TABLE I

PRECIPITATION OF BASIC LEAD(II) OXALATE

$[OH^-]$, molar	i_d arbitrary units	$[Pb^{II}]$ molar	$[Pb^{II}]/[OH^-]^{1.5}$
4.12×10^{-2}	27.00	1.645×10^{-3}	No ppt.
8.13×10^{-3}	25.30	1.543	2.10
6.85	23.57	1.438	2.54
5.50	21.13	1.289	3.15
4.52	18.13	1.106	3.64
3.47	10.05	0.613	3.00
2.48	8.15	.497	4.01
2.00	5.17	.315	3.54
1.66	3.54	.216	3.20
1.35	2.62	.160	3.22
1.08	1.87	.114	3.21
8.22×10^{-4}	0.95	.058	2.46
5.90	.60	.036	2.50
3.16	.34	.021	3.75
		Mean	$3.1_0 \pm 0.4_5$

water and acetone and dried over anhydrous magnesium perchlorate for 2 weeks was found to weigh 0.1240 g. It was decomposed by long standing under dilute sulfuric acid, and the lead sulfate thus resulting, after drying at 105°, weighed 0.1420 g. Assuming the precipitate to have the formula given above, the calculated weight of lead sulfate is 0.1433 g. The difference between the actual and calculated weights is probably due to water retained by the basic oxalate. Had the precipitate been the normal oxalate, the calculated weight of lead sulfate would have been 0.1513 g.

In 1.0 *F* potassium oxalate solutions equilibrium in this reaction is too slowly attained to permit accurate measurement of the diffusion current by the technique here employed. A few measurements which were made after the solutions had been permitted to stand for some hours are in approximate accord with the picture outlined above, but the values of *K* secured, due to the continuing slow precipitation, are much too erratic to aid in the assignment of a more accurate value than that given.

At *p*H values above about 12.3 the half-wave potentials in 1 *F* potassium oxalate (Fig. 5b) fall on a line parallel to that representing the data in 0.05 *F* oxalate, and are about 15 mv. more positive than the latter values. The difference is probably not significant, and the slope of this section of the curve indicates that it is the biplumbite ion which is the reducible species here also.

At lower *p*H values, however, the half-wave potential values becomes more negative than would be predicted by an extrapolation of this line, and between *p*H 7.4 and 10.7 in 1 *F* potassium oxalate $E_{1/2}$ is constant at -0.581 ± 0.002 v., in very good agreement with the value of -0.59 v. calculated from the dissociation constant of the $Pb(C_2O_4)_2^{=}$ ion given by Kolthoff, Perlich and Weiblen.[15]

NEW HAVEN, CONN. RECEIVED SEPTEMBER 6, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Raman Effect and Ultraviolet Absorption Spectra of Molybdenum and Tungsten Hexafluorides[1]

BY K. N. TANNER[2] AND A. B. F. DUNCAN

The Raman effect for MoF_6 and WF_6 has been studied and three lines were found for each molecule. Two of the lines are weak and diffuse, and the third is strong, sharp and highly polarized. This result indicates octahedral structure for these molecules. If this symmetry is assumed, the Raman inactive frequencies can be calculated from force constants obtained from the Raman active frequencies. Exploratory studies have been made on the ultraviolet absorption spectra of these molecules. A strong absorption band has been found for each, with a center probably around 1850 Å. for MoF_6 and about 1750 Å. for WF_6. This appears to represent the first allowed electronic transition. An interesting banded structure was found for this transition in MoF_6.

Introduction

Molecules of the type XY_6 are of some interest in the study of molecular structure, since symmetrical arrangements of atoms in molecules of this type may exist. The most symmetrical arrangement results when the Y atoms are located at the corners of a regular octahedron. This symmetry is characterized by several three and fourfold axes of rotation and a center of symmetry, and corresponds to the crystallographic group O_h.

A number of molecules of the type XY_6 have been studied, among them SF_6, SeF_6, TeF_6, UF_6, MoF_6 and WF_6. All have been subjected to electron diffraction experiments, and all but the last two have been studied by spectroscopic methods. All the evidence obtained so far indicates that SF_6, SeF_6 and TeF_6 have octahedral symmetry.[3] This work was undertaken to supply spectroscopic data on MoF_6 and WF_6.

In only a few cases has the electronic spectrum of molecules of cubic symmetry been studied. Since only transitions to triply degenerate excited states are allowed, the vibrational structure to be expected for such spectra would be very complicated and should appear as continuous or quasi-continuous bands.[4]

Experimental Details

The samples[5] of MoF_6 and WF_6 were prepared in metal systems and triply distilled *in vacuo* over anhydrous KF.

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(1) This work was supported in part under Contract No. N6onr-241, T. O. X, Project NR-019-118 with the Office of Naval Research, United States Navy.

(2) Part of the dissertation presented to the Faculty of the Graduate School of the University of Rochester in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

(4) H. Sponer and E. Teller, *Revs. Modern Phys.*, **13**, 92 (1941).

(5) We appreciate the kindness of Drs. Cady and Barber of the University of Washington who prepared these samples.

We received the samples in small Monel metal cylinders with brass needle valves.

Since these hexafluorides hydrolyze very readily, liberating HF, special precautions were used in handling the materials in glass systems. Small traces of water on the walls of the glass system convert the hexafluorides to oxyfluorides with the production of SiF_4 by a chain reaction.[6] The reaction can be broken by absorbing the HF formed in the process with NaF or KF. A gram or two of anhydrous NaF was placed in every glass storage bulb for this purpose.

MoF_6 and WF_6 also react with usual stopcock lubricants. To minimize reaction, the stopcocks were lubricated with a fluorochlorocarbon light grease supplied by Hooker Electrochemical Company.[7] A suitable grease was prepared by heating small portions of the Hooker fluorocarbon in a glass vacuum oven at 90–110° for 20 minutes to 1 hour, during which time about $^1/_3$ to $^1/_2$ of the sample distilled out, mostly as a clear oil. The consistency of the remaining grease depended on the time of heating and the temperature. The untreated grease always contained a very light fraction so that it was impossible to obtain a suitable vacuum. It was found possible to blend heavy and light treated samples to obtain a grease of the desired characteristics.

Since all heavy metal hexafluorides undergo large volume changes in passing through the melting point, it was necessary to use pear-shaped Pyrex glass bulbs with heavy walls whenever the compounds were frozen out. The Raman cell and the quartz ultraviolet cell were both equipped with pear-bulb reservoirs.

The compounds were handled in a Pyrex glass vacuum line. The Raman cell was isolated from the sample until all purification steps had been completed. Before any hexafluoride was admitted, the glass line was baked out and thoroughly pumped. No hexafluoride was admitted to the line until the total pressure including condensable gases (largely stopcock grease) was between 10^{-4} and 10^{-5} mm., measured with a Phillips type ionization gage.

The glass surface could be made somewhat resistant to attack by HF by baking in the presence of oil vapors from the fluorocarbon stopcock grease.

Since the compounds had been prepared so carefully and initially purified, it was considered necessary only to free them from small amount of oxygen, nitrogen, HF and SiF_4 before use. The procedure consisted of a series of evaporations into a one-liter expansion chamber followed by condensation into the pear-bulb with NaF and pumping out the residual gases. A stopcock above the bulb was closed and the residual pressure measured. The MoF_6 and WF_6 were condensed with a Dry Ice–acetone mixture until the pressure in the chamber was constant and approximately equal to the estimated vapor pressure.[8] After each condensation the compound was allowed to melt and mix intimately with the NaF. The sample was finally transferred to the pear-bulb on the Raman cell and sealed off at a constriction. A sample for ultraviolet work was obtained by the same process.

The WF_6 sample had become contaminated with a small amount of water vapor and was therefor subjected to a preliminary purification to free it from HF and other impurities. This was done by passing the compound several times through a tower containing dry powdered NaF and then into bulbs containing NaF. The pressure of the gas was kept low by freezing baths, but the condensation of HF was avoided since this tended to initiate reaction with glass.

It is felt that both compounds as finally obtained were quite pure. They are both clear, colorless liquids. NaF should combine with all volatile substances likely to result from handling in a glass system: HF, H_2O and SiF_4.[6] A small sample of MoF_6 was distilled into a glass tube without any NaF. Although the tube had been flamed repeatedly, a blue deposit developed in the tube after a day or two, and after little more than a week the hexafluoride had reacted completely. On the other hand, about 3 cc. of this compound which were used for the Raman experiments were kept stored over NaF in glass for almost a year with no apparent reaction. No additional Raman lines appeared during this time.

Raman Spectra.—The excitation was by six vertical AH-11 mercury arcs backed by elliptical reflectors which focused the light on the center of the Raman tube. The Raman tube was exposed to the light through an assembly of concentric chambers which contained the filter solution and cooling water. This equipment was constructed by soldering glass tubes between brass end plates through which connections were made to the chambers. The ends of the glass tubes were platinized and Woods metal used as a solder. This seal held water under considerable pressure and did not react with the filter solution. The upper end of the Raman tube was protected from the heat of the arcs by wrapping it with aluminum foil.

The usual filter was a solution of Rhodamine 5 GDN extra[9] in alcohol (48 mg./l.) which transmits about 75% at 4358 Å. (1 cm. layer). This was frequently used in conjunction with a cylinder of Wratten 2B gelatin filter.[10] The addition of *p*-nitrotoluene as recommended by Edsall and Wilson[11] caused a considerable decrease in the transmission of 4358 Å. by the filter during long exposures. To help bring out lines very close to the exciting line a 6–12 mm. thick layer of filter solution containing 32 mg. of Rhodamine 5 GDN extra and 120 g. of crude praseodymium nitrate per liter of alcohol was used.

The three prism spectrograph used was constructed in this Laboratory and equipped with a 16.5 cm., f/2.8 Zeiss camera lens. The definition at full aperture was excellent. The dispersion was 36.7 Å./mm. at 4358 Å. An exposure time of 2 minutes sufficed to photograph all of the principal lines of CCl_4 with a slit width of 20 μ.

The depolarization ratios were measured using the method of Crawford and Horwitz.[12] The light was collimated by a stack of blackened baffle plates and passed through concentric cylinders of type K Polaroid[13] and a Wratten 2B gelatin filter. The Rhodamine filter solution was circulated through the cell holder by a pump and cooled in a heat exchanger. In these exposures the lamp intensity was monitored by a photomultiplier tube. It was necessary to operate the arcs for over an hour before making these exposures to eliminate drift. Since the intensity of illumination depended so greatly on the sharpness of focus of the arcs, it is felt that even with good voltage and room temperature regulation the depolarization ratios determined with this type of excitation are not more accurate than 25%.

The intensity measurements for the depolarization ratios were made by the usual methods of photographic photometry with Eastman 103a-0 plates, which showed low reciprocity failure under our conditions. Calibrations were made from a series of timed Raman exposures. The high speed of the apparatus made it possible to use maximum exposure times of 16 minutes with a 50 μ slit width. Microphotometer tracings of depolarization exposures of WF_6 made under these conditions are shown in Fig. 1.

Colloidal particles of NaF from the reservoir caused a troublesome high background density. To minimize the amount of NaF carried over, the compound was distilled slowly into the Raman cell just before the exposure.

Ultraviolet Spectra.—The ultraviolet absorption spectra of MoF_6 and WF_6 vapors were obtained with a 40-cm. quartz cell. The pressure of the vapor was adjusted by controlling the temperature of the reservoir with a freezing mush. The pressure range was from 0.15 to 760 mm. The vapor pressures were calculated from the equations given by Ruff and Ascher.[8]

Most of the exposures were taken with a Hilger E.484 quartz spectrograph. The slit width was usually 50 μ. This spectrograph covered the ultraviolet region down to 1850 Å. Several exposures were made also with a one-meter grating in a vacuum spectrograph with the compound in a quartz cell. The windows of this cell limited observations to wave lengths above 1700 Å.

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[6] A. V. Grosse, Atomic Energy Commission Report MDDC-1038, declassified May, 1947.

[7] We are indebted to the Hooker Electrochemical Company and also to Professor Miller of Cornell University for supplying us with several samples of fluorocarbon greases and waxes.

[8] O. Ruff and E. Ascher, *Z. anorg. allgem. Chem.*, **196**, 413 (1931).

[9] We wish to thank the E. I. du Pont Company for a supply of this dye.

[10] The Wratten 2B filter replaces the Wratten 2A which is not as stable.

[11] J. T. Edsall and E. B. Wilson, Jr., *J. Chem. Phys.*, **6**, 124 (1938).

[12] B. L. Crawford, Jr., and W. J. Horwitz, *ibid.*, **15**, 268 (1947).

[13] We are indebted to Dr. C. D. West of the Polaroid Corporation for supplying us with the type K Polaroid. This Polaroid transmits about 33% of normally incident light at 436 mμ. The polarization is substantially complete.

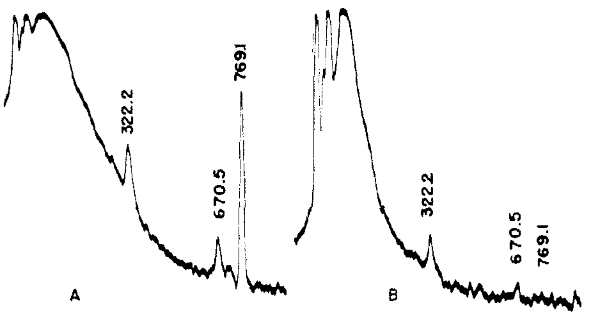

Fig. 1.—Tracings of depolarization exposures of WF_6: A, electric vector perpendicular to the tube axis; B, electric vector parallel to tube axis.

The light source in all cases was a hydrogen discharge tube operated with a current of 150 ma. Eastman III-O ultraviolet sensitized Spectroscopic Plates were used.

The source was photographed through the cell with the compound frozen with liquid nitrogen. Several timed source exposures were made which were used for intensity calibration, and CO band heads and lines from the Schumann–Runge bands were used as wave length standards. To measure wave lengths of the bands observed in the spectrum of MoF_6, an iron or aluminum spark comparison spectrum was used.

Results and Discussion of the Raman Effect

The experimental results are summarized in Table I. The species assignment is made on the basis of 0_h symmetry. The corresponding theoretical depolarization ratios are shown in column two. The experimental frequencies and experimental depolarization ratios are shown in columns three and four, with relative intensities of the lines given in parentheses after the frequency values. The intensity of the A_{1g}: frequency has been taken arbitrarily equal to 10. These frequencies are the result of independent measurements on several different plates. The agreement among the measured values lead us to believe that the accuracy is about 2 cm.$^{-1}$. On very long exposures all of these frequencies were found excited by the weaker mercury line 4347 as well as by 4358 A. Usually these lines could be measured accurately also.

TABLE I

RAMAN FREQUENCIES AND DEPOLARIZATION RATIOS (ρ) OF MoF_6 AND WF_6

Species	$\rho_{Theor.}$	Frequency, (cm.$^{-1}$)	$\rho_{Exptl.}$
		MoF_6	
ν_1A_{1g}	0.00	736 (10)	0.09
ν_2E_g	.87	641 (3)	.94
ν_3F_{2g}	.87	319 (3)	.98
		WF_6	
ν_1A_{1g}	0.00	769 (10)	0.04
ν_2E_g	.87	670 (3)	.76
ν_2F_{2g}	.87	322 (3)	.66

It can be concluded with some assurance by the appearance of only three lines, even with extended exposure times, that a high degree of symmetry exists. Reference to the tables of E. B. Wilson, Jr.,[14] shows that the only other structure consistent with three Raman lines is the regular hexagon (D_{6h}). The latter structure cannot be eliminated without further information, especially the infrared absorption spectrum.

It may be argued that the structure is slightly less symmetrical and that the resulting splitting of the degenerate frequencies of the octahedral model may be unresolved. For example, if the octahedron were compressed along one of its three-fold axes, with a resulting symmetry D_{3d}, the F_{2g} frequency in 0_h splits into one E_g and one $A1_g$ frequency of D_{3d}. If the distortion were small, this splitting might be unresolved. However, the unresolved line should have a totally symmetrical component, and should appear partially polarized. The high depolarization ratios for two lines in MoF_6 makes this situation appear unlikely. The evidence in case of WF_6 is not quite so good, but we believe that the corresponding two lines are actually depolarized to the limit in this case also.

Similar arguments serve to eliminate structures of lower symmetry. *It thus appears that the structure of a regular octahedron is most consistent with Raman effect for these molecules.* The unusual sharpness of ν_1 and its very low depolarization ratio provide additional evidence for this structure.

Information on the infrared absorption spectra would have been helpful in the conclusions on structure. Unfortunately we could not have observed any fundamentals below about 700 cm.$^{-1}$ with equipment available to us, and there is reason to suppose that the two fundamentals active in 0_h symmetry have lower values. Also the chemical reactivity of the compounds would have created additional experimental difficulties which we were not prepared to meet.

The conclusions drawn from electron diffraction data are not in harmony with the conclusions drawn in the present work. Braune and Pinnow[15] favor an orthorhombic symmetry V_h for MoF_6, WF_6 and UF_6, but they mention that the tetragonal octahedron or quadratic bipyramid D_{4h} model will fit their data also, with somewhat less accuracy. The former structure requires three different M–F distances and the latter structure four equal M–F distances and a shorter pair. Due to experimental difficulties these workers were able to obtain diffraction patterns showing only four rings for WF_6 and three for MoF_6. An analysis of their data is difficult for the former and impossible for the latter. However, their results are quite consistent with those obtained for UF_6 for which they were able to measure six maxima.

Bauer[16] has recently reinvestigated the structure of UF_6 by electron diffraction with considerably more accuracy. He concludes definitely that the structure of UF_6 is not octahedral, which is in disagreement with the spectroscopic data.[17]

A normal coördinate treatment of octahedral molecules has been made by Yost, Steffens and Gross[18] on the basis of central forces. These authors also quote a set of frequency formulas derived by E. B. Wilson, Jr., on the basis of "a very restricted type of valence–force potential function

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(14) E. B. Wilson, Jr., *J. Chem. Phys.*, **2**, 432 (1934).

(15) H. Braune and P. Pinnow, *Z. physik. Chem.*, **B25**, 239 (1937).

(16) S. H. Bauer, *J. Chem. Phys.*, **18**, 27 (1950).

(17) J. Bigeleisen, M. G. Mayer, P. C. Stevenson and J. Turkevich, *ibid.*, **16**, 442 (1948).

(18) D. M. Yost, C. C. Steffens and S. T. Gross, *ibid.*, **2**, 311 (1934).

involving only three constants...." We have computed these force constants from the formulas of E. B. Wilson, Jr., using the three observed Raman frequencies. The constants are shown in Table II (with the notation of ref. 18). The two infrared active frequencies may be estimated with two of these constants, and ν_4 is obtained directly from ν_3 from the valence-force formulas. The results are given in Table II.

TABLE II

FORCE CONSTANTS AND CALCULATED INFRARED ACTIVE AND INACTIVE FREQUENCIES OF MoF_6 AND WF_6

Force constant	MoF_6	WF_6
$k_{01} \times 10^{-5}$ (dynes/cm.)	5.087	5.556
p	0.244	0.266
k_φ	0.285	0.290
Frequency (cm.$^{-1}$)		
$\nu_4(F_{2u})$ (inactive)	226	227
$\nu_5(F_{1u})$	619	603
$\nu_6(F_{1u})$	328	296

Results and Discussion of the Ultraviolet Spectra

If WF_6 and MoF_6 actually have an octahedral structure the only allowed transition from the normal state is to a triply degenerate state of symmetry F_{1u}. It is to be expected that such a transition leads to a continuous or almost continuous spectrum.[4]

The absorption spectrum of MoF_6 appears to be continuous at 532 mm. pressure and extends from about 2815 Å. into the ultraviolet. However, on careful adjustment of the pressure to a value between 0.35 and 0.15 mm. a series of diffuse bands appeared which are shown in Fig. 2. The Schumann–Runge bands of oxygen are superimposed (positions of heads shown by × in Fig. 2) but do not obscure the bands assigned to MoF_6. Two bands at 1871 Å. and 2018 Å. are not shown on this figure. The average separation is 639 cm.$^{-1}$. This probably represents the totally symmetrical A_{1g} vibration in the excited state which would correspond to the 736 cm.$^{-1}$ frequency in the ground state. The lower value of this frequency appears to indicate a larger metal–fluorine distance in the excited state and weaker bonding. It was not possible to find exactly the high frequency end of the absorption band, and so the integrated absorption coefficient could not be determined. However, an attempt to approximate this coefficient was made.

The method used was to determine the absorption coefficient α[19] at the long wave length edge and to approximate the entire band by a symmetrical triangle. The absorption coefficients determined are shown in Table III. At pressures of 2.5 mm. and above the spectrum had a sharp red edge. The wave lengths corresponding to a transmission of 10%, or $\log I_0/I = 1$ were estimated visually for these pressures. At lower pressures and shorter wave lengths it was possible to obtain more reliable values for the absorption coefficients by photographic photometry.

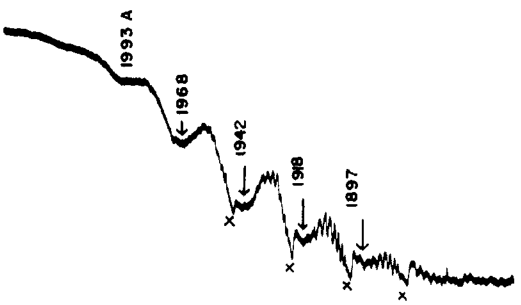

Fig. 2.—Ultraviolet absorption bands of MoF_6: crosses (×) indicate heads of O_2 bands.

TABLE III

ABSORPTION COEFFICIENTS FOR WF_6 AND MoF_6

Vapor pressure, mm.	α	Cm.$^{-1}$
	WF_6	
769	0.06	44643 (2240 Å.)
363	.13	45249
72.3	.65	46296
4.82	9.0	50505
0.60	9.4	51970
.60	14.6	52562
.60	23.2	53124 (1882 Å.)
	MoF_6	
532	0.09	35524 (2815 Å.)
7.06	6.8	41494
2.51	19	43290
0.34	57.6	48356
.34	61.4	48852
.34	68.4	49358
.34	82.6	49702
.34	127	50226
.34	176	50761 (1970 Å.)

Assuming a vibrational quantum of 639 cm.$^{-1}$, band widths of 12, 15 and 18 quanta were considered. The band centers estimated in this way are: 52684 cm.$^{-1}$ (1898 Å.), 53592 cm.$^{-1}$ (1866 Å.), and 54551 cm.$^{-1}$ (1833 Å.). The f numbers calculated for these band widths are, respectively, 0.056, 0.086 and 0.124. There is some reason to believe that the latter is more correct and that the ultraviolet band edge is near 1600 Å. An f number of this magnitude indicates an allowed transition.

The ultraviolet spectrum of WF_6 is similar to that of MoF_6 except that it is shifted about 100 Å. toward the ultraviolet. No structure was found. It is possible that similar bands exist at shorter wave lengths. No attempt was made to estimate an integrated absorption coefficient for WF_6 since the measurements were insufficient to determine the shape of the long wave length portion of the absorption curve.

ROCHESTER, N. Y.

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[19] This coefficient is defined by $\ln I/I_0 = \alpha l_0$ where l_0 is the path length in cm. at 0° and 76 cm. pressure, and I/I_0 is the fraction of light transmitted.