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Vibrational Spectrum and Thermodynamic Properties of Uranium Hexafluoride Gas*

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The Raman spectra of liquid UF_6 and of UF_6 dissolved in C_7F_{16} have been photographed. Three Raman lines are found for UF_6 at 200, 511, and 656 cm^{-1} . The infra-red spectrum of the gas has been obtained in the region between 2 and 17μ . A vibrational assignment of all the fundamental frequencies is made on the basis of the regular octahedral model. The calculated infra-red active overtones are in good agreement with experiment. Using 2.0\AA as the U-F distance from electron diffraction measurements, the entropy, heat capacity and $-(F^\circ - E_0^\circ/T)$ are calculated from 100°K to 1000°K for the gas. The calculated and experimental entropies are in good agreement.

I. INTRODUCTION

THE most regular form that a molecule of the type XY_6 can have is that of a regular octahedron. The molecules SF_6 , SeF_6 , and TeF_6 have been studied by electron diffraction,³ infra-red absorption,⁴ and Raman effect⁵ and have been found to be regular octahedra. The Raman effect of the ions SbCl_6^- , SnCl_6^- , seems to indicate that these ions too are octahedral.^{6,7} SnBr_6^- has a lower symmetry which is easily explained by steric effects.⁷ The hexafluorides of molybdenum, tungsten, and uranium have previously been studied by electron diffraction only⁸ and all three were found to have a lower symmetry than O_h .

Uranium hexafluoride has no dipole moment (less than 0.5 debye),⁹ which rules out a number of unsymmetrical configurations. The results of the infra-red and Raman measurements discussed in this paper show that uranium hexafluoride has the structure of a regular octahedron.

II. RAMAN EXPERIMENTS

The spectrograms were obtained in collaboration with Dr. R. F. Stamm of the Stamford Research Laboratories of the American Cyanamid Company. The spectrograph and the light sources have been described by Dr. Stamm.¹⁰ We wish to thank Dr. R. B. Barnes and Dr. R. F. Stamm for their cooperation in obtaining the Raman spectra.

Three sets of exposures under different exciting conditions were necessary before the complete spectrum could be obtained. In the first set of exposures the spectrum of liquid UF_6 was obtained using 4358Å excitation; in the second set the Raman spectrum of a solution UF_6 in C_7F_{16} was photographed using 4358Å excitation; finally, the spectrum of a solution of UF_6 in C_7F_{16} was photographed using 5461Å excitation. The cell used for all three sets of experiments is shown in Fig. 1. Great care was taken to keep the highly purified samples protected from ultra-violet light.

⁹ C. P. Smyth and N. B. Hannay, Princeton University report number A2130.

¹⁰ R. F. Stamm, *Ind. and Eng. Chem., anal. ed.* **17**, 318 (1945).

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³ L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.* **19**, 68 (1933).

⁴ (a) A. Eucken and H. Ahrens, *Zeits. physik. Chemie* **B26**, 297 (1934); (b) A. Eucken and F. Sauter, *ibid.* **B26**, 463 (1934); (c) H. Sachsse and E. Bartholomé, *ibid.* **B28**, 257 (1937).

⁵ D. M. Yost, C. C. Steffens, and S. T. Gross, *J. Chem. Phys.* **2**, 311 (1934).

⁶ O. Redlich, T. Kurz, and P. Rosenfeld, *Zeits. physik. Chemie* **B19**, 231 (1932).

⁷ O. Redlich, T. Kurz, and W. Stricks, *Monatshefte f. Chemie* **71**, 1 (1938).

⁸ H. Braune and P. Pinnow, *Zeits. physik. Chemie* **B35**, 239 (1937).

In spite of the precautions taken, the exposures of liquid UF_6 at 70°C using 4358A excitation had to be stopped after fifteen minutes. A considerable amount of fine fluffy solid appeared, which was caused by the photo-chemical reaction of the UF_6 and the glass, and gave rise to excessive Raleigh scattering. The gas bubbles of the boiling liquid also gave rise to a large amount of scattered primary light. The 4358A line was highly overexposed and the Rowland ghosts were very prominent so that no Raman lines below 300 cm^{-1} could be observed. In these experiments two Raman lines were found at $656 \pm 3\text{ cm}^{-1}$ and $511 \pm 3\text{ cm}^{-1}$. In the second set of experiments using first a sample of pure C_7F_{16} and then a 20-mole percent solution of UF_6 in C_7F_{16} to eliminate scattering by the gas bubbles, the photo-chemical reaction of UF_6 with either C_7F_{16} and/or the glass gave rise to significant amounts of fine solid. Here again no Raman lines below 300 cm^{-1} could be observed. Finally, using 5461A excitation, a two-hour exposure of UF_6 in C_7F_{16} showed three Raman lines. One line was definitely due to C_7F_{16} . The other two lines were at 666 cm^{-1} and 202 cm^{-1} . The Raman line of UF_6 at 511 cm^{-1} did not appear because of the weakness of the exposure. The results are tabulated in Table I.

The samples were prepared as follows. The UF_6 was a purified laboratory sample which was molten in the presence of fused KF in a sealed glass system which had been previously baked while connected to a high vacuum system. This process frees the UF_6 from traces of HF. The UF_6 was distilled under high vacuum into the storage bulb connected to the Raman cell. For the investigation of the Raman spectrum the solid UF_6 was heated to the melting point in the storage bulb. The liquid was poured into the connecting Raman tube which was heated to prevent freezing by means of a Nichrome wire wrapped around the tube. The C_7F_{16} was obtained from Dr. W. T. Miller formerly at the S.A.M. Laboratories. The C_7F_{16} was refluxed overnight with UF_6 in a closed dry system after which it was fractionally distilled into a glass vessel containing sodium. The sodium had been distilled in, under high vacuum. The C_7F_{16} was then distilled into another bulb containing UF_6 and KF solids. The solution of UF_6 in C_7F_{16} was

TABLE I. Raman lines of UF_6 .

Liquid (70°C)	Solution in C_7F_{16} (20°C)
656 ± 3	666 ± 3
511 ± 3	—
—	202 ± 3

then distilled from the solid KF into the Raman storage bulb. All operations were done in high vacuum systems which had been thoroughly baked and outgassed.

III. INFRA-RED SPECTRUM

The infra-red spectrum of UF_6 from 2 to 17μ was obtained on the Princeton rocksalt spectrometer described by W. W. McCarthy and J. Turkevich.¹¹ The uranium hexafluoride used was a highly purified sample obtained from the S.A.M. Laboratories through the courtesy of Professor Anthony Turkevich to whom we are highly indebted for counsel and aid. A portion of this material was distilled in high vacuo into an infra-red absorption cell. The latter was made out of glass and had at the ends rocksalt

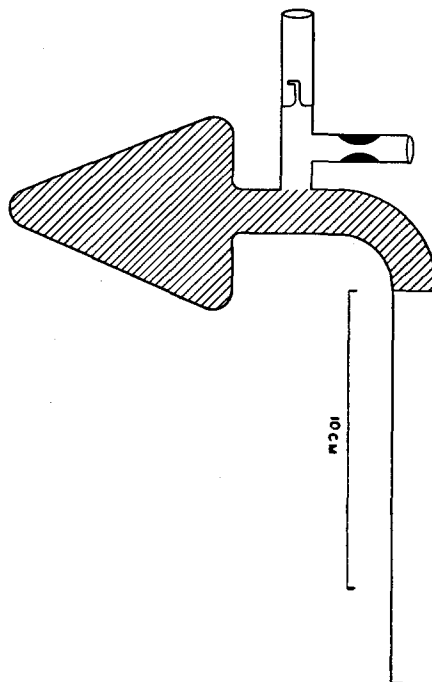


FIG. 1. Raman cell for UF_6 . The shaded portion is made of "Pyrex Lifetime Red" glass.

¹¹ W. W. McCarthy and J. Turkevich, J. Chem. Phys. 12, 461 (1944).

TABLE II. Fundamental vibrations of UF_6 .

	Fre- quency	Sym- metry	Degen- eracy	Activity	Observed
ν_1	656	A_{1g}	1	Raman	656 ± 3
ν_2	511	E_g	2	Raman	511 ± 3
ν_3	200	T_{2g}	3	Raman	202 ± 3
ν_4	130	T_{2u}	3	Inactive	—
ν_5	200	T_{1u}	3	Infra-red	—
ν_6	640	T_{1u}	3	Infra-red	623 or larger

windows baked on in vacuum at 150°C with glyptal. The length of the cell was 20 cm. A side tube on the cell always contained some solid UF_6 . The pressure of the UF_6 in the absorption cell was regulated by controlling the vapor pressure of the solid UF_6 in the side tube by use of appropriate temperature baths. During the course of repeated measurements a slight reaction of the UF_6 and the moisture in the rocksalt took place. This resulted in the formation of a slight film whose absorption was determined by freezing out the UF_6 from the cell into the side tube by liquid air. The infra-red spectrum of UF_6 was taken at several pressures and the results are tabulated in Table III.

IV. CONFIGURATION OF URANIUM HEXAFLUORIDE

If uranium hexafluoride has the structure of a regular octahedron, one would expect to find three Raman lines and two infra-red active vibrations, one of which should be of low frequency. In the region in which the infra-red measurements were made one would expect to find one active fundamental. Table III shows one line at 623 cm^{-1} which is about one hundred times stronger than any other line. However, inspection of the infra-red data indicates that there may be an accidental degeneracy. The absorption line at 675 cm^{-1} is two to three times stronger than any other line in the spectrum, except for the line at 623 cm^{-1} . It seems reasonable to assume that the fundamental frequency is actually somewhat higher, say at 640 cm^{-1} ; and that a double overtone falls at about the same point. Thus the two lines at 623 cm^{-1} and 675 cm^{-1} would originate from the interaction of the two levels at about 640 cm^{-1} . The experimental results of the number and the positions of active lines both in the infra-red and Raman

spectra are strong arguments in favor of this completely symmetrical model.

On this basis the following assignment of the fundamental frequencies is made (Table II).

The results of x-ray diffraction on single crystals of uranium hexafluoride of Hoard and Stroupe¹² are in agreement with the symmetrical model, although they can also be reconciled with a less symmetrical structure. Hoard and Stroupe propose a configuration in which there are two sets of U—F distances. Two opposite U—F distances are assumed to be equal and longer than the remaining four. This reduction in symmetry would introduce a splitting of all but the breathing vibration, A_{1g} . One component of the vibration T_{2u} would become infra-red active.

Electron diffraction measurements of the gas have been made by Braune and Pinnow⁸ and more recently by Bauer.¹³ Both workers do not find a completely symmetrical structure. Bauer considers a model in which there are two sets of U—F distances and the U—F bonds are at right angles. This is not in agreement with Hoard and Stroupe's results. With this model all triply degenerate frequencies in Table II split. In addition, all Raman active frequencies should be infra-red active and *vice versa*. One component of the inactive vibration, ν_4 , should also be infra-red and Raman active.

It is conceivable that the deviations from regular octahedral symmetry might be small enough so that the splitting is not resolvable and the new lines are too weak to be observed. In that case, there is still one argument left in favor of complete symmetry. In Section VI the

TABLE III. Infra-red spectrum of UF_6 .

	Calculated	Observed	Strength
ν_5	200 cm^{-1}	—	
$\nu_4 + \nu_3$	330	—	
$\nu_6 + \nu_3$	400	—	
ν_6	640	623	1000
$\nu_4 + \nu_2$	641	675	10
$\nu_6 + \nu_2$	711	713-719	$\frac{1}{2}$
$\nu_6 + \nu_3$	840	825	2
$\nu_6 + \nu_1$	856	850	$\frac{1}{2}$
$\nu_6 + \nu_2$	1151	1163	4
$\nu_6 + \nu_1$	1296	1295	3
		2053	$\frac{1}{2}$

¹² J. L. Hoard and J. D. Stroupe, Columbia Report A 1242, March, 1944. Declassified October 7, 1946.

¹³ S. H. Bauer, Columbia Report A-1209. Declassified October 14, 1946.

entropy of the gas is calculated from the frequency assignment of Table II with the use of the symmetry number 24. This is shown to be in good agreement with, although somewhat lower than the experimental value. On the basis of the Hoard and Stroupe model the calculated entropy will be raised by $R \ln 3 = 2.18$ e.u., and Bauer's model would be higher by $R \ln 8 = 4.13$ e.u. Both of these results are in poor agreement with the experimental entropy. We are therefore led to believe that the gas UF₆ has the structure of a regular octahedron.

V. ANALYSIS OF INFRA-RED DATA

With the help of the assignment of the fundamentals it is possible to calculate all the infra-red active double combination frequencies. The assignment of the inactive frequency, ν_4 , was made to obtain an accidental degeneracy by combining ν_4 with ν_2 to give 641 cm^{-1} , which is accidentally degenerate with the active fundamental at 640 cm^{-1} . The calculated and observed values are compared in Table III.

VI. THERMODYNAMICS OF URANIUM HEXAFLUORIDE

The vibrational spectra together with the interatomic distances provide a basis for the calculation of the thermodynamic functions of uranium hexafluoride gas. The vibrational assignment given in Table II was used. The structure of the molecule was taken as a regular octahedron in conformity with the vibrational assignment. The six uranium to fluorine distances were taken as 2.0Å. This is very close to the average of the distances given by Bauer¹³

TABLE IV. Thermodynamic properties of UF₆ from spectroscopic data.

T°K	S° in cal. deg. ⁻¹ mole ⁻¹	C _p in cal. deg. ⁻¹ mole ⁻¹	-(F° - E ₀ °)/T cal. deg. ⁻¹ mole ⁻¹
100	62.99	18.93	50.91
150	71.58	23.45	56.41
200	78.81	26.74	61.14
273	87.65	30.13	67.08
298	90.34	31.00	68.92
323	92.89	31.75	70.69
348	95.22	32.38	72.33
373	97.47	32.93	73.93
400	99.86	33.46	75.65
500	107.45	34.80	81.25
750	122.37	36.35	92.99
1000	132.58	36.94	101.37

TABLE V. Calculated and experimental entropy of UF₆ gas.

T°K	S° Exp.	S° Calc.	S° Exp. - S° Calc.
273	88.21	87.65	+0.56
298	90.76	90.34	+0.42
323	92.96	92.89	+0.07
348	94.97	95.22	-0.25

and by Braune and Pinnow.⁸ In any case, there is little error introduced into the rotational contributions if the distances differ from 2.0Å by as much as five percent. In accordance with the usual convention the entropies of nuclear spin and isotope mixing are neglected. The symmetry number was taken as 24. The results for the ideal gas are given in Table IV.

The calculated values may be compared in part with the best experimental data available. Brickwedde, Hoge, and Scott¹⁴ have determined the heat capacity of solid uranium hexafluoride from 20°K to 337.2°K and of the liquid from 337.2°K to 370°K. Crist and Weinstock¹⁵ have measured the vapor pressures of uranium hexafluoride from 273°K to 358°K. From these measurements and the critical constants of the gas, Crist and Weinstock have calculated the entropy of the gas at several temperatures. Their experimental entropies are compared with some of the entropies calculated from spectroscopic data in Table V.

It will be seen that the calculated entropies agree with the experimental ones to better than 0.7 percent. The differences are within the probable limits of error of either determination. There is a somewhat larger than usual uncertainty in the third law entropy of the condensed phases.¹⁴ The entropy of sublimation has not been directly determined and may be in error by about 0.2 cal. deg.⁻¹ mole⁻¹. There are nine vibrational frequencies below 200 cm^{-1} , which have been treated as harmonic. This approximation will give a low calculated entropy. In addition if one of the triply degenerate frequencies ν_4 or ν_5 has been incorrectly assigned by about 10 cm^{-1} , the calculated entropy will be changed by about 0.5 cal. deg.⁻¹ mole⁻¹.

¹⁴ F. G. Brickwedde, H. J. Hoge, and R. B. Scott, J. Chem. Phys.

¹⁵ R. H. Crist and B. Weinstock, J. Chem. Phys.