

Electron diffraction studies of hot molecules. IV. Asymmetries of nonbonded distribution functions of SF₆, SiF₄, and CF₄

Lawrence S. Bartell and John F. Stanton

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

(Received 16 May 1984; accepted 29 June 1984)

Highly significant improvements in the agreement between observed and calculated intensities of electrons diffracted by hot molecules were obtained by optimizing the skew parameter \hat{a} for the nonbonded distributions. Derived \hat{a} values ($\pm 2\sigma$) were 2.75(11), 0.72(13), and 2.0(4) Å⁻¹ for SF₆, SiF₄, and CF₄, respectively. These measured skew parameters are approximately 2 Å⁻¹ higher in each case than values previously proposed on the basis of Morse asymmetry factors and the nonlinear transformation between curvilinear and normal coordinates of molecules. The principal factor responsible for the increase is the previously unknown intrinsic anharmonicity in bending deformations. Silicon tetrafluoride has a lower \hat{a} value than the other molecules studied primarily because its bending force constant is lower, relative to stretching. Practical as well as theoretical implications of present findings are discussed.

INTRODUCTION

In recent electron diffraction studies of hot molecules¹⁻³ an anomalous "shrinkage effect" was observed that became progressively larger, the hotter the molecules. This effect, which made the apparent distances between nonbonded atoms too short to conform with measured bond lengths, was not understood until the concluding days of the research. The explanation of this anomaly proved to be simple. Bending anharmonicity skews nonbonded distributions to a degree not allowed for in conventional least-squares refinements of electron intensities. When an incorrect distribution is incorporated into refinements, part of the misfit is absorbed by displacing derived internuclear distances from their proper values. It was found, too late to carry out systematic corrections, that when the coefficients of skewness of the nonbonded distributions are refined as well as the first and second moments, the intensity residuals drop significantly and a geometrically consistent set of internuclear distances can be recovered. What is most significant about this result that warrants further analysis is as follows. It was discovered that a very simple mechanical model of the force field for bending can account for the observed skewing with no freely adjustable parameters.⁴ Preliminary tests suggested that this model whose scope has not heretofore been appreciated, may be of general applicability.^{5,6} Because existing experimental knowledge about bending anharmonicity is extremely limited, it is worthwhile to extract as quantitatively as possible the information latent within the diffraction intensities. Another reason for pursuing the problem is that, until the anharmonic shrinkage can be treated quantitatively, the accuracy of electron diffraction determinations of polyatomic structures will be degraded in some measure.

In the following we outline the analysis of diffraction patterns of hot molecules of SF₆, SiF₄, and CF₄.

PROCEDURE

Experimental procedures used in the recording of the present diffraction patterns of gaseous fluorides have been described elsewhere along with preliminary analyses of the

patterns.^{1,2} Also discussed for the AF_n molecules investigated was the normal "shrinkage"⁷

$$\delta = 2r_g(\text{AF})\sin(\alpha_{\text{FAF}}/2) - r_g(\text{FF}), \quad (1)$$

a foreshortening effect expected to occur in any vibrating polyatomic molecule. What is sought is a measure of the skew in F...F distribution peaks which can ultimately be related to anharmonicity in the potential energy surface as analyzed recently.^{4,8-10} This skew is most conveniently expressed by the parameter

$$\hat{a} = A_3/l_g, \quad (2)$$

where A_3 is the standard coefficient of skewness of the peak and l_g is the rms displacement from the mean internuclear distance. In the special case of a Morse diatomic oscillator in its ground state, \hat{a} is identical to a , the Morse asymmetry constant. To an adequate accuracy for the present purposes, \hat{a} is related to the frequency modulation parameter of the diffracted intensity function by

$$\kappa = \hat{a}l_g^4/6. \quad (3)$$

In the present treatment \hat{a} values for bonds and (in SF₆) *trans* nonbonded distances were fixed at the theoretically expected values assigned in Ref. 1. Two alternative procedures, I and II, were applied to determine \hat{a} for geminal nonbonded distances. Refinements were carried out upon the leveled experimental intensities. In procedure I, the shrinkage inferred from vibrational frequencies was imposed as a constraint in least squares computations performed with various fixed values of \hat{a}_{FF} . Amplitudes of vibration and bond lengths were allowed to vary freely. The preferred value known, hereafter, as \hat{a}_I was taken to be that which minimized intensity residuals under the imposed constraint.

In procedure II, nonbonded distances were allowed to refine independently of bond distances, and amplitudes were refined, as well, at various fixed values of \hat{a}_{FF} . For this procedure the preferred value of \hat{a}_{II} is that yielding the correct shrinkage δ . This parameter, denoted \hat{a}_{II} , can be seen to lie on the regression line of δ on \hat{a} , whereas \hat{a}_I lies on the regression line of \hat{a} on δ . If the correct value of δ happens to lie at a

minimum in the full parameter space including \hat{a} and δ , then a_I and a_{II} will agree, of course. Otherwise, by virtue of the meaning of regression lines,¹¹ \hat{a}_I is the best available compromise for the skew parameter. Uncertainties in \hat{a} can be estimated roughly by the scatter in the derived results from various diffraction plates. An alternative approximate scheme used to estimate standard deviation corresponding to individual plates invoked

$$\sigma_I^2(\hat{a} + \sigma_a) = \sigma_I^2(\hat{a}) \{ 1 + [B_{aa}(B^{-1})_{aa}/(n-m)] \}. \quad (4)$$

In this equation σ_I is the standard deviation in intensity when parameter \hat{a} is set (left-hand side) one standard deviation from its optimum value or (right-hand side) at its optimum value. Diagonal elements of the information matrix B and its inverse are for parameter \hat{a} . In the absence of parameter correlation the product $B_{aa}(B^{-1})_{aa}$ would be unity. For correlation between \hat{a} and δ , characterized by correlation coefficient $\rho_{a\delta}$, it can be seen that when $\rho_{a\delta} > 0$, $\hat{a}_{II} > \hat{a}_I$ and when $\rho_{a\delta}$ changes sign, so does $(\hat{a}_{II} - \hat{a}_I)$. Because experimental values of \hat{a}_{II} scatter around \hat{a}_I for the hotter plates, it appears $\rho_{a\delta}$ scatters around zero. For lack of further information about other correlations, we arbitrarily took $B_{aa}(B^{-1})_{aa}$ to be 2. This scheme yielded standard deviations not greatly different from the values implied by the scatter in \hat{a} measurements.

RESULTS

In accord with preliminary analyses,^{2,4} it was found that introducing the nonbonded asymmetry parameter as an additional variable in least squares refinements led to a systematic and highly significant improvement between experimental and calculated intensities. In the prior treatment,^{1,2} refinement with \hat{a}_{FF} constrained to a small value (including only effects of Morse asymmetry and nonlinear transformation between internal and normal coordinates), least-squares rms residuals had increased markedly as temperature increased. As shown in Fig. 1 for SF₆, this systematic deficiency has been largely remedied in the present work. Illustrating the nonrandom quality of intensity misfits is a typical pattern of residuals in Fig. 2 corresponding to one of the hotter plates of SF₆. While these residuals are delocalized over scattering angle, Fourier transformation identifies the source of the trouble to be principally in the region of the geminal F...F distance, as can be seen in Fig. 3.

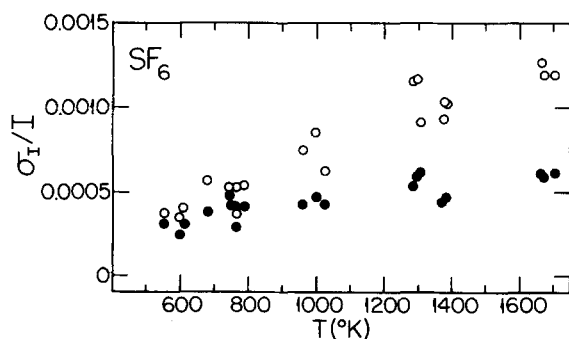


FIG. 1. Temperature dependence of standard deviation between observed and calculated electron diffraction intensities. Open circles, Ref. 1 where refinements froze \hat{a} (FF_{cls}) at values proposed in Ref. 13. Solid points, same experimental data, where refinements optimized \hat{a} (FF_{cls}).

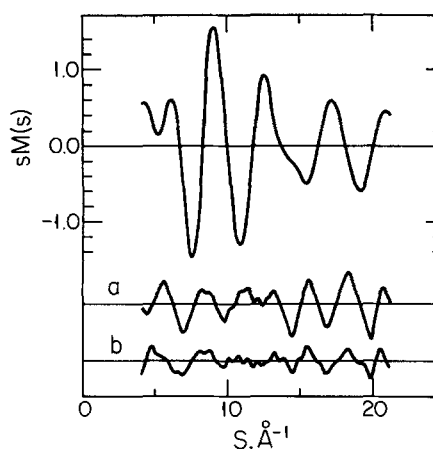


FIG. 2. Upper curve, characteristic diffraction pattern for SF₆ at 1700 K. Lower curves, intensity residuals magnified tenfold, (a) based on frozen \hat{a} values of Ref. 1, (b) with optimized \hat{a} (FF_{cls}). The remaining systematic residuals are associated with multiple scattering and assumption of spherical atoms in intensity calculations.

Asymmetry parameters deduced from the diffraction patterns of SF₆, SiF₄, and CF₄ at various temperatures are plotted in Fig. 4. Methods I and II yielded comparable results for the two heavier molecules, each of which was readily scavenged by the cold trap. In the case of CF₄, the two methods differed systematically and appreciably, suggesting that caution in accepting the results would be prudent. This warning is reinforced by the substantially greater standard deviations for CF₄. The source of this imperfection is thought to be the relatively high and variable background pressure in the diffraction chamber arising because the sample did not condense on the liquid nitrogen trap after passage through the probing electron beam. Scattering from delocalized gas beneath the nozzle has an effect on diffraction features qualitatively similar to that of altered \hat{a} values. Since it operates differently on peaks of different mean amplitude, it influences the apparent shrinkage as well as the peak shapes.

To investigate whether the improved refinements in

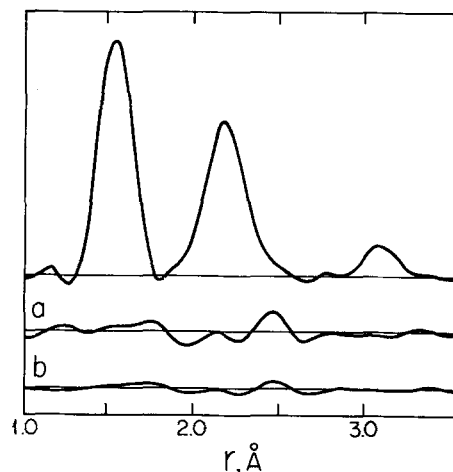


FIG. 3. Fourier transforms of data in Fig. 2. Upper curve, radial distribution function (the largest distortions are due to termination ripples unimportant for present purposes). Lower curves corresponding to (a) and (b) of Fig. 2 identify region of misfit between observed and calculated distribution functions. This misfit is magnified fivefold in the plots.

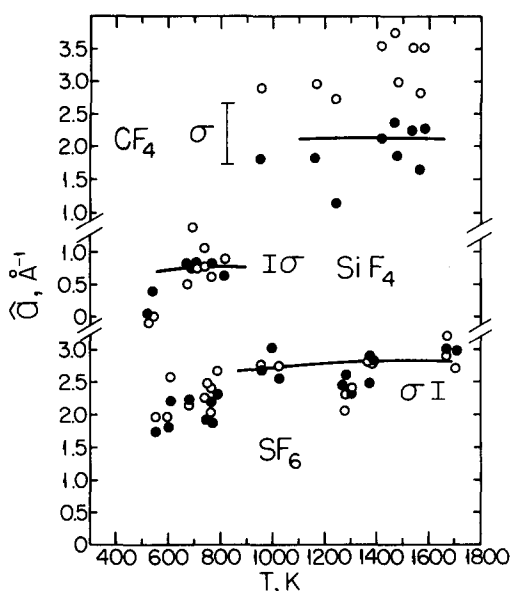


FIG. 4. Values of skew parameter $\hat{a}(\text{FF}_{cl})$ determined for SF_6 , SiF_4 , and CF_4 at various temperatures. Error bars, characteristic standard deviations for individual diffraction plates estimated according to Eq. (4). Solid points, optimum least squares values, \hat{a}_I . Open circles, \hat{a}_{II} values. See the text for meaning.

this work appreciably changed the pattern of derived amplitudes of vibration, we compared thermal increases in amplitudes of nonbonded distances with corresponding increases for bonded distances. Results presented in Figs. 5–7 verify a significant systematic shift away from the points reported previously,¹ towards the theoretically computed curves.

DISCUSSION

When amplitudes of bond bending are large, either because of idiosyncrasies of the molecular force field¹² or because of high temperature (as in this research), the agreement between observed and calculated molecular diffraction pat-

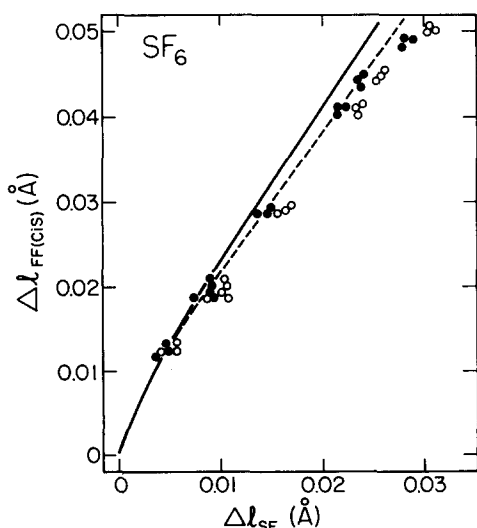


FIG. 5. Thermally induced increase in rms FF_{cl} amplitude of vibration vs corresponding increase in rms SF amplitude for SF_6 , $300 < T < 1700$ K. Solid line represents normal coordinate calculations based on harmonic force field. Dashed line corresponds to calculation treating bonds as Morse oscillators, after Kuchitsu, Ref. 14. Points, see caption for Fig. 1.

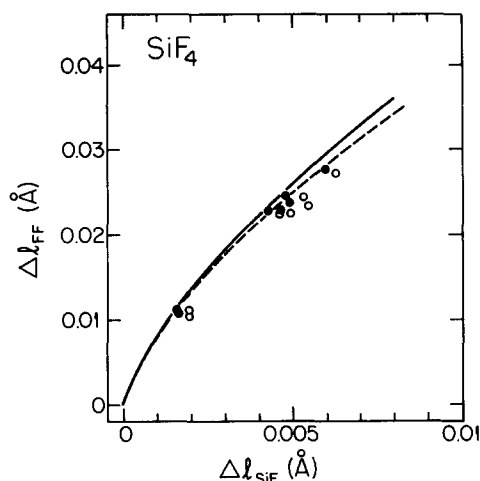


FIG. 6. Increase in rms FF amplitude vs corresponding increase in SiF amplitudes for SiF_4 , $300 < T < 815$ K. See the caption for Fig. 5.

terns can be improved materially by incorporating a suitable coefficient of skewness into nonbonded distribution functions. Values of the skew parameter \hat{a} for nonbonded distances minimizing residuals for the present fluorides are similar in magnitude to values reported earlier,⁴ based on a few individual plates, but are believed to be appreciably more reliable. Weighted averages derived from the data of Fig. 3 are, for the hotter plates, $2.75 \pm 0.11 \text{ \AA}^{-1}$ for SF_6 ($900 < T < 1700$ K), $0.72 \pm 0.13 \text{ \AA}^{-1}$ for SiF_4 ($700 < T < 815$ K), and $2.0 \pm 0.4 \text{ \AA}^{-1}$ for CF_4 ($955 < T < 1560$ K). Listed uncertainties represent estimates of 2σ for the averages, neglecting systematic errors whose magnitudes we are as yet ignorant of. There is weak experimental evidence and reasonable theoretical evidence^{4,8} that \hat{a} falls off at lower temperatures where refinements become insensitive to \hat{a} .

In principle it should be possible to deduce \hat{a} from analyses of spectra of ground and excited vibrational states of molecules. Unfortunately, no studies of the present molecules appear to have been carried out with the requisite precision and detail. Plausible model anharmonic force fields have been proposed,⁸ however, that incorporate semiempirical molecular orbital estimates⁶ of bending anharmonicity.

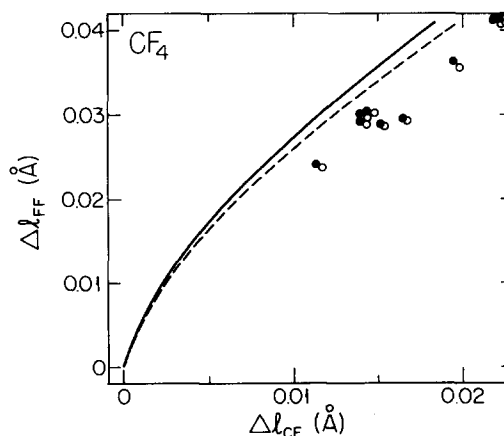


FIG. 7. Increase in rms FF amplitude vs corresponding increase in CF amplitude for CF_4 , $300 < T < 1580$ K. See the caption for Fig. 5.

Preliminary values of skew parameters deduced^{8,9} from these for temperatures comparable to our experimental temperatures are 2.65, 1.3, and 2.2 Å, respectively, for the above listed molecules. In view of uncertainties both in the experiments and in the model force fields, it is premature to speculate upon the source of the minor discrepancies between them. More significant is the general agreement.

Factors that distinguish SiF₄, with its low value of \hat{a} , from the others were identified fairly well by a simple predictive model¹³ not depending upon a detailed knowledge of the *intrinsic* anharmonic potential constant (i.e., those of the natural curvilinear coordinates). The most important difference between the molecules, all of which strongly resist stretching displacements, is that bonds in SiF₄ are significantly freer to bend. This is manifested in \hat{a} through the propagation of the Morse stretching anharmonicity into the nonbonded distribution and via the nonlinear transformation from curvilinear to rectilinear coordinates. Intrinsic stretching anharmonicities, before propagation, are quite similar but stretching displacements contribute relatively much less than the bending displacements to the total F...F mean square amplitude in SiF₄ than in CF₄ and SF₆. Therefore the Morse influence is nearly obliterated in the silicon compound. The greater freedom of bending in SiF₄ also leads to more strongly arced fluorine trajectories which then contribute an appreciably larger skew component. The reason this decreases the net skew is because, as a simple analysis shows, the effect is opposite in sign to that of intrinsic bending anharmonicity and other factors making $\hat{a} > 0$.

Not only did optimizing \hat{a} yield substantially better agreement between experimental and calculated electron intensities, it led to an improved consistency between amplitudes of vibration of bonded and nonbonded distances. Contrary to some previous conjectures, the nonbonded \hat{a} parameter is correlated significantly with mean amplitudes. Unexpectedly, the nonbonded \hat{a} value influenced the mean amplitude of the bond distance as well as that of the non-

bonded distance, even though the two distances are well resolved. As shown in Figs. 5 and 6 the experimental and calculated¹⁴ plots of I (nonbonded) vs I (bonded) are reconciled for SF₆ and SiF₄ when \hat{a} is properly chosen. In the case of CF₄, which is marred by a delocalized sample distribution, the improvement is less conspicuous.

Results of this research corroborate the important role of bending anharmonicity in molecular force fields. Before its magnitude was known, when skewing of nonbonded distances was estimated solely on the basis of Morse anharmonicity and nonlinear transformation effects,^{1,13} \hat{a} values for the present molecules were thought to be about 2 Å⁻¹ lower than they have turned out to be. At higher temperatures this led to discrepancies of over 0.01 Å in intermolecular distances, distances which can be measured with a precision of better than 0.001 Å. Practical as well as theoretical implications of this finding are evident. Work is currently under way to simplify computations relating anharmonic potential constants to observable skew parameters.⁹

¹S. R. Goates and L. S. Bartell, *J. Chem. Phys.* **77**, 1866 (1982).

²S. R. Goates and L. S. Bartell, *J. Chem. Phys.* **77**, 1874 (1982).

³L. S. Bartell, W. Vance, and S. R. Goates, *J. Chem. Phys.* **80**, 3923 (1984).

⁴L. S. Bartell, *J. Mol. Struct.* **84**, 117 (1982).

⁵L. S. Bartell, *Croat. Chem. Acta* (in press).

⁶L. S. Bartell and Y. Z. Barshad, *J. Am. Chem. Soc.* (in press).

⁷See S. J. Cyvin, *Molecular Vibrations and Mean Square Amplitudes* (Elsevier, Amsterdam, 1968).

⁸L. S. Bartell, *J. Mol. Struct.* **116**, 279 (1984).

⁹J. F. Stanton and L. S. Bartell (unpublished research).

¹⁰R. L. Hilderbrandt and D. A. Kohl, *Theochem.* **2**, 25 (1981); D. A. Kohl and R. L. Hilderbrandt, *ibid.* **2**, 325 (1981).

¹¹W. C. Hamilton, *Statistics in Physical Science* (Ronald, New York, 1964).

¹²E. J. Jacob and L. S. Bartell, *J. Chem. Phys.* **53**, 2235 (1970).

¹³L. S. Bartell, *J. Mol. Struct.* **63**, 259 (1981).

¹⁴Normal coordinate treatment with bond amplitude corrected for Morse anharmonicity as by K. Kuchitsu, *Bull. Chem. Soc. Jpn.* **40**, 498, 505 (1967).