

Inference of vibrational anharmonicity in hot SF₆: An electron diffraction study

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(Received 31 January 1979)

In an investigation of gaseous SF₆ at temperatures ranging from 298 to almost 1000 K, the observed thermal expansion of the mean bond length as a function of the mean-square amplitude of vibration was found to be much too large to be accounted for by the commonly invoked model of Morse anharmonicity. Experimental results can be reproduced quantitatively, however, with the aid of existing potential constants fed into an anharmonic, modified Urey-Bradley force field proposed previously.

INTRODUCTION

A fortunate accident has led to the measurement of a useful index of the anharmonicity of SF₆. Substantial increases in the S-F bond length were observed in fortuitously heated samples. These increases were roughly twice those expected from Morse anharmonicity alone but could be accounted for quantitatively by a simple model field^{1,2} with previously determined potential parameters. In view of the great interest in the potential function of SF₆³ and its bearing on multiphoton absorption in intense radiation fields, we hereby report the results.

EXPERIMENTAL

An electron diffraction investigation of gaseous SF₆ was carried out while the sample was being subjected to a modest irradiation by an infrared beam from a 40 W cw CO₂ laser. While the beam was being focused on the sample by a 5 in. *f*/1. lens, it was accidentally allowed to graze and thereby heat the nozzle, a 6 mm stainless steel needle of 0.1 mm I.D. This action yielded a series of runs with heated gaseous samples ranging in temperature from 300 K to almost 1000 K. Since results were uncorrelated with laser wavelength or with sample pressure which, at the nozzle exit, ranged from about 0.3 to 10 Torr, we conclude that the heating was not due to direct absorption of radiation. Except for the conditions noted above, experimental details and analyses of diffraction intensities were similar to those described for the recent study of SF₆ at room temperature.⁴ Indices of resolution averaged 0.90, with a 0.03 average scatter uncorrelated with mean-square amplitudes.

ANALYSIS OF DATA

Temperatures were inferred from the amplitudes of vibrations of the three internuclear distances, S-F, F...F (*cis*) and F...F (*trans*), the second of which was the most sensitive measure of temperature. For comparison, amplitudes were calculated as a function of temperature by a normal coordinate treatment⁵ based on the force constants of Weinstock and Goodman.⁶ In order to compensate roughly for minor systematic errors due to the limited range of experimental intensities ($4.1 \text{ \AA}^{-1} \leq s \leq 21.4 \text{ \AA}^{-1}$) and due to the neglect of anharmonicity in the normal coordinate treatment, experimental mean-square amplitudes \bar{l}_i^2 were adjusted by small additive

constants so that they would agree with calculated amplitudes at 298 K. Each internuclear peak in a given run then yielded the same temperature to within experimental error.⁷ It is probable that the temperatures so deduced exhibit an increasing systematic error, as *T* increases, because of the neglect, at this stage, of anharmonicity. But, since temperature is essentially a dummy variable in this study, the crucial variable being the mean-square amplitude, the problem is not serious.

As is illustrated in Fig. 1, a convenient representation of results is given by a plot of experimental bond

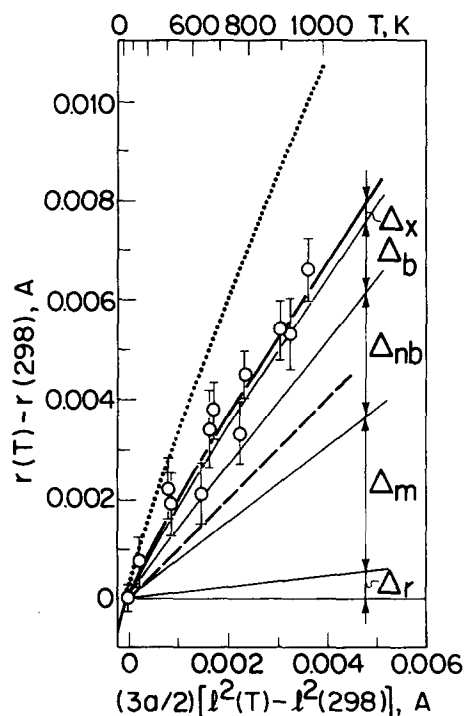


FIG. 1. Thermal expansion of mean bond lengths in SF₆ plotted against the theoretical expansion expected for a (nonrotating) diatomic S-F molecule of the same temperature. Also illustrated are the contributions from rotational centrifugal stretch, Morse anharmonicity, nonbonded repulsion, bond bending centrifugal stretch, and the minor remaining terms Δ_x , as calculated according to the force field proposed in the text. Dashed line, $(3a/2)[\bar{l}^2(T) - \bar{l}^2(298)]$. Dotted line, proposed anharmonic Urey-Bradley field of Ref. 3. Error bars represent standard errors inferred from diffracted intensities. Horizontal errors are roughly one fourth as large as vertical. Estimated temperatures are recorded at the top of the figure.

length displacements, $r_e(T) - r_e(298)$ against the displacements $(3a/2) [l_e^2(T) - l_e^2(298)]_{SF}$ expected for a diatomic molecule at the same temperature,⁸ where a is the Morse parameter and l_e is the rms amplitude calculated for the S-F bond at the weighted-average temperature of the run. Calculated amplitudes $l_e(S-F)$ were used instead of experimental amplitudes, because they were established with greater precision [mainly by the experimental F...F (*cis*) peak], but the difference was minor, the scatter of 0.001₂ Å between observed and calculated amplitudes being comparable to the standard error in $l_e(S-F)$ inferred from diffracted intensities.

As is well known, mean displacements $\langle\Delta r\rangle$ of bond lengths from their equilibrium values can be calculated for vibrating molecules if the potential energy function is assumed to be known. Unfortunately, only for a handful of polyatomic molecules are the force fields known well enough by spectroscopic measurements to permit such a calculation. As is outlined in the preceding paper,² however, an anharmonic, modified Urey-Bradley force field, which has been shown to give reasonable results for some molecules^{4,9} leads, in the case of SF₆, to the following simple expression² for $\langle\Delta r\rangle$:

$$\langle\Delta r\rangle = \Delta_r + \Delta_m + \Delta_{nb} + \Delta_b + \Delta_x, \quad (1)$$

where the rotational centrifugal stretch is

$$\Delta_r = 3kT/6f_{11}r_e, \quad (2)$$

the Morse anharmonic stretch is

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

the stretch associated with the increased force of collision between nonbonded atoms as amplitudes of vibration increase is

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

the centrifugal stretch associated with bending vibrations is

$$\Delta_b \approx (6f_{11}r_e)^{-1} \sum_{i=bond} (h\nu_i/2) \coth(h\nu_i/2kT), \quad (4)$$

and a minor residual term is

$$\Delta_x = 8^{1/2}(F'K_{xx} + F\delta_{xx})/f_{11} - (F - F')r_e\langle(\Delta\alpha)^2\rangle/f_{11}. \quad (5)$$

Notation in the above equations follows conventional Urey-Bradley and general usage and is explained in detail in the preceding paper.²

ESTIMATION OF PARAMETERS

Parameters required were estimated as follows. From the experimental S-F internuclear distance $r_e = 1.561$ Å, together with Eq. (1), an equilibrium length of $r_e = 1.555$ Å was found. A Morse parameter $a = 1.8$ Å⁻¹ was taken from Herschbach and Laurie.¹⁰ Nonbonded force constants were estimated from *ab initio* and semi empirical calculations by Woehler¹¹ yielding $149 \exp(-3.75q)$ for $V_{FF}(q)$, in mdyne Å. Urey-Bradley constants were augmented by assuming that fluorines each bear 0.15 excess electrons (a rather trivial correction) to give values of -0.072, 0.559,

and -4.56 mdyne/Å for F' , F , and F_3 , respectively. Force constants $f_{11} = 6.845$ mdyne/Å and frequencies were taken from McDowell *et al.*,¹² and $K = 4.47$ mdyne/Å was derived from McDowell's general valence constants as outlined elsewhere.¹³

RESULTS AND DISCUSSION

Potential constants, as initially determined in the preceding section, were found to account quantitatively for the observed bond lengths immediately without adjustment, as shown in Fig. 1. After this comparison was made we learned of the Urey-Bradley field of Kim, Souder, and Claassen¹⁴ for SF₆ and its extension to anharmonic terms by Person and Kim.³ This extension had been carried out in an attempt to account for vibrational anharmonicity constants. The nonbonded force constants of Person and Kim, extrapolated to the cubic constant by imposing a 6-12 potential,³ were considerably larger than those estimated by ourselves and resulted in excessive corrections [$r_e(T) - r_e(298)$], as shown by the dotted line in Fig. 1. We conclude that our experimental results, while not leading to a detailed force field, at least provide useful constraints.

ACKNOWLEDGMENTS

This research was supported by a grant from the National Science Foundation. We gratefully acknowledge computing time made available by the Michigan Computing Center. We express our gratitude to Mr. Michael Kacner for carrying out the normal coordinate analysis with the program MSAV graciously donated by Professor R. L. Hilderbrandt.

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