

Electronic spectroscopy of UF_6 and WF_6 by electron impact^{a)}

Ronald Rianda,^{b)} Robert P. Frueholz, and Aron Kuppermann

Arthur Amos Noyes Laboratory of Chemical Physics, ^{c)} California Institute of Technology, Pasadena, California 91125

(Received 21 March 1978)

The electron-impact excitation spectra of uranium hexafluoride (UF_6) and tungsten hexafluoride (WF_6) have been studied experimentally at impact energies of 30, 50, and 75 eV and at scattering angles from 5° to 80° . Eleven features in UF_6 are observed with maxima at 3.26, 4.2, ~ 4.7 , 5.8, 7.0, 7.86, 9.26, 11.01, 11.75, 12.5, and 13.2 eV. Four features in WF_6 are observed with maximum intensity at 7.25, 7.9, 8.5, and 9.85, in good agreement with optical work. In addition, three previously unobserved features in WF_6 at 11.75, 12.6, and 13.5 eV are reported. Similarity between the spectra of UF_6 and WF_6 suggests that the primary contribution to the absorption intensity in UF_6 above 5.8 eV and in WF_6 results from charge transfer transitions from fluorine p orbitals to metal d orbitals. Tentative assignments based in part on recent theoretical studies are made.

I. INTRODUCTION

A potential uranium isotope separation scheme involves isotopically specific vibrational excitation of the ν_3 mode of $^{235}\text{UF}_6$ followed by the electronic excitation of the vibrationally excited species by one or two ultraviolet photons to a dissociative or predissociative state. In order to determine the positions and nature of the electronically excited states, which might prove important to such a scheme, the electron-impact spectrum of UF_6 has been studied. As an aid to assignment of the spectrum of UF_6 , the electron-impact spectrum of WF_6 has also been determined.

In previous studies the technique of low-energy variable-angle electron-impact spectroscopy has been primarily applied to molecules composed of light nuclei (first- and second-row elements) with principal emphasis on the detection of spin-forbidden transitions.¹⁻⁴ In these systems the differential cross section (DCS) as a function of angle is a sensitive probe of the spin forbiddenness or allowedness of a transition. Typically, the DCS for an optically allowed transition decreases by approximately two orders of magnitude as the scattering angle is increased from 10° to 80° . In contrast, the DCS for a spin-forbidden excitation (one in which the spin quantum number changes by unity) remains relatively constant, within a factor of 2 or 3, over a similar angular range. Electron impact spectroscopy is also suitable for studying molecules containing heavy nuclei⁵⁻⁷ such as UF_6 and WF_6 , but in these systems spin-orbit coupling may be significant. The resultant mixing of states of different spin multiplicities causes the correlation between the angular behavior of the DCS and the spin nature of the transition to become less clear.⁵

Both UF_6 and WF_6 possess O_h symmetry.⁸ From the viewpoint of ligand field theory the valence electrons of

the central metal atom (the $5f$, $6d$, and $7s$ electrons of uranium and the $5d$ and $6s$ electrons of tungsten) are assumed to be transferred to the fluorine atoms yielding a complex of the form $\text{M}^{6+}\text{F}_6^{8-}$. This is a crude approximation which nevertheless is helpful in explaining the observed spectra. In this model, transitions correspond to charge transfer from ligand fluorine atom orbitals to the $5f$, $6d$, and $7s$ orbitals of uranium and the $5d$ and $6s$ orbitals of tungsten.

Previous theoretical studies of UF_6 have considered only transitions from ligand orbitals to uranium $5f$ orbitals and therefore assignment of only the low energy portion of the spectrum was attempted.⁹⁻¹¹ The most reliable calculation to date is that of Koelling, Ellis, and Bartlett¹¹ using the relativistic, self-consistent, Dirac-Slater model. They have obtained one-electron energy levels, charge distributions, ligand-to-uranium $5f$ orbital transition energies, and ionization potentials which agree well with experiment. Figure 1 shows the orbital energy diagram obtained for UF_6 based in part on their calculations. There have been no theoretical studies of the electronic structure of WF_6 to date.

Prior to our investigation numerous optical absorption studies of UF_6 in the region below 6 eV have been performed.¹²⁻¹⁶ Agreement between these previous experimental results and the theoretical calculations is fair. However, considering the density of predicted transitions, any apparent agreement may be fortuitous. McDiarmid has performed the only optical studies of UF_6 and WF_6 above 6 eV.^{17,18} In addition to the optical work, previous electron-impact studies of UF_6 have been performed by Chutjian *et al.*⁶ and Srivastava *et al.*⁷ from which photoabsorption cross sections were obtained. Attempts at interpreting the observed spectra were limited.

II. EXPERIMENTAL

The electron-impact spectrometer used in this study was that reported by Kuppermann *et al.*¹ with the surfaces of all electron optical elements having been gold-plated. With unplated surfaces (oxygen-free, high-puri-

^{a)}This work was supported by the Department of Energy (Contract No. EX-76-G-03-1305).

^{b)}Work completed in partial fulfillment of the requirements for the PhD in chemistry at the California Institute of Technology.

^{c)}Contribution No. 5753.

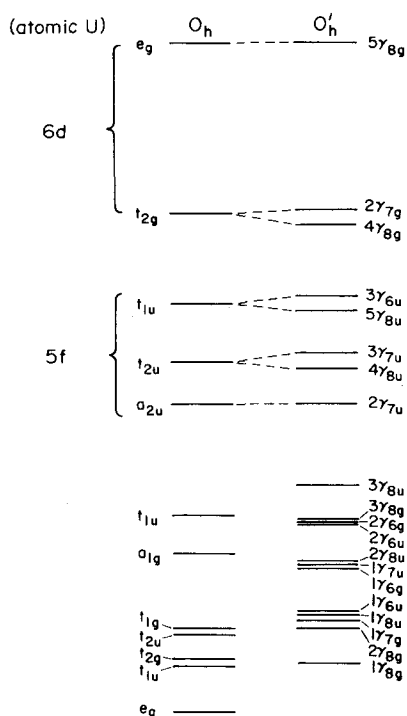


FIG. 1. Valence orbital energy ordering for UF_6 . Symmetry designations listed under O_h are those appropriate for the octahedral point group, while those beneath O_h' are appropriate for the octahedral double point group. The $5\gamma_{8g}$ is about 13.2 eV above the $1\gamma_{8u}$. The location of the others is approximate. The levels $3\gamma_{8u}$ and below represent fully occupied valence orbitals involved in the U-F bonding.

ty copper lenses and hemispherical analyzers and molybdenum apertures) operation of the instrument was limited to periods of 1 to 2 h before complete disassembly and cleaning of the electron optics was required, due to the reactivity of the hexafluorides. After gold-plating, continuous operation for periods up to one week was possible.

Spectra of UF_6 and WF_6 in the energy-loss region 0–18 eV were taken at impact energies of 30, 50, and 75 eV at scattering angles from 5° to 80° . The sample chamber pressure was typically 2 mTorr as indicated by an uncalibrated Schulz-Phelps ionization gauge, while the incident electron beam current was approximately 40 nA. Instrumental resolution was electron-optimally set at approximately 0.18 eV. Accumulation times for typical spectra ranged from 3 h for a 10° spectrum to about 12 h for an 80° spectrum. This corresponds to a 10 meV channel width accumulation time of between 10 sec and 40 sec. Spectra presented in Figs. 2–5 were digitally smoothed using an 11 to 19 channel least-squares cubic polynomial convolution. Before smoothing, typical signal-to-noise ranged from about 3:1 on weak features in high-angle spectra to approximately 100:1 for strong features in low-angle spectra.

The UF_6 was supplied by Varlacoid Chemical Co.¹⁹ with a stated purity of 99.9%. The WF_6 was obtained from PCR Inc.²⁰ with a stated purity of 99%. Both samples were used without further purification.

III. RESULTS

Figures 2 and 3 show the electron-impact spectrum of UF_6 and WF_6 at an impact energy of 50 eV and scattering angles of 10° and 70° . The higher energy-loss regions of both UF_6 and WF_6 are shown in greater detail at 75 eV impact energy in Figs. 4 and 5. The ratios of DCS's of several features in the spectrum of UF_6 at 50 eV to the DCS of the 5.8 eV feature are shown in Fig. 6. Similarly, for WF_6 , DCS ratios with respect to the 8.5 eV feature are shown in Fig. 7.

The most significant changes with angle in the spectra of UF_6 occur in the 3–5 eV region and at the 11.01 eV feature. At an impact energy of 50 eV the integrated intensity under the 3.26 eV feature increases by about an order of magnitude relative to that under the feature at 5.8 eV as the scattering angle is increased from 10° to 80° . The major portion of this change occurs between scattering angles of 10° and 20° . Chutjian *et al.*⁶ found a change in this ratio by a factor of about 3.5 in going from 20° to 135° , at an impact energy of 20 eV. There is no inconsistency between these two observations. For molecules with light nuclei, such behavior would be consistent with three possible interpretations: (a) this feature is due to a spin-forbidden transition;

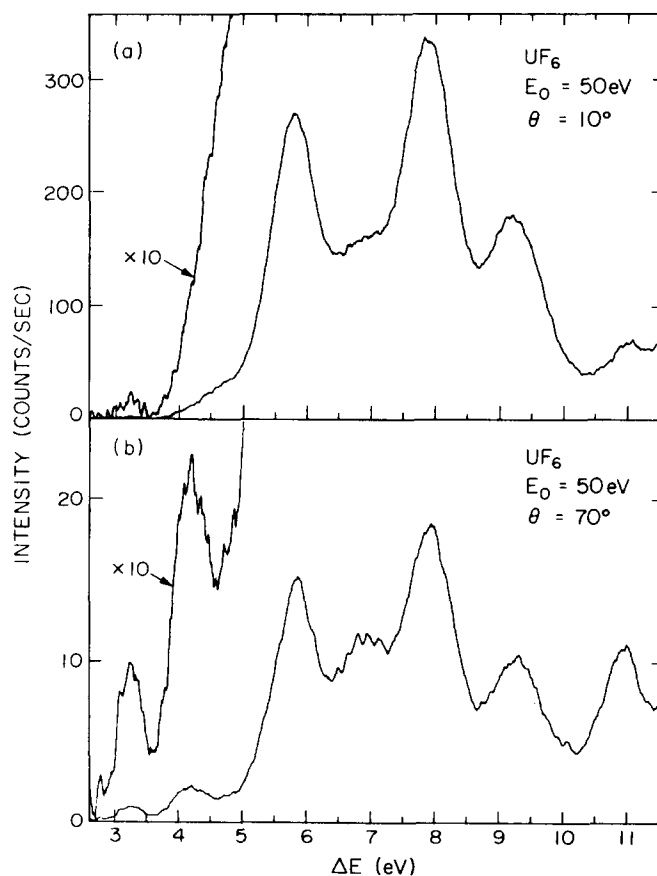


FIG. 2. Electron energy loss spectrum of UF_6 at (a) 10° and (b) 70° ; 50 eV incident electron energy; 4×10^{-8} A incident beam current; 2 mTorr sample pressure reading from an uncalibrated Schulz-Phelps gauge; resolution approximately 0.18 eV (fwhm).

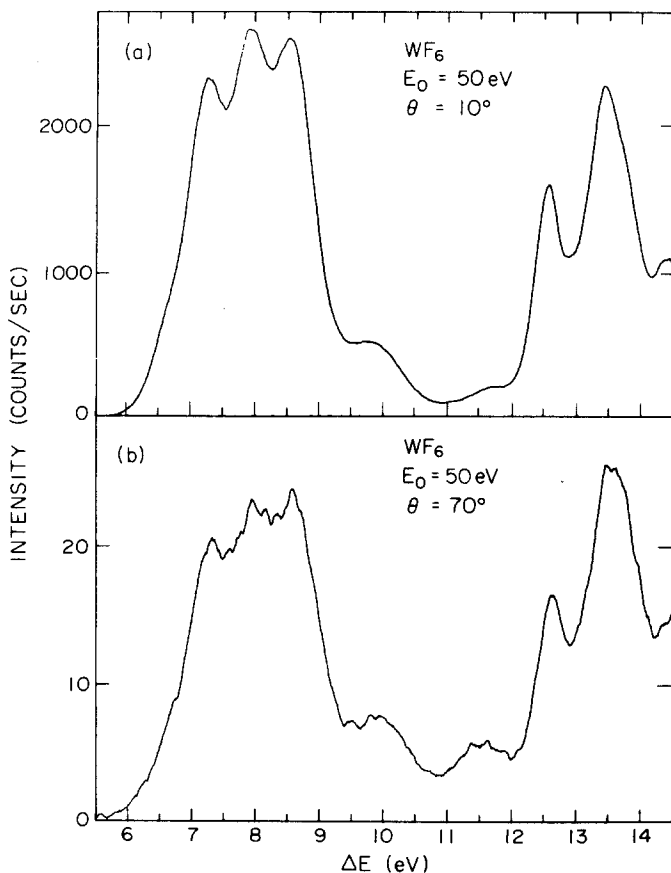


FIG. 3. Electron energy loss spectrum of WF_6 at (a) 10° and (b) 70° ; 50 eV incident electron energy; 7×10^{-8} A incident beam current; 1 mTorr sample pressure reading from an uncalibrated Schulz-Phelps gauge; resolution approximately 0.18 eV (fwhm). No absorption is observed for ΔE below 5.5 eV.

(b) it is due to a spin-allowed but symmetry-forbidden transition; and (c) it results from a spin-allowed transition with an underlying spin-forbidden transition, a possibility that would have been considered to be the most likely.

However, the relationship of the variation of the DCS

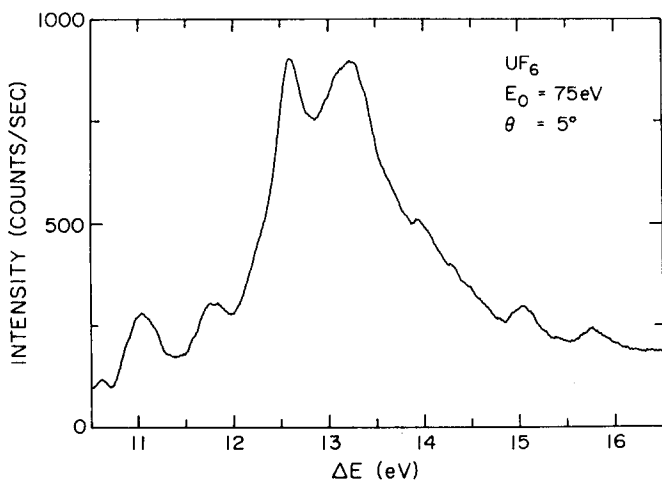


FIG. 4. Electron energy loss spectrum of UF_6 at 5° ; 75 eV incident electron energy; other experimental parameters are similar to those in Fig. 2.

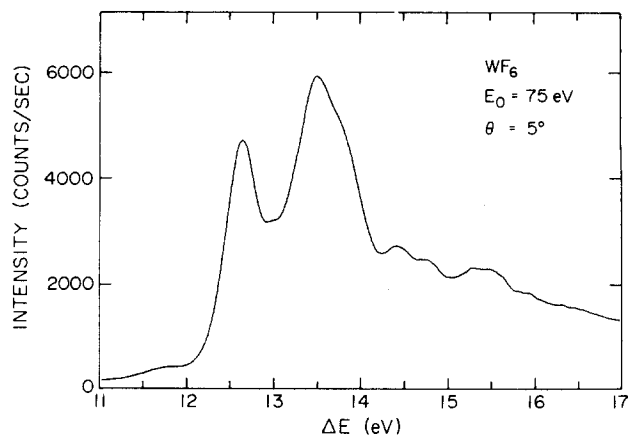


FIG. 5. Electron energy loss spectrum of WF_6 at 5° ; 75 eV incident electron energy; other experimental parameters are similar to those in Fig. 3.

with scattering angle and the spin allowedness of a transition is ambiguous for molecules such as UF_6 and WF_6 which contain heavy nuclei. In these systems the "goodness" of the orbital and spin angular momentum quantum numbers L and S is questionable. Both theoretical and experimental information regarding the spin-orbit interaction as applied to the spin nature of the wavefunc-

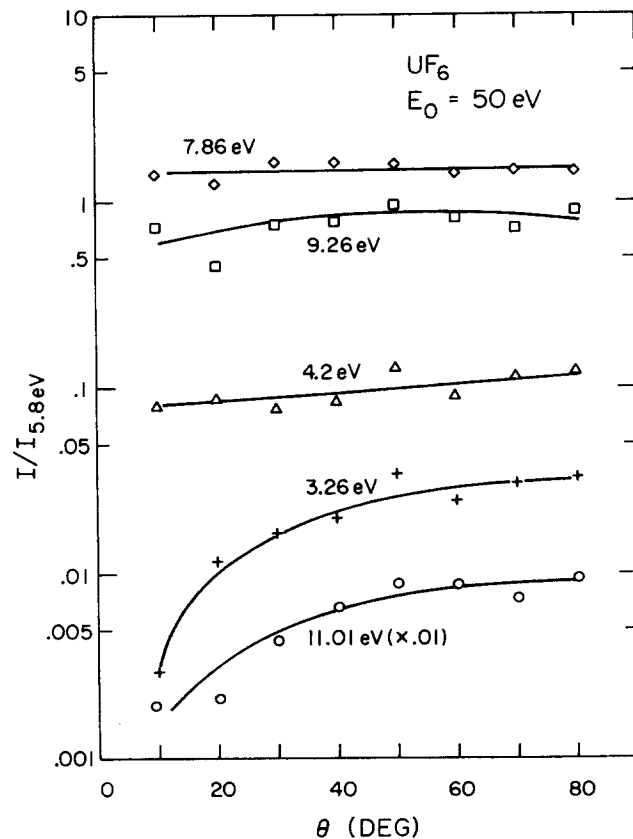


FIG. 6. Integrated intensities of several electronic transitions in UF_6 divided by the integrated intensity of the 5.8 eV feature as a function of scattering angle θ at an incident electron energy of 50 eV; the transition energies for each of the curves are indicated. The intensity ratio for the 11.01 eV transition was multiplied by 0.01 before plotting.

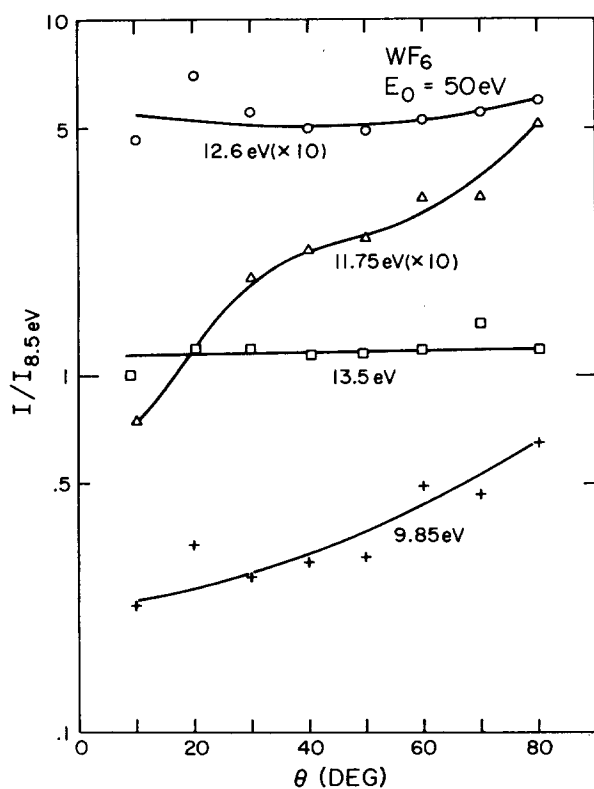


FIG. 7. Integrated intensities of several electronic transitions in WF₆ divided by the integrated intensity of the 8.5 eV feature as a function of θ at an incident electron energy of 50 eV; the transition energies for each of the curves are indicated. The scale factors in parentheses indicate the coefficients by which the intensity ratios were multiplied before being plotted.

tion is lacking. Similarly, attempts at correlating the electron impact DCS with the magnitude of the spin-orbit interaction have been limited to a study of Xe by Williams, Trajmar, and Kuppermann.⁵ The results of this study indicate that for atoms with significant spin-orbit interactions, DCS variations with angle may no longer be used with reliability to assign the spin nature of a transition. In molecular systems containing a heavy central atom in a strong ligand field provided by surrounding atoms, the influence of that field on the central atom orbitals may predominate over the spin-orbit interaction.²¹⁻²³ However, the implication of this effect on DCS variations is unknown.

In the 4–5 eV region the low-angle spectrum shows an unresolved feature with an apparent (deconvoluted) intensity maximum at approximately 4.7 eV, while the high-angle spectrum shows a feature with a distinct maximum at 4.2 eV. This observed shift in position indicates the overlap of at least two electronic transitions. In the previous electron-impact study of UF₆,⁶ these features were also observed at 4.2 and 4.8 eV. The former was attributed to an optically forbidden transition and the latter to a weak dipole-allowed transition. However, Koelling *et al.*,¹¹ on the basis of the relativistic SCF $X\alpha$ calculations, assign both as dipole-allowed transitions. Optically, a feature is observed at 4.77 eV as well as two much weaker transitions at 4.13 and 3.87 eV.¹⁵ The intensity under the 11.01 eV feature in-

creases by a factor of 5 relative to that under the 5.8 eV one as the scattering angle is increased from 10° to 80°. This increase is significant and will be used in discussing the assignment of the 11.01 eV transition in Sec. IV.

In the spectrum of WF₆ there is no detectable absorption below 5.5 eV. The only significant change with angle in the spectrum of this molecule occurs at 11.75 eV. The integrated intensity under this feature increases by a factor of about 7 relative to that under the 8.5 eV one as the scattering angle is increased from 10° to 80°.

The similarities between the spectra of UF₆ and WF₆ are quite apparent from comparison of Figs. 2–5. In addition to the absence of the low-lying absorptions in WF₆, the principal difference is that the WF₆ spectrum is shifted to higher energy by about 1 eV with respect to the UF₆ spectrum. Table I summarizes our results for UF₆ and WF₆, respectively.

V. DISCUSSION

In order to assign the bands in the UF₆ spectrum it is worthwhile to make use of the similarities between it and the WF₆ spectrum. Since WF₆ does not possess low-lying unoccupied *f* valence orbitals, we believe all transitions observed below 14 eV in this molecule correspond to a valence charge transfer from fluorine ligand σ and π orbitals to tungsten 5*d* orbitals. The possibility exists that features observed in the region of the spectrum above approximately 10 eV are due to Rydberg excitations. We do not think this to be a correct assignment for the features at 12.6 and 13.5 eV for the following reason. The intensities of these transitions are

TABLE I. Energy-loss features in UF₆ and WF₆.^{a, b}

Transition	UF ₆	WF ₆
$3\gamma_{8u} \rightarrow 2\gamma_{7u}, 4\gamma_{8u}, 3\gamma_{7u}$	3.26	
$3\gamma_{8g} \rightarrow 2\gamma_{7u}$	4.2	
$3\gamma_{8g} \rightarrow 4\gamma_{8u}$	~4.7	
$3\gamma_{8u} \rightarrow 4\gamma_{8g}, 2\gamma_{7g}$	5.8 ^c	7.25
$2\gamma_{6u} \rightarrow 4\gamma_{8g}, 2\gamma_{7g}$	7.0 ^c	7.9
$2\gamma_{8u}, 1\gamma_{7u} \rightarrow 4\gamma_{8g}, 2\gamma_{7g}$	7.86 ^c	8.5
	9.26	9.85
	11.01	
	11.75	11.75
$2\gamma_{8u}, 1\gamma_{7u} \rightarrow 5\gamma_{8g}$	12.5	12.6
$1\gamma_{6u}, 1\gamma_{8u} \rightarrow 5\gamma_{8g}$	13.2	13.5

^aThe energy losses are in eV and have an accuracy of ± 0.05 eV.

^bThe assignments in this table are based in part on the calculations of Ref. 11; the energy losses are those of the present experiments.

^cThere may also be contribution to these features from ligand-to-5*f* transitions.

significantly greater than would be expected for Rydberg excitations. The oscillator strength for the transition at 13.5 eV in WF₆ may be estimated in the following manner. The generalized electron-impact oscillator strength,²⁴ f_{e1} , is given by

$$f_{e1} = \frac{W}{2} \frac{k_0}{k_n} K^2 \sigma,$$

where W is the excitation energy, k_0 and k_n are the incident and scattered electron momenta, respectively, K is the change in momentum suffered by the electron as a result of the collision, and σ is the differential cross section for the transition being considered. Since we have not obtained absolute DCS's we are only able to estimate ratios of f_{e1} . Lassetre *et al.*²⁴ have shown that as K^2 approaches zero, f_{e1} approaches the optical oscillator strength f_{opt} . From the optical data of McDiarmid¹⁷ we estimate f_{opt} of the 8.5 eV feature to be 0.3.²⁵ Using our 50 eV incident energy spectra, and extrapolating the f_{e1} vs K^2 curve monotonically to $K^2=0$, we obtained an unnormalized f_{opt} for the 8.5 eV transition.²⁶ Since this must correspond to the value of f_{opt} (absolute) obtained from the data of Ref. 17, we are able to calculate the normalization factor which makes our measurements absolute. This factor is independent of the transition being considered and is hence the same for the 13.5 eV feature. The resulting absolute value of f_{opt} for this transition (obtained from a similar extrapolation²⁶ to $K^2=0$ of the corresponding f_{e1}) is about 0.8, which is roughly 3 times greater than the maximum oscillator strength expected for a Rydberg excitation.²⁷ The transition at 11.75 eV in WF₆ is significantly weaker than that at 13.5 eV, making differentiation between valence or Rydberg states unclear.

The similarity of the UF₆ spectrum above 5 eV energy loss to that of WF₆ suggests that the primary contribution to the spectrum in this region is also due to transitions from fluorine ligand σ and π orbitals to uranium 6d orbitals, although the apparently increased intensity of the features at 5.8 and 7.86 eV in UF₆ relative to the corresponding features in WF₆ may indicate an additional contribution in UF₆ from ligand-to-5f orbital excitations.

Use of the orbital energy ordering for UF₆ as well as excitation energies calculated by Koelling *et al.*¹¹ (orbital energy diagram shown in Fig. 1) allows a more specific assignment of some of the transitions. Orbital designations are those appropriate for the O_h double group²⁸ required by the spin-orbit interactions in these systems. Since no electronic structure calculations have been reported for WF₆, we assume in our analysis that the orbital ordering in that molecule is the same as for the corresponding orbitals in UF₆. Transitions below 5.8 eV in UF₆ have been assigned by Koelling *et al.* as ligand to 5f orbital excitations.¹¹ These assignments are consistent with our results and are summarized in Table I. The 5.8 eV feature in UF₆ has been assigned as a ligand-to-5f transition for which the calculated excitation energy is 6.31 eV. However, comparison with our WF₆ results indicates that a significant fraction of the intensity of this feature is due to excitation to the uranium 6d($4\gamma_{8g}$, $2\gamma_{7g}$) orbitals (see Fig. 1). Therefore,

the most reasonable explanation would be that this UF₆ feature results from a superposition of at least the $3\gamma_{8g} \rightarrow 5\gamma_{8u}$ and $3\gamma_{8u} \rightarrow 4\gamma_{8g}$, $2\gamma_{7g}$ one-electron excitations. Analogously, the 7.25 eV feature in WF₆ is assigned to the $3\gamma_{8u} \rightarrow 4\gamma_{8g}$, $2\gamma_{7g}$ transitions. The next two excitations in UF₆ at 7.0 and 7.86 and in WF₆ at 7.9 and 8.5 eV are assigned as the $2\gamma_{6u} \rightarrow 4\gamma_{8g}$, $2\gamma_{7g}$ and $2\gamma_{8u}$, $1\gamma_{7u} \rightarrow 4\gamma_{8g}$, $2\gamma_{7g}$ one-electron transitions, respectively. In the ligand field theory approach, using O_h symmetry, among the most intense transitions is expected to be the transition from the fluorine $p\sigma(t_{2u})$ orbital to the metal e_g orbital (from spatial overlap considerations). Therefore we assign the intense features at 13.5 eV in WF₆ and 13.2 eV in UF₆ as the $1\gamma_{6u}$, $1\gamma_{8u} \rightarrow 5\gamma_{8g}$ transitions. In UF₆ the nearly degenerate $1\gamma_{7u}$ and $2\gamma_{8u}$ orbitals are calculated to lie approximately 0.6 eV higher in energy than the $1\gamma_{6u}$ and $1\gamma_{8u}$ orbitals. Excitation from these orbitals is allowed and is expected to be about 0.6 eV below the $1\gamma_{6u}$, $1\gamma_{8u} \rightarrow 5\gamma_{8g}$ transition. Therefore we tentatively assign the 12.5 eV feature in UF₆ and the 12.6 eV feature in WF₆ to the $1\gamma_{7u}$, $2\gamma_{8u} \rightarrow 5\gamma_{8g}$ excitations. The angular behavior of the features at 3.26 and 11.01 eV in UF₆ and at 11.75 eV in WF₆ is distinctly different from that of the other features in the spectra. Figure 6 displays the ratios of integrated intensities of some bands of UF₆ relative to the 5.8 eV feature. Figure 7 shows the corresponding ratios for features of WF₆ relative to the integrated intensity of the 8.5 eV band. The ratios demonstrate that the features at 3.26 and 11.01 eV in UF₆ and at 11.75 eV in WF₆ display a significant increase in relative intensity as the scattering angle is increased. While the concept of singlet and triplet states is not well defined for these molecules (see Sec. I), this angular behavior is very similar to that displayed by transitions which have been definitively assigned as singlet-triplet in systems containing only light nuclei.¹⁻⁴ A possible explanation for the angular behavior of the 11.01 eV feature in UF₆ and the 11.75 eV feature in WF₆ is that these transitions contain significant singlet-triplet contributions. It is possible that the ligand-field interaction is sufficiently strong to predominate over the spin-orbit interaction yielding states which are either primarily singlet or primarily triplet in nature.²¹⁻²³ In addition to the feature at 11.01 eV in UF₆ there is also a transition at 11.75 eV which appears to display similar angular behavior, suggesting that it too may be due to a singlet-triplet transition. Unfortunately, this transition is heavily overlapped with the 12.5 eV feature and reliable integrated intensity ratios were not obtainable.

The feature at 3.26 eV in UF₆ has been previously assigned to overlapping singlet-singlet and singlet-triplet transitions.¹⁶ This transition is presumably due exclusively to a ligand-to-uranium 5f orbital excitation, and consequently care must be taken when attempting to assign it using an *LS* coupling scheme. This is due to the fact that the ligand field interaction for the 5f orbitals is significantly weaker than that for the 6d orbitals and is expected to be of the same order as the spin-orbit interaction, weakening the argument in behalf of an *LS* coupling scheme.²¹⁻²³

Three additional optically allowed excitations, $1\gamma_{6u} - 1\gamma_{8u} - 4\gamma_{8g}$, $2\gamma_{7g}$, $3\gamma_{8u} - 5\gamma_{8g}$ and $2\gamma_{6u} - 5\gamma_{8g}$ are predicted by the ordering scheme of Fig. 1. They may lie in the 8–11 eV region where only one feature is apparent in our spectra: the 9.26 eV feature in UF₆ and the 9.85 eV feature in WF₆. Several higher lying transitions are also observed in both WF₆ and UF₆ above 14 eV which we tentatively assign as Rydberg excitations.

VI. CONCLUSIONS AND SUMMARY

We have obtained electron-impact spectra of UF₆ and WF₆ at several different impact energies and scattering angles from 5° to 80°. Our measurements for UF₆ are in good agreement with previous ones. For WF₆ the results of our experiments are also in good agreement with previous limited optical studies. We have reported several previously unobserved transitions at higher energy losses. Assignments of the spectra of both UF₆ and WF₆ are proposed using the theoretical results of Koelling *et al.*¹¹ and relying heavily upon similarities in the UF₆ and WF₆ spectra. Below 14 eV we assign all transitions in WF₆ as ligand-to-tungsten 5*d* orbital charge transfer excitations, with the exception of the feature at 11.75 eV, the possible Rydberg nature of which cannot be excluded. The spectrum of UF₆ between 5 and 14 eV is very similar to that of WF₆, and the primary contribution to this region is similarly assigned to ligand-to-uranium 6*d* orbital excitations. Correspondingly, transitions in UF₆ below 5 eV are assigned exclusively to ligand-to-5*f* excitations.

ACKNOWLEDGMENT

The authors express their appreciation to Professor H. B. Gray for useful discussions.

¹(a) A. Kuppermann, J. K. Rice, and S. Trajmar, *J. Phys. Chem.* **72**, 3894 (1965); (b) J. K. Rice, Ph.D. thesis, California Institute of Technology, Pasadena, CA, 1969.

²S. Trajmar, J. K. Rice, and A. Kuppermann, *Adv. Chem. Phys.* **78**, 15 (1970).

³(a) O. A. Mosher, W. M. Flicker, and A. Kuppermann, *J. Chem. Phys.* **59**, 6502 (1973); (b) O. A. Mosher, W. M.

Flicker, and A. Kuppermann, *J. Chem. Phys.* **62**, 2600 (1975).

⁴R. P. Frueholz, W. M. Flicker, O. A. Mosher, and A. Kuppermann, *Chem. Phys. Lett.* **52**, 86 (1977).

⁵W. Williams, S. Trajmar, and A. Kuppermann, *J. Chem. Phys.* **62**, 3031 (1975).

⁶A. Chutjian, S. K. Srivastava, S. Trajmar, W. Williams, and D. C. Cartwright, *J. Chem. Phys.* **64**, 4791 (1976).

⁷S. K. Srivastava, D. C. Cartwright, S. Trajmar, A. Chutjian, and W. X. Williams, *J. Chem. Phys.* **65**, 208 (1976).

⁸R. S. McDowell, L. B. Aspree, and R. T. Paine, *J. Chem. Phys.* **61**, 3571 (1974).

⁹D. H. Maylotte, R. L. St. Peters, and R. P. Messmer, *Chem. Phys. Lett.* **39**, 181 (1976).

¹⁰M. Boring and J. W. Moskowitz, *Chem. Phys. Lett.* **38**, 185 (1976).

¹¹D. D. Koelling, D. E. Ellis, and R. J. Bartlett, *J. Chem. Phys.* **65**, 3331 (1976).

¹²G. H. Dieke and A. B. F. Duncan, *Spectroscopic Properties of Uranium Compounds* (McGraw-Hill, New York, 1949).

¹³G. P. Sheretmet'ev, *Opt. Spektrosk.* **1**, 181 (1956).

¹⁴H. J. Hurst and P. W. Wilson, *Spectr. Lett.* **5**, 275 (1972).

¹⁵G. L. De Poorter and C. K. Rofer-De Poorter, *Spectr. Lett.* **8**, 521 (1975).

¹⁶W. B. Lewis, L. B. Aspree, L. H. Jones, R. S. McDowell, S. W. Rabideau, A. H. Zeltmann, and R. T. Paine, *J. Chem. Phys.* **66**, 2707 (1976).

¹⁷R. McDiarmid, *J. Chem. Phys.* **65**, 168 (1976).

¹⁸R. McDiarmid, *J. Chem. Phys.* **61**, 3333 (1974).

¹⁹Varlacoid Chemical Co., 666 S. Front St., Elizabeth, NJ 07202.

²⁰PCR Inc., Research Chemicals Division, P.O. Box 1466, Gainesville, FL 32602.

²¹W. Moffitt, G. L. Goodman, M. Fred, and B. Weinstock, *Mol. Phys.* **2**, 109 (1959).

²²N. J. Reisfeld and G. A. Crosby, *Inorg. Chem.* **4**, 65 (1965).

²³G. C. Allen and K. D. Warren, *Coord. Chem. Rev.* **16**, 227 (1975).

²⁴E. N. Lassetre, A. Skerbele, and N. A. Dillon, *J. Chem. Phys.* **50**, 1829 (1969).

²⁵Value of f_{opt} obtained using data of Ref. 17 and a path length of 10 cm (personal communication, R. McDiarmid).

²⁶The values of K^2 ranged from about 0.15 to about 2.4, over which range the unnormalized f_{el} increased by a factor of only about 2.1 for the 8.5 eV transition and about 1.6 for the 13.5 eV feature. Therefore, the extrapolations to $K^2 = 0$, although approximate, should be adequate²⁴ for the present purposes.

²⁷M. B. Robin, *Higher Excited States of Polyatomic Molecules* (Academic, New York, 1974), Vol. I, p. 30.

²⁸N. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill, New York, 1964), pp. 75–80.