6}) H_3 r_e^2 (\Delta \alpha_{ij})^3] + \sum_{i < j} [F' q_e (\Delta q_{ij}) + \frac{1}{2} F (\Delta q_{ij})^2 + (\frac{1}{6}) F_3 (\Delta q_{ij})^3 + \dots] \quad (2)$$

where the symbols have their usual meaning^{5,6,14} and an additional potential function V_A , described in Ref. 14, and included in order to make the quadratic field perfectly general.¹⁵ Of the force constants over and above those in V_{UB} , the most important one for hydrides has been found to be G , that portion of the stretch-stretch interaction not accounted for by the nonbonded constants F' and F . Accordingly, we write

$$V_A = \sum_{i < j} G \Delta r_i \Delta r_j + \dots \quad (3)$$

It is assumed that cubic terms in V_A will be smaller than those in V_{UB} . An exception to this is briefly discussed in the last section.

Values of force constants

Linear force constants K' , H' , and F' are interrelated by the equilibrium conditions. Bending anharmonicity as expressed in constant H_3 is small and neglected in the following. We shall also neglect H' and the related

"intramolecular tension" parameter found in a previous study⁶ to make trivial contributions to $\langle \Delta r \rangle$. Morse bond stretching anharmonicity is embodied in the Morse parameter a in Eq. (2). It is usually approximately 2 \AA^{-1} , and more accurate values for common bonds can be found in tabulations by Herschbach and Laurie.¹⁶ The most poorly characterized force constants, and the most controversial, are the nonbonded constants F' , F , and F_3 . Nevertheless, results to date^{11,13} indicate that it is better to include them than exclude them. Moreover, there are several ways they can be estimated. First, a reasonable value for F can be estimated by a Urey-Bradley analysis of vibrational frequencies or, better, from stretch-bend interaction constants (see Ref. 14) if they are available from a more complete analysis. In order of magnitude, it is expected that $F \approx -10F' \approx -0.1F_3$ if the nonbonded potential falls as Aq^{-n} with n in the range of 9 to 12. Therefore, a measure of F serves as a measure of F' and F_3 , also. A number of nonbonded potential functions, some better than others, have been constructed from empirical data. Deriva-

tives of these functions yield $F'q$, F , and F_3/q directly. Lastly, *ab initio* quantum calculations of nonbonded functions are becoming available.

Calculation of mean displacement

From Ehrenfest's theorem¹⁷ for the motion of wave packets it can be deduced that the space average potential energy derivative vanishes,

$$\langle \partial V / \partial z_i \rangle = 0 \quad (4)$$

for stationary states or equilibrium distributions among stationary states,¹⁸ where z_i is a Cartesian displacement coordinate of any particle in the system. For the present problem we adopt the conventional notation with Δx_i and Δy_i representing the Cartesian displacement coordinates of atom i perpendicular to and Δz_i the displacement along the bond axis as illustrated in Ref. 5. Then letting $V = V_{UB} + V_A$, designating the number of bonds in AX_n adjacent to AX_i as m , and carrying out the differentiation of Eq. (4), we find

$$K' r_e \langle \partial r_i / \partial z_i \rangle + K \langle \Delta r_i \partial r_i / \partial z_i \rangle - \left(\frac{3}{2}\right) a K \langle (\Delta r_i)^2 \partial r_i / \partial z_i \rangle + m H r_e^2 \langle \Delta \alpha_{ij} \partial \alpha_{ij} / \partial z_i \rangle + m F' q_e \langle \partial q_{ij} / \partial z_i \rangle + m F \langle \Delta q_{ij} \partial q_{ij} / \partial z_i \rangle + m (F_3 / 2 q_e) \langle (\Delta q_{ij})^2 \partial q_{ij} / \partial z_i \rangle + m G \langle \Delta r_j \partial r_j / \partial z_i \rangle + \dots = 0, \quad (5)$$

disregarding the minor H' and H_3 terms. Making use of the z_i dependence of r_i , r_j , α_{ij} , and q_{ij} given explicitly in Eqs. (14)–(19) of Ref. 5, and noting that $\langle \Delta q \rangle = 2s \langle \Delta r \rangle - \delta_{xx}$ where $s = \sin(\alpha_{ij}/2)$ and $\delta_{xx} = 2sK_{AX} - K_{XX}$ is the "shrinkage" of the nonbonded distance for which¹⁹

$$K_{ab} = \langle (\Delta x_{ab})^2 + (\Delta y_{ab})^2 \rangle / 2r_{ab}, \quad (6)$$

we obtain

$$(K' r_e + m s F' q_e) + (K + 2m s^2 F + m G) \langle \Delta r \rangle_v - (3aK/2) \langle (\Delta r)^2 \rangle - (mH/2r_e) \langle (r_e \Delta \alpha)^2 \rangle - m s (F' K_{xx} + F \delta_{xx}) + (m F_3 / 4 r_e) \langle (\Delta q)^2 \rangle = 0. \quad (7)$$

Note that the term in the first parentheses vanishes by the condition for equilibrium of the minimum potential energy structure and that $(K + 2m s^2 F + m G)$ is the force constant f_{11} for the totally symmetric stretching mode of AX_n . Equation (7) relates the mean A-X bond stretching $\langle \Delta r \rangle_v$ to mean-square amplitudes of vibrations arising, at low temperatures, from zero-point vibrations and increasing, at high temperatures, with thermal excitation. Zeroth-order mean-square amplitudes for the molecule vibrating in a quadratic force field can be calculated directly from normal coordinate theory.¹⁹ It is shown in Ref. 18 that, at least for Morse stretching, the use of zeroth-order mean-square amplitudes in place of the corrected mean-square amplitudes calculated for the anharmonic force field compensates quite well for the other error of truncating the potential energy function beyond cubic terms.

To the $\langle \Delta r \rangle_v$ arising from anharmonic vibration should be added the centrifugal stretch, Δ_r , due to rotation. Solving Eq. (7) for $\langle \Delta r \rangle_v$ and adding the rotational stretch, we arrive at

$$\langle \Delta r \rangle = \Delta_r + \Delta_m + \Delta_{nb} + \Delta_b + \Delta_x \quad (8)$$

with the following simple physical components. Centrifugal stretching is easily shown for AX_n to be

$$\Delta_r = 2 \bar{E}_{\text{rot}}^{K \cdot E} / n f_{11} r_e \quad (9)$$

where $\bar{E}_{\text{rot}}^{K \cdot E}$ is kT or $3kT/2$ for linear or nonlinear molecules, respectively. Morse anharmonic stretching is

$$\Delta_m = (3a \langle (\Delta r)^2 \rangle / 2) \cdot (K / f_{11}), \quad (10)$$

or just the diatomic expression of Eq. (1) modified by the factor (K/f_{11}) whose value is near unity. Stretching due to the enhancement of nonbonded repulsions as atoms vibrate and become effectively larger is given by

$$\Delta_{nb} = -(m F_3 / 4 f_{11} r_e) \langle (\Delta q)^2 \rangle. \quad (11)$$

Recall that $F_3 < 0$. Then, to put the remaining terms into perspective we add to H in Eq. (7) the quantity $(-s^2 F' + c^2 F)$, where $c = \cos(\alpha/2)$, in order to bring the Urey-Bradley bending force constant H up to the valence bending force constant f_α . We then subtract the same correction from the next term in Eq. (7) so that there is no net change in $\langle \Delta r \rangle$. The resulting contributions to $\langle \Delta r \rangle$ become, then,

$$\Delta_b = \Delta_{bH} + \Delta_{bUB} = m(H - s^2 F' + c^2 F) \langle (r_e \Delta \alpha)^2 \rangle / 2 f_{11} r_e \quad (12)$$

and

$$\Delta_x = \Delta_{xUB} - \Delta_{bUB} = m s (F' K_{xx} + F \delta_{xx}) / f_{11} - m(-s^2 F' + c^2 F) \langle (r_e \Delta \alpha)^2 \rangle / 2 f_{11} r_e, \quad (13)$$

where the last term Δ_x , of minor importance, arises from various crossterms and nonlinearities in the trans-

TABLE I. Contributions to $\langle \Delta r \rangle$, in Å, for methane in its ground vibrational state according to the KB field.^a See text for definitions.

Molecule	Δ_m	Δ_{nb}	Δ_b			Δ_x	Δ_r^b
			Eq. (12)	Eq. (17)	Eq. (18)		
CH ₄	0.0151	0.0049	0.0028	0.0028	0.0027	0.0001	0.0005
CD ₄	0.0109	0.0034 ₅	0.0021	0.0021	0.0020	0.0001	0.0005

^aReference 6.^bAt 298 K.

formations between nonbonded distances and internal coordinates. More substantial is Δ_b , a term most easily interpreted as a centrifugal stretching of bonds as the peripheral atoms X travel over their arced trajectories in bending vibrations (see Ref. 18). It is possible to simplify Δ_b with little loss in accuracy in the cases investigated to date. If coordinates are transformed from internal to rectilinear symmetry coordinates (see Ref. 8 for notation and details), the bending term becomes, very nearly,

$$\Delta_b \approx -(2n^{1/2}f_{11})^{-1} \sum_{i=\text{bend}} f_{i11}^T \langle S_i^2 \rangle \quad (14)$$

where the bend-bend-stretch cubic constant is

$$f_{i11}^T = \sum_r (f_{r1} T_r^{11} + f_{r1} T_r^{11}), \quad (15)$$

in which only quadratic force constants occur, and in which S_i is the totally symmetric stretch coordinate. This term arises because of the nonlinear transformation

$$\bar{S}_k = S_k + \frac{1}{2} \sum_i \sum_j T_k^{ij} S_i S_j + \dots \quad (16)$$

between curvilinear \bar{S}_k and rectilinear S_k coordinates. Because of the simple form of the stretch-bend elements of the transformation tensor T , Eq. (14) reduces to

$$\Delta_b \approx (nf_{11}r_e)^{-1} \sum_{i=\text{bend}} f_{i11} \langle S_i^2 \rangle, \quad (17)$$

where $f_{i11} \langle S_i^2 \rangle$ represents twice the mean potential energy associated with the pure bend i . For a simple harmonic oscillator, with $\langle T \rangle = \langle V \rangle$, twice the potential energy is the total energy of the oscillator, or $(h\nu_i/2) \coth(h\nu_i/2kT)$ on the average, at temperature T . If we neglect coupling of modes and make the aforementioned identification, Eq. (17) becomes

$$\begin{aligned} \Delta_b &\approx (nf_{11}r_e)^{-1} \sum_{i=\text{bend}} (h\nu_i/2) \coth(h\nu_i/2kT) \\ &= (\bar{E}_{\text{bend}}^{\text{tot}})/nf_{11}r_e = 2(\bar{E}_{\text{bend}}^{\text{K.E.}})/nf_{11}r_e. \end{aligned} \quad (18)$$

Note the similarity between the form of the bending centrifugal contribution of Eq. (18) and the rotational centrifugal contribution of Eq. (9). Note, also, that Δ_{nb} increases in proportion to the number of adjacent bonds. Accordingly, this term is much larger in SF₆, say, than in triatomic molecules.

Numerical illustrations of the various contributions to $\langle \Delta r \rangle$ are given in the next section.

DISCUSSION

In the foregoing we have presented an elementary procedure for calculating the anharmonic stretching in AX_n molecules. It is essentially equivalent to but enormously less laborious than the perturbation approach applied previously. For illustrative purposes we present in Table I numerical values for the contributions to the vibrational bond lengthening in CH₄ and CD₄, among other things comparing values of Δ_b calculated from the three different equations offered above. For sake of ease of comparison, we adopt the potential constants for methane proposed in Ref. 6 and also adopt the perturbed rather than zeroth-order values of $\langle (\Delta r)^2 \rangle$ and $\langle (\Delta q)^2 \rangle$. All the necessary ingredients have been tabulated in Ref. 6. More modern estimates change little except for the nonbonded cubic constant F_3 ; this constant is almost halved in the quite successful MUB-2 field.²⁰ The net sums of terms for $\langle \Delta r \rangle$ in Table I for CH₄ and CD₄ are slightly larger than the net values obtained in the original perturbation calculations,⁶ principally because the first-order perturbation treatment renormalized the first-order wave function via a factor λ_0 which has since been found to worsen results. When that factor is eliminated the perturbation results agree with the present results to within a few ten thousandths of an angstrom unit.

As a word of caution it should be mentioned that the good agreement between the Δ_b values of Eqs. (12), (17), and (18) shown in Table I may not always be found in other cases. One other case, carbon dioxide, was studied in detail and, since it has no other modes corresponding to the symmetry of the bend, Eqs. (12), (17), and (18) are in agreement. On the other hand, however, CO₂ is a special case whose π -bond overlap is diminished, weakening the C=O bond, as the O=C=O angle is bent. This shows up as an additional bend-bend-stretch cubic term²¹ comparable to that of Eq. (15). Such a term has not been modeled into the KB field. This deficiency leads to an underestimation of $\langle \Delta r \rangle$ for CO₂ by about 10%. If known, however, such a term can be easily treated via an equation analogous to Eq. (14).⁸

The greatest virtue of the present treatment is that it permits an easy estimate—and an excellent estimate if the actual force field is well modeled by the KB field with available parameters—of the effect of molecular excitation upon bond length. Alternatively, it permits an estimation of the correction from an experimental mean bond length, r_e , to the equilibrium length, r_e . Complexities customarily associated with perturbed

normal coordinate treatments vanish in the transformations employed and only the standard results of normal coordinate calculations, such as those routinely furnished by R. L. Hilderbrandt's program MSAV, are needed.²² Results have been found to account quantitatively for the structure of very hot sulfur hexafluoride, as described in the following paper.³

ACKNOWLEDGMENT

This research was supported by a grant from the National Science Foundation.

- ¹See, for example, V. P. Spiridonov, N. G. Rambidi, and N. V. Alekseev, *Zhur. Struct. Khim.* **4**, 779 (1963); I. Hargittai, M. Hargittai, V. P. Spiridonov, and E. V. Erokhin, *J. Mol. Struct.* **8**, 31 (1971); S. M. Tolmachev and N. G. Rambidi, *High Temperature Sci.* **5**, 385 (1973).
- ²See, for example, N. Bloembergen and E. Yablonovitch, *Physics Today* **31**, 23 (1978); R. V. Ambartzumian and V. S. Letokhov, *Accts. Chem. Res.* **10**, 61 (1977).
- ³L. S. Bartell, S. K. Doun, and S. R. Goates, *J. Chem. Phys.* **70**, 4585 (1979), following paper.
- ⁴L. S. Bartell, *J. Chem. Phys.* **23**, 1219 (1955).
- ⁵K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.* **36**, 2460 (1962).
- ⁶K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.* **36**, 2470 (1962).
- ⁷I. M. Mills, *J. Phys. Chem.* **80**, 1187 (1976).
- ⁸L. S. Bartell and S. Fitzwater, *J. Chem. Phys.* **67**, 4168 (1977).
- ⁹B. Kirtman, W. E. Palke, and C. S. Ewig, *J. Chem. Phys.* **64**, 1883 (1976); **67**, 5980 (1977).
- ¹⁰K. Kuchitsu and Y. Morino, *Bull. Chem. Soc. Jpn.* **38**, 804, 814 (1965); *Spectrochim. Acta* **22**, 33 (1966); Y. Morino, *Pure Appl. Chem.* **18**, 323 (1969).
- ¹¹L. S. Bartell, S. Fitzwater, and W. J. Hehre, *J. Chem. Phys.* **63**, 3042 (1975).
- ¹²P. Pulay, W. Meyer, and J. E. Boggs, *J. Chem. Phys.* **68**, 5077 (1978).
- ¹³L. S. Bartell and K. Kuchitsu, *J. Chem. Phys.* **68**, 1213 (1978).
- ¹⁴L. S. Bartell and K. Kuchitsu, *J. Chem. Phys.* **37**, 691 (1962).
- ¹⁵In the case of AX₃, the UB field would need also an out-of-plane bend constant not shown in Eq. (2). Perhaps the OVFF field of D. C. Heath and J. W. Linnett [*Trans. Faraday Soc.* **44**, 873, 878, 884 (1948); **45**, 264 (1949)] expanded out to cubic terms in stretch and nonbonded terms would be better for most molecules in general, and for AX₃ molecules, in particular. But see H. Kim, P. A. Souder, and H. H. Claassen [*J. Mol. Spectrosc.* **26**, 46 (1968)] for comments on errors in the work of Heath and Linnett. In the present work, the deficiency of Eq. (2) for AX₃ molecules is compensated for in the approximation of Eq. (18) for Δ_β and the remainder of the effects of bending are taken into account properly by correctly calculated values of ⟨(Δq)²⟩, ⟨(Δα)²⟩, K_{xx}, and δ_{xx} of Eqs. (11) and (13).
- ¹⁶D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.* **35**, 485 (1961).
- ¹⁷P. Ehrenfest, *Z. Phys. (Leipzig)* **45**, 455 (1927).
- ¹⁸L. S. Bartell, *J. Chem. Phys.* **38**, 1827 (1963).
- ¹⁹S. J. Cyvin, *Molecular Vibrations and Mean Square Amplitudes* (Elsevier, Amsterdam, 1968).
- ²⁰S. Fitzwater and L. S. Bartell, *J. Am. Chem. Soc.* **98**, 5107 (1976).
- ²¹J. Pliva, in *Crit. Eval. Chem. Phys. Struct. Inf. Proc. Conf.* 1973, edited by D. R. Lide (Natl. Acad. Sci., Washington, D.C., 1974), pp. 436-48.
- ²²R. L. Hilderbrandt, *J. Chem. Phys.* **51**, 1654 (1969).