

## Two photon spectroscopy of UF<sub>6</sub> in the near ultraviolet

E. R. Bernstein and P. M. Kennedy

Citation: *The Journal of Chemical Physics* **74**, 2143 (1981); doi: 10.1063/1.441372

View online: <http://dx.doi.org/10.1063/1.441372>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/74/4?ver=pdfcov>

Published by the AIP Publishing

---

### Articles you may be interested in

Photoelectron spectroscopy and theoretical studies of UF<sub>5</sub> – and UF<sub>6</sub> –

*J. Chem. Phys.* **136**, 194304 (2012); 10.1063/1.4716182

Twofrequency multiphoton absorption in UF<sub>6</sub>

*J. Appl. Phys.* **54**, 2827 (1983); 10.1063/1.332316

Ultravioletlaser induced fluorescence of UF<sub>6</sub> isolated in argon matrices

*J. Chem. Phys.* **68**, 4540 (1978); 10.1063/1.435558

Polyhalide photofragment spectra. II. Ultraviolet photodissociation dynamics of UF<sub>6</sub>

*J. Chem. Phys.* **68**, 4195 (1978); 10.1063/1.436283

Vibrational spectroscopy of matrixisolated UF<sub>6</sub> and UF<sub>5</sub>

*J. Chem. Phys.* **64**, 3081 (1976); 10.1063/1.432574

---



# Two photon spectroscopy of $\text{UF}_6$ in the near ultraviolet<sup>a)</sup>

E. R. Bernstein and P. M. Kennedy

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523  
(Received 29 August 1980; accepted 7 November 1980)

The two photon excited fluorescence excitation spectrum of  $\text{UF}_6$  has been observed in the region 410 to 315 nm. The spectrum is virtually indistinguishable from the one photon absorption in this region. No vibronic structure was observed in absorption or dispersed emission. These data indicate a high density of  $u$  and  $g$  states for  $\text{UF}_6$  in this energy range and facile photochemical decomposition. Emission intensity is found to be proportional to laser power to the 3.0 to 3.6 power.

## I. INTRODUCTION

Uranium hexafluoride has been the subject of intense spectroscopic investigation for the past 40 years.<sup>1-9</sup> The one photon gas phase absorption spectrum exhibits only broad charge transfer bands with maxima at 214, 260, and 368 nm. To a first approximation, these bands may be considered as resulting from an electron being promoted from a fluorine  $2p$  orbital to a uranium  $5f$  orbital. Lewis and co-workers<sup>4</sup> have published a more detailed band assignment which takes into account the strong spin-orbit coupling in  $\text{UF}_6$ . In their scheme, the uppermost filled molecular orbital (primarily a ligand  $t_{1u}$  orbital) transforms as  $\Gamma_{8u}$ , and the five lowest (primarily metal) unfilled orbitals transform as  $\Gamma_{7u}$ ,  $\Gamma_{8u}$ ,  $\Gamma_{7u}$ ,  $\Gamma_{8u}$ , and  $\Gamma_{6u}$  in order of increasing energy. Thus, the 260 and 368 nm bands are assigned to electric dipole forbidden, magnetic dipole allowed  $u \rightarrow u$  transitions, while the first electric dipole allowed transition occurs from the molecular orbital immediately below the highest filled MO (a  $\Gamma_{8g}$  orbital) and is identified with the 214 nm band. It would therefore appear profitable to study multiphoton, and in particular two photon, spectroscopy of  $\text{UF}_6$  since the selection rules are complementary to the selection rules for one photon spectroscopy.

Low temperature solid state  $\text{UF}_6$  emission and excitation spectra exhibit detailed vibronic structure.<sup>5,9</sup> The one photon gas phase absorption spectrum of  $\text{MoF}_6$ , a molecule similar to  $\text{UF}_6$ , has been reported to show a progression in  $\nu_1$  in the ultraviolet.<sup>10,3</sup> Thus, the possibility of observing two photon vibronic structure provides a further motivation for two photon absorption experiments with  $\text{UF}_6$ .

A third impetus for these investigations is provided by Lewis's<sup>4</sup> molecular orbital diagram which places the two highest occupied molecular orbitals in  $\text{UF}_6$  in the reverse order from that observed in most other hexahalides. Thus,  $t_{1g}\pi$  is predicted to be below  $t_{1u}\sigma$  in  $\text{UF}_6$  whereas  $t_{1u}\sigma$  is more stable in most other hexahalides. This point is discussed in a review by Jorgensen.<sup>11</sup> Two photon spectroscopy might reasonably be expected to provide additional information regarding this reversal.

Finally, elucidation of the low-lying electronic and vibronic states of  $\text{UF}_6$  would be an important step towards

an understanding of its photophysical and photochemical behavior.

## II. EXPERIMENTAL

The experimental apparatus used in this investigation has been described previously.<sup>12,13</sup> Briefly, the purified (triply distilled *in vacuo*)  $\text{UF}_6$  is contained in a stainless steel can which is attached to the optical cell with stainless steel tubing. The cell is constructed of stainless steel and quartz windows with indium seals. A beam from a Nd/YAG-pumped dye laser (Quanta Ray) is focused into the cell and fluorescence is observed at  $90^\circ$  to the beam direction via an RCA 8850 photomultiplier tube. The signal from the PM tube is fed into channel A of a PAR boxcar integrator. The beam, after passing through the optical cell, impinges upon a power meter, the signal from which is fed into channel B of the boxcar. Spectra are recorded as  $A/B^2$  in an attempt to normalize intensity to dye output and minimize pulse-to-pulse laser variations. A  $\text{CuSO}_4$  filter is placed between the cell and the PM tube to remove scattered laser light, and suitable sharp-cut filters are placed on the cell to remove unwanted dye-laser harmonics and incoherent fluorescence. To obtain sufficient power in the low energy region of the spectrum, a Raman shifter is employed with some of the dyes to shift the wavelength by  $4155 \text{ cm}^{-1}$ . The Raman shifter contains hydrogen at a pressure of 100 psi. The following dyes are used to scan the wavelength ranges indicated:

DCM,	628–670 nm,
Carbazine 720,	684–720 nm,
Rhodamine 590 (Raman shifted),	716–750 nm,
Rhodamine 610 (Raman shifted),	746–774 nm,
Kiton red (Raman shifted),	760–784 nm,
Rhodamine 640 (Raman shifted),	794–816 nm,
DCM (Raman shifted),	815–910 nm.

In the DCM and Carbazine 720 dye regions, absorption spectra were also obtained photoacoustically as described in Ref. 12. Essentially the same two photon spectra are obtained by both techniques.

In addition to the absorption spectra, an attempt was made to disperse the  $\text{UF}_6$  emission upon excitation at two separate wavelengths: 640 nm (DCM dye—260 nm band) and 775 nm (Kiton red dye—368 nm band). Ex-

<sup>a)</sup>Supported in part by the Office of Naval Research.

citation at 640 nm yields a weak continuous emission over the wavelength range 300–450 nm. No structure whatsoever was observed. Excitation at 775 nm yielded an emission signal too weak to be dispersed.

### III. RESULTS AND DISCUSSION

If it is assumed that two photons are absorbed simultaneously, the wavelength range covered corresponds to a range which includes the low energy side of the 260 nm band to the low energy side of the 368 nm band of the one photon spectrum (342–410 nm). In the one photon spectrum, a minimum is observed in this region at 340 nm, with strong absorption to high energy and weak absorption to the low energy side of this minimum. No absorption is observed above 410 nm.<sup>3,4</sup> The multiphoton (fluorescence) excitation spectrum exhibits the same overall shape as the one photon spectrum in the wavelength range studied with the minimum shifting to 354 nm. Strong absorption is observed to high energy and weak absorption to the low energy side of this minimum. No absorption is observed above 410 nm. Similar results obtain for the photoacoustic spectra.

In order to determine the number of photons simultaneously absorbed, a power dependence study was performed on several of the dyes (R610, R590, and C720) by plotting fluorescence intensity vs laser power on a log–log graph. The slopes of the lines obtained were generally between 3.0 and 3.6, suggesting the absorption of three or four photons. This is believed to be the result of two effects: (1) real, superquadratic multiphoton absorption and (2) the buildup of a  $\text{UF}_5$  or  $(\text{UF}_5)_n$  “snow” within the cell which strongly scattered the incoming beam and lead to a spuriously high “fluorescence” intensity.<sup>14</sup>  $\text{UF}_6$  is known to photolyze rapidly to  $\text{UF}_5$  which then polymerizes.<sup>15</sup> The sensitivity of the PM tube was sufficiently high that even a few photons passing through the  $\text{CuSO}_4$  filter would yield higher than normal intensities. As more experiments were performed between cell cleanings, the number of photons apparently absorbed became higher, indicating a buildup of material within the cell.

The above mentioned difficulties notwithstanding, we believe that both photoacoustic and emission signals originate with resonant two photon absorption in the region 340–410 nm for the following two reasons: (1) No absorption is observed on the low energy side of 410 nm even though there are states which would be resonant for greater-than-two photon absorption; and (2) the interpretation of the spectra of other molecules (pyrazene,<sup>12</sup> triazine,<sup>13</sup> and osmium tetroxide<sup>16</sup>) in the same experimental apparatus using similar laser power levels is only possible by assuming a two photon resonant absorption even though emission may arise from higher states and/or photochemically generated species.

Polarization studies were performed using both photoelectric and photoacoustic detection. However, little

significant difference could be found between the two spectra. This is to be expected considering there is so little difference between one and two photon spectra and that there are no pronounced features in either spectra.

### IV. CONCLUSIONS

Two photon absorption spectroscopy of gas phase  $\text{UF}_6$  yields a spectrum which, in its main features, is indistinguishable from the one photon absorption spectrum. No vibronic structure is observed. Two photon excited emission is weak and continuous for the 260 nm band and about a factor of 10 weaker for the 360 nm band. Again, no vibronic structure is observed. These results are indicative of the difficulty in performing experiments on a molecule which rapidly and efficiently photolyzes. However, the similarity of the one and two photon spectra does indicate that the density of excited states accessible to  $\text{UF}_6$  must be very high in this energy range.

Investigations of the solid state of  $\text{UF}_6$  appear much more promising in this regard. Well-resolved emission and excitation spectra have been obtained in matrix-isolated and pure and mixed crystal  $\text{UF}_6$ .<sup>5,9</sup> The solid state and low temperatures employed appear to suppress the fast photochemistry to a significant extent.

<sup>1</sup>G. H. Dieke and A. B. F. Duncan, *Spectroscopic Properties of Uranium Compounds* (McGraw-Hill, New York, 1949), Chap. 8.

<sup>2</sup>G. D. Sheremet'ev, *Opt. Spektrosk.* **2**, 99 (1957); **1**, 181 (1956).

<sup>3</sup>R. McDiarmid, *J. Chem. Phys.* **65**, 168 (1976).

<sup>4</sup>W. B. Lewis, L. B. Asprey, L. H. Jones, R. S. McDowell, S. W. Rabideau, and A. H. Zeltmann, *J. Chem. Phys.* **65**, 2707 (1976).

<sup>5</sup>J. C. Miller, S. W. Allison, and L. Andrews, *J. Chem. Phys.* **70**, 3524 (1979).

<sup>6</sup>R. C. Oldenberg, W. W. Rice, and F. B. Wampler, *J. Chem. Phys.* **69**, 2181 (1978).

<sup>7</sup>W. W. Rice, F. B. Wampler, R. C. Oldenberg, W. B. Lewis, J. J. Tiee, and R. T. Pack, *J. Chem. Phys.* **72**, 2948 (1980).

<sup>8</sup>W. B. Lewis and A. H. Zeltmann, *J. Photochem.* **12**, 51 (1980).

<sup>9</sup>E. R. Bernstein, G. R. Meredith, and J. D. Webb, *J. Chem. Phys.* **68**, 4066 (1978).

<sup>10</sup>K. N. Tanner and A. B. F. Duncan, *J. Am. Chem. Soc.* **73**, 1164 (1951).

<sup>11</sup>C. K. Jorgensen, *Prog. Inorg. Chem.* **12**, 101 (1970).

<sup>12</sup>J. D. Webb, K. M. Swift and E. R. Bernstein, *J. Mol. Struct.* **61**, 285 (1980).

<sup>13</sup>J. D. Webb, K. M. Swift, and E. R. Bernstein, *J. Chem. Phys.* **73**, (1980).

<sup>14</sup>Similar results have recently been reported: E. Borsella, F. Catoni, and G. Freddi, *J. Chem. Phys.* **73**, 316 (1980).

<sup>15</sup>W. B. Lewis and A. H. Zeltmann, *J. Photochem.* **12**, 51 (1980).

<sup>16</sup>E. R. Bernstein and K. M. Swift (unpublished results).