

## Vibrational spectroscopy of matrixisolated UF6 and UF5

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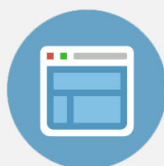
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The above result does not preclude the existence of a  $C_{3v}$  minimum with substantially different geometrical parameters, but the work of GHH and our previous theoretical work<sup>16</sup> argues against such a structure. It seems clear that further experimental and theoretical work is needed to resolve these structural ambiguities and account for the molecular spectra and dipole moment of this molecule.

The author thanks Professor H. F. Schaefer III for helpful discussions and computing time. This work was completed during the author's tenure as a Miller Fellow at the University of California, Berkeley.

<sup>1</sup>The structure of crystalline beryllium borohydride has been established with certainty: D. S. Marynick and W. N. Lipscomb, *Inorg. Chem.* **11**, 820 (1972); J. W. Nibler, D. F. Shriver, and T. H. Cook, *J. Chem. Phys.* **54**, 5257 (1971); D. S. Marynick and W. N. Lipscomb, *J. Am. Chem. Soc.* **93**, 2322 (1971).

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<sup>6</sup>T. H. Cook and G. L. Morgan, *J. Am. Chem. Soc.* **91**, 774 (1969).

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<sup>8</sup>J. W. Nibler and T. Dyke, *J. Am. Chem. Soc.* **92**, 2920 (1970).

<sup>9</sup>See T. H. Cook and G. L. Morgan, *J. Am. Chem. Soc.* **92**, 6493 (1970), footnote 11.

<sup>10</sup>T. H. Cook and G. L. Morgan, *J. Am. Chem. Soc.* **92**, 6493 (1970).

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<sup>12</sup>G. Gundersen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.* **59**, 3777 (1973). The electron diffraction work is also consistent with a structure of  $C_{3v}$  symmetry and a linear Be-B-B framework, but this structure was eliminated on chemical grounds. STO calculations on the B-Be-B  $C_{3v}$  and Be-B-B  $C_{3v}$  models indicate that the Be-B-B model is roughly 130 kcal/mol less stable.

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<sup>17</sup>T. H. Dunning, *J. Chem. Phys.* **53**, 2823 (1970); the scale factor for all functions on hydrogen was taken as 1.15, optimum for  $BeH_2$ .

<sup>18</sup>The basis set for beryllium was taken from an optimized set for the  $^3P$  state of the beryllium atom: D. R. Yarkony and H. F. Schaefer III, *J. Chem. Phys.* **61**, 4921, (1974). The  $p$  orbital scale factors were taken as 1.09 (inner) and 0.95 (outer), optimum for  $BeH_2$ .

<sup>19</sup>The optimized parameters found with the extended basis set calculations are: B-Be, 1.75 Å; B-H<sub>b</sub>, 1.255 Å; H<sub>t</sub>-B-H<sub>b</sub>, 114.3°. The B-H<sub>t</sub> distance was taken as 1.18 Å, optimum for a minimum basis set (Ref. 16).

<sup>20</sup>Using a 6-31 G basis set [W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* **56**, 2257 (1972)] and near Hartree-Fock optimized geometries for  $D_{3d}$  and  $C_{3v}$  ammonia [R. M. Stevens, *J. Chem. Phys.* **55**, 1725 (1971)] the calculated inversion barrier is 38% too low (D. S. Marynick, unpublished results).

<sup>21</sup>The  $D_{3d}$  to  $C_{3v}$  distortion consistent with the electron diffraction data involves a shift of the beryllium atom position only ca. 0.05 Å, and similar changes in the B-H<sub>b</sub> bond lengths. In terms of bond angles, the distortions are smaller than those associated with the  $NH_3$  inversion mode.

## Vibrational spectroscopy of matrix-isolated $UF_6$ and $UF_5$

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We report here the vibrational spectrum of  $UF_6$  molecules isolated in Ar, Xe, and CO matrices, and the infrared spectrum of monomeric  $UF_5$  molecules produced in these matrices by photolysis with ultraviolet radiation.

The experimental apparatus consisted of a Displex model DE202S closed-cycle 1-W helium refrigerator system (Air Products and Chemicals, Inc., Allentown, PA) with an Air Products APD-IC-1 temperature controller.  $UF_6$  and the desired matrix gas were premixed in a 2.5 l Monel cylinder. The mixed sample passed through a Monel metering valve to a stainless steel inlet orifice opposite the cooled sample target, which was a CsI window for the infrared studies and a polished copper flat for the Raman spectra. Spectra were

obtained on a Perkin-Elmer model 180 infrared spectrometer and a Cary model 82 laser Raman spectrometer using 5145 Å  $Ar^+$  excitation. An Oriel model 6242 source fitted with a 1-kW mercury-xenon lamp and a Schoeffel model GM-250 monochromator were used for the photolysis experiments.

Most of the work reported here was carried out using inert gas/ $UF_6$  ratios of 1000, but dilution ratios of 200 were used to measure the weaker combination bands; peak positions were not dilution sensitive over this range provided that the deposition conditions were otherwise identical. Increasing the dilution ratio to  $10^4$  resulted in no significant improvement in the quality of the spectra. Deposition at about 1 mmol/h at 20 K produced the best spectra; annealing the sample

rarely improved spectral quality. The spectra were recorded with the matrices held at about 10 K.

The infrared and Raman measurements are summarized in Table I. The stretching fundamental  $\nu_3$  in an argon matrix is shown in Fig. 1(A), and is typical in that the main absorption is accompanied by several weaker features, indicating the presence of multiple trapping sites and/or slight matrix perturbations of the equilibrium  $O_h$  symmetry of  $UF_6$ . (Lowered symmetry is also suggested by the fact that  $\nu_1$  is not observed to be completely polarized in the Raman; its measured depolarization ratio is  $\sim 0.5$ .) Details of these secondary features depend on the matrix gas and on the rate and temperature of deposition, as do the magnitudes of the frequency shifts from the vapor band positions.<sup>1</sup> The principal infrared absorption peaks were 0.3 to 0.7  $cm^{-1}$  wide in Ar and Xe matrices (measured full widths at half absorbance, minus the spectral slitwidth); in CO the secondary structure is so prominent that no meaningful linewidth measurements are possible.

Photolysis was initially carried out with broad-band ultraviolet radiation. In Ar matrices the photolytic decomposition proceeds rather rapidly; the 619- $cm^{-1}$   $UF_6$  peak decreases in intensity and two new peaks grow in at 561 and 584  $cm^{-1}$  (Fig. 1), which we attribute to the expected<sup>2</sup> photolysis product  $UF_5$ . In the bulk solid,  $\alpha$ - $UF_5$ <sup>3</sup> and  $\beta$ - $UF_5$ <sup>4</sup> both have polymeric fluorine-bridged structures, with strong, broad U-F stretching absorptions at 570–610  $cm^{-1}$  and equally strong, broad U-F-U bridging modes at 390–400  $cm^{-1}$ .<sup>5</sup> The sharpness of the matrix peaks, and the complete absence of any absorption near 400  $cm^{-1}$ , indicate that we are observing isolated  $UF_5$  molecules. After some hours of photolysis a steady state is reached and the relative intensities of the  $UF_5$  and  $UF_6$  absorptions do not change further. Annealing the matrix at this point reverses the dissociation, and about 80% of the original intensity of the  $UF_6$  peak can be recovered.

We were unable to produce sufficient  $UF_5$  to obtain a satisfactory Raman spectrum, so the structure of isolated  $UF_5$  must remain speculative at present. Two

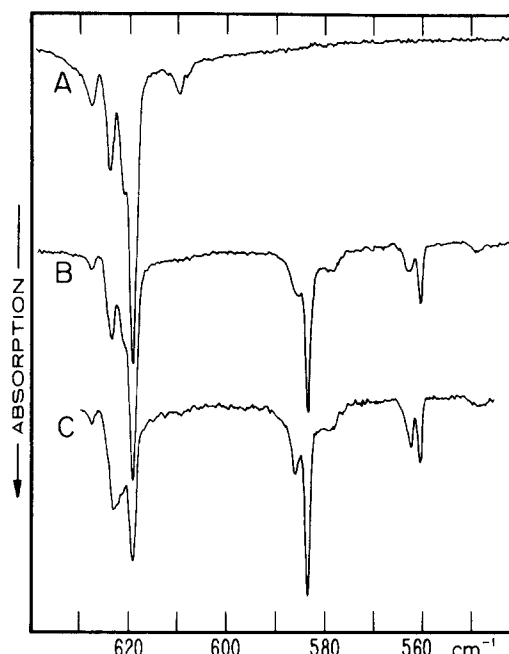


FIG. 1. Infrared spectra of a 1000:1 Ar: $UF_6$  matrix at  $\sim 10$  K: (A) before photolysis; (B) after 30 min broad-band ultraviolet irradiation; (C) after 4.5 h irradiation. Spectral slit width approximately 0.8  $cm^{-1}$ .

infrared-active U-F stretches would be expected for the trigonal bipyramidal ( $D_{3h}$ ) and three for the square pyramidal ( $C_{4v}$ ) structure, but one of the latter three would be expected to be weak,<sup>6</sup> so the infrared data alone are inconclusive.

The wavelength dependence of the photodecomposition was studied using monochromatized radiation (10 nm bandpass). The relative quantum efficiency for  $UF_6$  dissociation per unit absorbance of  $UF_6$  is relatively constant over the region 250–300 nm, in the strong allowed  $\bar{B} - \bar{X}$  absorption band of  $UF_6$ ,<sup>7</sup> but then drops rapidly as the edge of the  $\bar{B} - \bar{X}$  transition (330 nm<sup>7</sup>) is reached. Radiation in the forbidden  $\bar{A} - \bar{X}$  band of  $UF_6$  (340–410 nm<sup>7</sup>) is at most  $10^{-4}$  as efficient in effecting conversion to  $UF_5$  as is that at  $\sim 280$  nm.

In CO matrices, which should be efficient fluorine-atom scavengers, the photolysis is very rapid: all of the  $UF_6$  can be decomposed in a few minutes using a broad-band source. Three sharp infrared bands appear at 533, 543, and 568  $cm^{-1}$  with relative absorbances of about 0.5, 0.7, and 1.0, respectively, in addition to numerous bands elsewhere in the spectrum that can be assigned to FCO, (FCO)<sub>2</sub>, and F<sub>2</sub>CO.<sup>8</sup> We attribute the absorptions in the 530–570  $cm^{-1}$  region to  $UF_5$  perturbed by the influence of CO molecules, perhaps even to the point of forming a compound such as  $UF_5CO$ . This decomposition is not reversible on annealing, and if photolysis continues a new, broader band appears at 499  $cm^{-1}$  and continues to grow; this may be due to  $UF_4$  or to polymerized  $UF_5$ . We could not effect photodecomposition in a xenon matrix even after several hours of irradiation.

We thank F. B. Wampler for assistance with the photolysis experiments.

TABLE I. Vibrational frequencies of matrix-isolated  $UF_6$  ( $cm^{-1}$ ).

Assignment	Ar: $UF_6$	Xe: $UF_6$	CO: $UF_6$	$UF_6$ vapor <sup>a</sup>
$\nu_1 + \nu_3$ (ir)	1281.3			1290.9
$\nu_2 + \nu_3$ (ir)	1145.8			1156.9
$\nu_1 + \nu_4$ (ir)	847.3			852.8
$\nu_3 + \nu_5$ (ir)	816.9			$\sim 824$
$\nu_2 + \nu_4$ (ir)	712.3			719.1
$\nu_2 + \nu_6$ (ir)	673.2			$\sim 674$
$\nu_1$ ( $A_{1g}$ stretch; R)	665.8		666	667.1
$\nu_3$ ( $F_{1u}$ stretch; ir)	619.3	617.0	618.4 <sup>b</sup>	625.5
$\nu_2$ ( $E_g$ stretch; R)	529.6		530	534.1
$\nu_5$ ( $F_{2g}$ bend; R)	199.7		205	200.4
$\nu_4$ ( $F_{1u}$ bend; ir)	183.5			186.2

<sup>a</sup>At 298 K, from Ref. 1.

<sup>b</sup>Strongest peak; other peaks, nearly as strong, at 620.4 and 621.8  $cm^{-1}$ .

\*This work was supported by the U. S. Energy Research and Development Administration.

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## Static dielectric constant of pyroelectric crystals

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In a previous paper,<sup>1</sup> Urano and the author have extended the Fröhlich<sup>2</sup> formula for static isotropic dielectric constants in such a way that it can be applied to anisotropic dielectrics which are assumed not to be pyroelectrics. In this note, we drop this assumption and present a formula for the static dielectric constant of pyroelectric crystals.

When we consider a pyroelectric crystal the relation between the electric displacement  $\mathbf{D}$  and the electric field  $\mathbf{E}$  is

$$\mathbf{D}_i = \mathbf{D}_{0i} + \sum_k \epsilon_{ik} \mathbf{E}_k, \quad (1)$$

where  $\mathbf{D}_{0i}$  is a constant vector, and  $\epsilon_{ik}$  is the dielectric tensor. In our case the electric polarization  $\mathbf{P}$  takes a form as

$$\mathbf{P} = \mathbf{P}_0 + \mathbf{P}_{in}, \quad (2)$$

where  $\mathbf{P}_0$  is the spontaneous polarization, and  $\mathbf{P}_{in}$  is the induced polarization. An electric dipole moment  $\mathbf{M}$  is related simply to the electric polarization  $\mathbf{P}$  by the following equation:

$$\mathbf{M} = V' \mathbf{P}, \quad (3)$$

where  $V'$  is the volume of the crystal. The electric dipole moment can be divided into two parts as in (2), namely,

$$\mathbf{M} = \mathbf{M}_0 + \mathbf{M}_{in}, \quad (4)$$

where  $\mathbf{M}_0$  and  $\mathbf{M}_{in}$  are the spontaneous and the induced part of  $\mathbf{M}$ , respectively.

We take the coordinates axes  $x$ ,  $y$ ,  $z$  along the principal axes of the dielectric tensor  $\epsilon_{ik}$ . Without loss of generality we may take the field  $\mathbf{E}$  to be along the  $z$  axis and we shall use this condition hereafter. Therefore, from Eqs. (1)–(4) and the well-known relation  $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$ , we obtain

$$\epsilon^{(z)} - 1 = \frac{4\pi}{V} \frac{(\mathbf{M}_z - \mathbf{M}_{0z})}{\mathbf{E}_z}, \quad (5)$$

where  $\epsilon^{(z)}$  is the  $z$  principal value of the dielectric tensor. This equation is a pyroelectric version of (1.9) of Ref. 2 and it affords the relation between macroscopic and atomic theory.

The method which will be used is quite similar to the

method which has been used by Fröhlich.<sup>2</sup> We select from the crystal a macroscopic spherical region of volume  $V$  which consists of a number of elementary charges  $e_i$ , each of which can undergo a displacement from the equilibrium position. This displacement is denoted by  $\mathbf{r}_i$ . A set of all the displacement vectors will be collectively denoted by  $X$ . We shall calculate the average electric moment of the sphere in the direction of the field  $\mathbf{E}$ . We treat the inside of the sphere using classical statistical mechanics. The outside, however, will be considered as a continuous dielectric medium. The potential energy  $U(X, E)$  of the sphere in the configuration  $X$ , in the presence of the field  $\mathbf{E}$  is given by<sup>2</sup>

$$U(X, E) = U(X) - \mathbf{M}_{inz}(X) \mathbf{G}_z, \quad (6)$$

where  $U(X)$  is the potential energy in the absence of the field  $\mathbf{E}$ , and  $\mathbf{G}_z$  is the  $z$  component cavity field which has been calculated as<sup>3</sup>

$$\mathbf{G}_z = \frac{\epsilon^{(z)}}{\epsilon^{(z)} - n^{(z)}(\epsilon^{(z)} - 1)} \mathbf{E}_z. \quad (7)$$

Here  $n^{(z)}$  is the  $z$  component of depolarization coefficient and it is defined in Refs. 1 and 3.

Therefore, the average electric dipole moment  $\mathbf{M}_{inz}$  can be calculated with the aid of (6) and (7):

$$\begin{aligned} \mathbf{M}_{inz} &= \frac{\int \mathbf{M}_{inz}(X) e^{-U(X, E)/kT} dX}{\int e^{-U(X, E)/kT} dX}, \\ &= \frac{\epsilon^{(z)}}{\epsilon^{(z)} - n^{(z)}(\epsilon^{(z)} - 1)} \frac{\mathbf{E}_z}{kT} \langle \mathbf{M}_{inz}^2 \rangle, \end{aligned} \quad (8)$$

where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature and  $\langle \rangle$  is the statistical average value in the absence of the field  $\mathbf{E}$ . In the derivation we have used  $\langle \mathbf{M}_{inz} \rangle = 0$  and a weak field approximation:

$$e^{-U(X, E)/kT} \approx e^{-U(X)/kT} [1 + \mathbf{M}_{inz}(X) \mathbf{G}_z/kT]. \quad (9)$$

Inserting the Result (8) into (5) and using  $\mathbf{M}_{inz} = (\mathbf{M}_z - \mathbf{M}_{0z})$ , we have come to the following conclusion:

$$\epsilon^{(z)} - 1 = \frac{4\pi}{V} \frac{\epsilon^{(z)}}{\epsilon^{(z)} - n^{(z)}(\epsilon^{(z)} - 1)} \frac{\langle (\mathbf{M}_z - \mathbf{M}_{0z})^2 \rangle}{kT}. \quad (10)$$

Evidently, this Formula (10) agrees with (9) of Ref. 1 when the spontaneous polarization is absent in the crystal.