Electron diffraction studies of hot molecules. II. "Anharmonic shrinkage effects" in SF_6, CF_4, and SiF_4

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Least squares refinements of diffraction intensities for SF_6, CF_4, and SiF_4 yielded nonbonded internuclear distances that lagged increasingly behind values expected from the bond lengths, the higher the temperature. The observation that observed nonbonded shrinkages greatly exceed calculated shrinkages cannot be attributed to a deficiency in the theoretical expressions customarily invoked. It is explained, instead, by anharmonic effects in bending modes that give the illusion of anomalous shrinkage where it does not, in fact, exist. These effects, which skew the nonbonded distribution functions and displace the true mean distances from the peak maxima, contain heretofore unexploited information about anharmonic potential constants.

I. INTRODUCTION

Now that a fairly convenient procedure has been devised for studying structures of polyatomic molecules systematically over an unprecedented range of temperature by electron diffraction (see paper I[1]), it seemed advisable to test it with molecules that are quite stable and reasonably well understood. Therefore, we selected the simple binary compounds SF_6, CF_4, and SiF_4 for study. What lends novelty to the investigation of these frequently studied compounds is the substantially larger amplitudes of vibration that are attained. These lead to exaggerated manifestations of two effects encountered also at ordinary temperatures that have not yet been satisfactorily settled. The first, the "shrinkage effect,"[2,3] is a foreshortening of mean nonbonded internuclear distances relative to hypothetical distances that would occur in a rigid molecule with the same mean bond lengths and angles. This effect is primarily harmonic in nature. The other effect is that of anharmonicity. In molecules larger than triatomic,[4] the consequences have to date been more a matter of speculation than of hard facts. What *is* known is that, in precise studies, calculated and observed shrinkages have often been observed to be in poor agreement for obscure reasons. Greatly magnified discrepancies of this sort were indeed found in the present investigation, and their systematic behavior showed the way to a resolution of the problem, as discussed in the following.

II. ANALYSIS OF DATA

In the preceding paper[1] a description was given of our experimental procedure and treatment of data. A crucial feature of our treatment turned out to be the adoption of a recently proposed model[5] to predict the temperature dependent asymmetry parameter $\hat{a}$[6] defined by

$$\hat{a} = \langle (r - \langle r \rangle)^3 \rangle / l_g^4 \tag{1}$$

and related to the frequency modulation parameter κ in diffraction intensity by[7]

$$\kappa \approx \hat{a}\, l_g^4/6 + \cdots \quad . \tag{2}$$

Previously, for nonbonded distances, this subtle quantity has been left to guesswork or has been refined as an independent parameter. In an effort to reduce arbitrariness we chose to adopt a predictive model[5] which incorporates in a plausible manner the essential anharmonicity for a three-atom fragment X–A–X arising from the nonlinearity of transformation between internal and normal coordinates and from the stretching anharmonicity of the constituent A–X bonds.

Shrinkages derived from our experiments have been calculated from the observed mean internuclear distances for bonded (AF) and nonbonded (FF) atom pairs according to

$$\delta = 2r_{g(\mathrm{AF})} \sin(\alpha/2) - r_{g(\mathrm{FF})} \quad , \tag{3}$$

where δ is the "practical shrinkage"[3] and α is the equilibrium bond angle. Theoretical shrinkages for comparison were calculated following Cyvin.[3] In the case of molecules with O_h and T_d symmetry, such as the fluorides of this study, the theoretical shrinkage can be expressed in the simple form

$$\delta^{\mathrm{theor}} = 2K_{\mathrm{AF}} \sin(\alpha/2) - K_{\mathrm{FF}} \quad , \tag{4}$$

where the shrinkage components K_{ij} can be determined from normal coordinate calculations.[3] It may be noted that the anharmonic contributions to bond lengthening discussed in paper I[1] do not appear in Eq. (4). They cancel and play no role in the determination of either experimental or theoretical shrinkages. Calculated K_{ij} terms were obtained over a range of temperatures for each molecule with a normal coordinate routine[8] using published force fields[9-11] for SF_6, CF_4, and SiF_4. Shrinkages were then calculated as a function of temperature from the normal coordinate K_{ij} terms. Experimental temperatures were inferred from the amplitudes of vibration of bonded atoms, as described in Ref. 1.

It was noted in paper I[1] that refinements of diffraction intensities for SF_6 at room temperature yielded negative values for the *cis* and *trans* shrinkages. Similar results for SF_6 have been obtained by Kelley and Fink.[12] These negative shrinkages were considered an artifact connected with the large nonrandom residuals encountered at small scattering angles discussed in Ref. 13; such residuals represent systematic deficiencies of standard scattering expressions of modest significance in the derivation of the parameters sought in this work. The diffraction data were, therefore, con-

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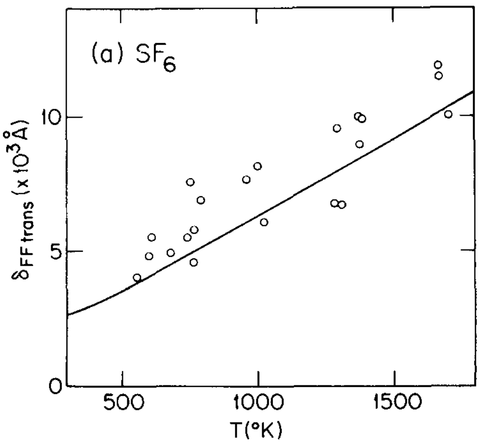

FIG. 1. Points, experimental shrinkages for the *trans FF* distance in SF_6 derived as a function of temperature with constraints described in the text. Solid curve, shrinkages calculated by Morino–Cyvin method.

strained through the $\overline{\Delta M_r}(s)$ correction to yield room temperature shrinkages which matched, on the average, the theoretical room temperature shrinkages (see Ref. 13 and paper I, Sec. III). Over the entire temperature range the effect of the $\overline{\Delta M_r}(s)$ correction was simply to increase all experimentally derived shrinkages by roughly the same amount as at room temperature. [Compare, for example, Figs. 2 and 5(b).]

III. RESULTS

Experimentally derived shrinkages are shown in Figs. 1–4 as a function of temperature and compared with calculated shrinkages. Also shown in Fig. 2 are the data of Kelley and Fink.[12,14] Experimental points deviate systematically and conspicuously from calculated values. The reasons for this and the new information latent within the plots are discussed in the next section.

IV. DISCUSSION

A. Observation of large apparent shrinkages

With the exception of the *trans* shrinkage in SF_6, which is reasonably well accounted for by the model treatment,[5] markedly increasing deviations of experimental shrinkages from theoretical shrinkages with increasing temperature (Figs. 1–4) are apparent in our data. Because of the well-behaved thermal expansions of the bonds,[1] it appears that the large experimental shrinkages arise primarily from unforeseen trends in the nonbonded distances rather than in the bond distances.

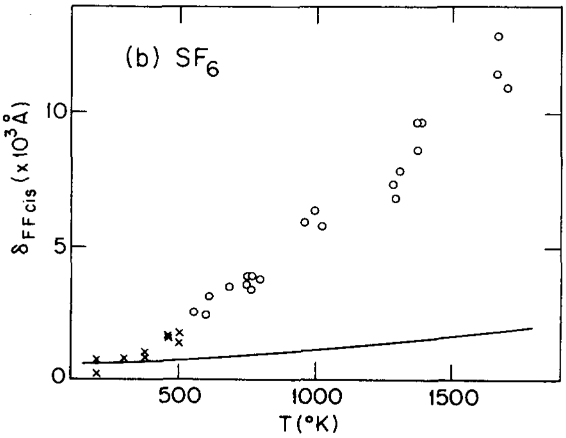

FIG. 2. Shrinkages for the *cis FF* distances in SF_6. See the caption, for Fig. 1.

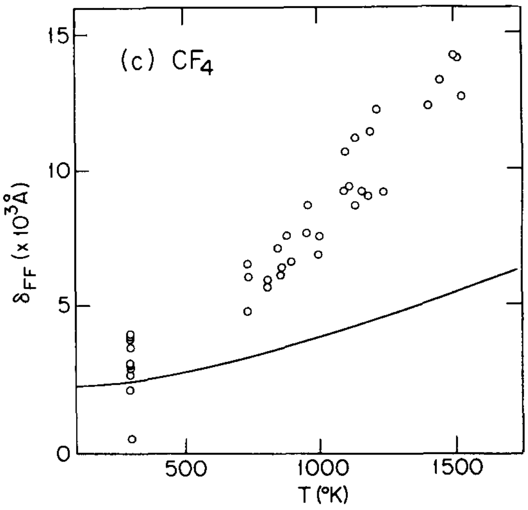

FIG. 3. Shrinkages for *FF* distance in CF_4. See the caption for Fig. 1.

The possibility that systematic error due to certain experimental features is the source of the shrinkage anomalies seems to be limited by the agreement of our results for SF_6 with those of Kelley and Fink.[12] Kelley and Fink used a nozzle much different from ours and a nonphotographic technique for recording diffraction intensities.

A possible source of error in the determination of shrinkage in CF_4 might be the high background pressures of CF_4 in the diffraction chamber during expo-

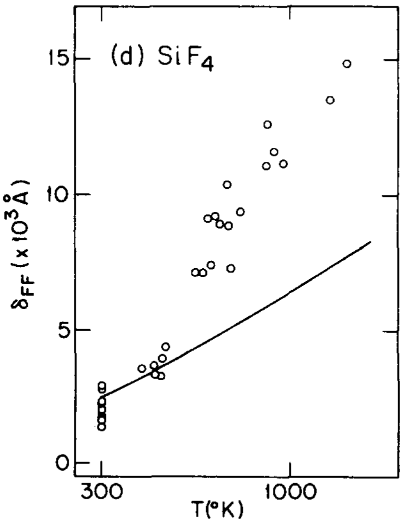

FIG. 4. Shrinkages for *FF* distance in SiF_4. See the caption for Fig. 1.

sures. Uncertainty in the derivation of bond lengths in CF_4 due to high background pressures was discussed previously in paper I, Sec. III. Derivations of nonbonded distances would be affected as well. However, just as the determination of the overall trend of *changes* in mean bond lengths does not seem to be seriously affected by background pressure, so also is it likely that the derivation of *changes* in the nonbonded distances is insensitive to background pressure. We discount, therefore, the effect of background pressure as an explanation of the shrinkage misfit for CF_4.

B. Explanation of anomalous shrinkage

If the observed "shrinkages" are *bona fide* shrinkages in the sense of Eqs. (3) and (4), a failure of theory to account for experiment within experimental error would have to be blamed upon the (conventional) truncation of the K_{ij} expansion at the mean-square perpendicular amplitude terms $\langle(\Delta x)^2 + (\Delta y)^2\rangle / 2r_g$. Conceivably, the larger-amplitude motions of hot molecules might require extension to terms of higher order. We carried out the expansion to higher order, evaluated magnitudes of the new terms, and found them trivial. Therefore, we conclude that the observed "shrinkages" are not true shrinkages at all but are artifacts of the method of analysis. That is, the parameter derived to represent the mean nonbonded distances are not authentic mean internuclear distances. Instead, they represent some compromise parameter leading to a least-squares minimum when the least-squares procedure is subject to an incorrect constraint. Inasmuch as the first two moments of the distribution functions for nonbonded distances are allowed to vary freely (as r_g and l_g are refined) the trouble must lie with the third moment, or $\hat{a}$ [cf., Eq. (1)]. Because this parameter was chosen in accordance with the "predictive model" of Ref. 5, it is clear that the predictive model is inadequate for the present hot molecules. In view of indiscriminate usage of $\hat{a}$ in the literature (where $\hat{a}$ is usually written without a caret, a practice that confuses it with a, the temperature-independent Morse potential constant) we comment upon its correct meaning. Parameter $\hat{a}$ was introduced to help characterize the skewness of a nearly Gaussian peak with standard coefficient of skewness

$$A_3 \equiv \langle(r - \langle r\rangle)^3\rangle / \langle(r - \langle r\rangle)^2\rangle^{3/2}$$
$$\equiv \langle(r - \langle r\rangle)^3\rangle / l_g^3 \ . \qquad (5)$$

A convenient form for such a peak, and one that is quite appropriate in many vibrational studies, is afforded by the *ground state* probability distribution function for a Morse oscillator.[15] In place of a *distribution of excited* Morse oscillator functions corresponding to the fixed potential constant a, a single distribution function with the mathematical form of a ground state function is adopted but given flexibility by adjusting parameters l_g and $a \equiv \hat{a}$ as needed to get the desired skewness. For this specific choice of function it can be shown that

$$A_3 = \hat{a}\, l_g \ . \qquad (6)$$

Unfortunately, it is difficult to predict $\hat{a}$ for an arbitrary radial distribution peak. In order to test the effects of alternative choices of asymmetry values $\hat{a}$, we carried out least-squares refinements on three uncorrected SF_6 plates with different values of $\hat{a}_{FF}(cis)$. Results for *cis* shrinkage from these refinements are depicted in Fig. 5(b). Shown in Fig. 5(a) are the *cis* shrinkages resulting if the practice of keeping $\hat{a}_{SF}$ constant with temperature and setting $\hat{a}_{FF}$ equal to zero or to $\hat{a}_{SF}$ is adopted. Figure 5(b) clearly implies much larger values for $\hat{a}_{FF}(cis)$ than those calculated from the "predictive model" of Ref. 5, which were nearly zero at all temperatures. Kelley and Fink[12] had also adopted a value of zero for $\hat{a}_{FF}(cis)$ in their study. In the case of SiF_4, the value of $\hat{a}_{FF}$ at 1000 K which makes the experimentally derived shrinkage agree with the theoretical shrinkage is about 1 $Å^{-1}$, or 2 $Å^{-1}$ larger than the model $\hat{a}_{FF}$.

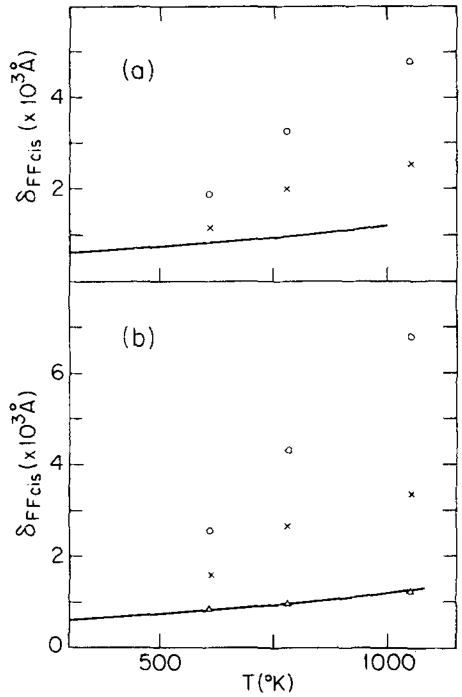

FIG. 5. Effect on the determination of the *cis* shrinkage in SF_6 of imposing various alternative constraints upon the asymmetry parameter $\hat{a}$. Results for three uncorrected plates are compared with theoretical shrinkages (solid lines). (a) Crosses, $\hat{a}_{SF} = \hat{a}_{FF}(cis) = \hat{a}_{FF}(trans) = 1.8$ $Å^{-1}$; circles, $\hat{a}_{SF} = 1.8$ $Å^{-1}$, $\hat{a}_{FF}(cis) = \hat{a}_{FF}(trans) = 0$. (b) Parameters $\hat{a}_{FF}$ and $\hat{a}_{FF}(trans)$ are assigned the temperature dependent values from Fig. 1, Ref. 1; circles $\hat{a}_{FF}(cis) = 0$; crosses, $\hat{a}_{FF}(cis) = \hat{a}_{FF}(trans)$; triangles, $\hat{a}_{FF}(cis) = 3.0$, 3.25, and 3.5 $Å^{-1}$ for the three plates, in increasing order of temperature.

Graphic evidence of the skewing of the SF_6 *cis* distribution is evident in the radial distribution function for SF_6 at higher temperatures (see Fig. 6). The more a peak is skewed, the more does the position of its maximum shift from its true center of gravity. It should be noted, however, that we found virtually no effect of $\hat{a}$ upon the derivation of vibrational amplitudes, and changes in the asymmetry parameter associated with one internuclear distance did not produce changes in the r_g value derived for other internuclear distances when the distances were refined independently.[16] Therefore, the results of the previous paper are not com-

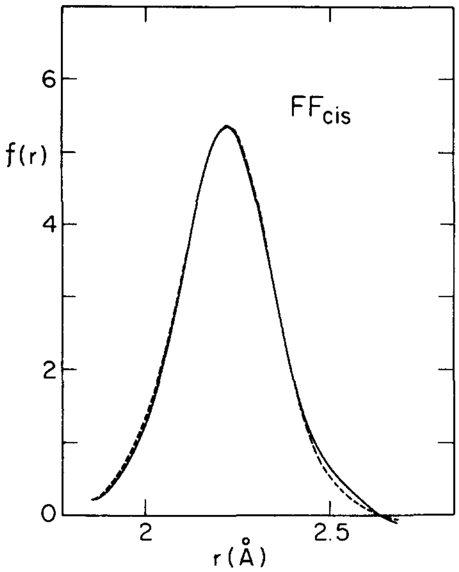

FIG. 6. *Cis FF* peak in radial distribution function for SF_6 at 1700 K. Solid curve, calculated from experimental intensities. Broken curve, derived from best fit of experimental intensities with $\hat{a}_{FF}(cis) = 0$.

promised by our nonoptimum choice of nonbonded asymmetry factors.

In retrospect, what is clear now that was not anticipated at the outset of this study is that ordinary molecules in excited vibrational states exhibit large pseudoshrinkage effects that are exactly analogous to the so-called "anharmonic shrinkage" effects[17] observed a decade ago for cool molecules possessing unusual potential functions, namely, XeF_6,[18] IF_7,[19] and ReF_7.[17] All in all, it is apparent that the diffraction information provides substantial information about bending anharmonicity in molecules that is not embodied in the predictive model of Ref. 5, and that is not simple to derive from spectroscopy. What is useful about the predictive model is its provision of a baseline from which the specific bending anharmonicity can be reckoned, the anharmonicity which couples together bending modes of different symmetries. Procedures for exploiting this new potentiality are under development. They promise to lead, on the one hand, to more precise and less arbitrary structure determinations, particularly in cases where low symmetry makes it impossible to distinguish between true and pseudoshrinkage effects. They offer the hope, on the other hand, of obtaining new knowledge about the character of intramolecular forces.

ACKNOWLEDGMENTS

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