

## OPTO-ACOUSTIC SPECTROSCOPY AND THE ENERGY OF PHOTO-DISSOCIATION OF URANIUM HEXAFLUORIDE

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### Summary

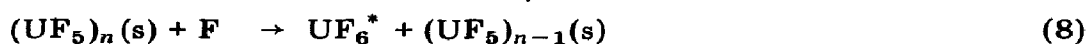
Opto-acoustic spectroscopy of uranium hexafluoride ( $UF_6$ ) with a tunable pulsed dye laser in the region of its weakest absorption band (A band) was observed. In contrast to the normal opto-acoustic response where most of the photon energy rapidly reappears as thermal energy, the response with  $UF_6$  represents only a small fraction of the absorbed photon energy. Since  $UF_6$  is photodissociated with essentially a quantum yield of unity in this band, most of the photon energy is consumed in the dissociation process. Only the excess energy contributes to the opto-acoustic response. The dependence of the response on wavelength or photon energy is determined both by the photons absorbed and by the excess energy over that required to dissociate  $UF_6$ . The dependence of the response on other factors is also discussed. In spite of the very fast post-photolytic kinetics of the exothermic reactions known to follow the dissociation of  $UF_6$ , no evidence of their contribution to the opto-acoustic response was detected. Even the deliberate addition of  $H_2$ , which rapidly reacts with the fluorine atoms produced during photolysis of  $UF_6$ , fails to contribute to the response through the release of additional chemical energy. However, some enhancement of the response results from the presence of  $H_2$  or  $D_2$ , because of their effectiveness in relaxing the vibrationally or rotationally excited products of the  $UF_6$  photolysis. Their effectiveness exceeds that of  $UF_6$  or  $WF_6$ . Other gases such as nitrogen, helium and argon have a negligible effect.

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### 1. Introduction

Although opto-acoustic detection is currently a widely employed technique in spectroscopy, it has rarely been used to detect photochemical reactions. The near-ultraviolet absorption of photons by uranium hexafluoride ( $UF_6$ ) results in essentially 100% dissociation into  $UF_5$  molecules and fluorine atoms at all wavelengths in the absorption band greater than about 222 nm [1, 2]. At shorter wavelengths the photons have enough energy to

dissociate  $\text{UF}_6$  into  $\text{UF}_4$  and  $\text{F}_2$  molecules, and at less than 172 nm  $\text{UF}_4$  molecules and fluorine atoms may be formed. Stepwise photodissociation of  $\text{UF}_6$  with two photons would be thermodynamically possible at wavelengths as long as 294 nm, but that would require maintaining  $\text{UF}_5$  in the vapor phase until the second photon was absorbed, a condition which is likely to be achieved only within the time interval corresponding to a laser pulse width. As far as we are aware, however,  $\text{UF}_4$  has not been identified in the product from the photolysis of  $\text{UF}_6$  by KrF lasers at 248 nm. The opto-acoustic signal in  $\text{UF}_6$ , which results from the release of thermal energy, can therefore represent only a relatively small fraction of the energy in the absorbed photons since most of that energy is required to dissociate the  $\text{UF}_6$ . The thermal energy release following the photodissociation of  $\text{UF}_6$  is certainly complex since the primary products,  $\text{UF}_5$  molecules and fluorine atoms, undergo further reactions before achieving stable states. The processes which are known [1, 2] or assumed to occur are (in order of decreasing rate or later sequence in time) the following:



The superscript \* indicates excited states of any kind and may include any combination of electronic, vibrational, rotational or translational excitation that is present to a greater degree than it is in the thermal distribution at room temperature.

The energy associated with the sum of reactions (1) - (3) will be 10 kcal  $\text{mol}^{-1}$  or less for dye lasers operating at 360 nm or greater, and is only a small fraction of the photon energy per einstein. For pure  $\text{UF}_6$  the velocity of sound is 8390  $\text{cm s}^{-1}$  at room temperature and the shock wave from an absorbed laser pulse would move 0.1 mm or 40% of the diameter of the irradiated volume in about 1.2  $\mu\text{s}$ . Any chemistry occurring after that lapse of time is not likely to be detectable. At the molecular densities produced in typical nitrogen-pulsed dye laser photolysis, only reactions (2) - (7) are fast enough to be important [2]. Of these, reactions (2) and (3) will contribute

a total of 0 - 10 kcal mol<sup>-1</sup> available from the energy in excess of the minimum 69 kcal mol<sup>-1</sup> needed to dissociate UF<sub>6</sub> [3]. However, reactions (4) and (5), and (6) and (7), are exceedingly exothermic and would not have to progress more than a few per cent towards completion before contributing a detectable amount of thermal energy.

The present investigation was undertaken to identify the processes which contribute to the opto-acoustic signal associated with the photodissociation of UF<sub>6</sub>.

## 2. Experimental

The opto-acoustic cell consisted of a brass cylinder with an inside diameter of 0.75 in and having an acoustical cavity defined by two irises separated by 4.0 in. The ends of the cylinder were provided with quartz Brewster angle windows. The opto-acoustic detector was a 0.25 in Brüel and Kjaer Model 4135 microphone with Model 2615 preamplifier adapter. The microphone was sealed inside a side arm to the cell and was connected electrically to the preamplifier by means of a feed-through connector. The signal was further amplified with a PAR model 131 preamplifier and the principal frequency, corresponding to the fundamental diaphragm frequency of the microphone, was passed through a Krohn-Hite Model 3342 tunable bandpass filter. With the 0.25 in microphone and with the aid of a Nicolet Model 444 Mini-Ubiquitous fast Fourier transform spectrum analyzer it was observed that acoustic mode frequencies were relatively weak at the pressure of 20 Torr employed in most of this work. The diaphragm frequency, however, was considerably more intense in this pressure range. Because the diaphragm frequency was about 45 kHz in the 0.25 in microphone, it also had the advantage of being relatively isolated from acoustic modes and therefore had a simple exponential decay envelope.

The filtered spectrophone signal (approximately 45 kHz) entered a half-wave rectifier. The rectified signal was then fed to a Molecron LSDS System, the basic component of which was a dual-channel boxcar integrator. The second channel simultaneously sampled the pulse intensity in a portion of the laser beam via a reference signal from a PIN diode.

Because of variations in the PIN diode sensitivity with wavelength as well as with imperfections in optical components which tend to be a strong function of wavelength, it was particularly important to determine the ratio of the split beams since this generally varies with the wavelength of the dye laser. The effect of this variation in splitting ratio on the spectrum was compensated for in the computer calculation.

Two identical scans were made for each wavelength region. In one the ratio of the spectrophone signal to the laser power was determined. In the other the spectrophone was replaced by a second PIN diode and the beam splitting ratio was determined.

During a spectral scan the signals from the two detectors were passed to dual-channel voltage-to-digital converters. The digitized signals were stored in a DEC PDP 11/40 computer where individual signals could be averaged and a ratio of the averaged signals in the two channels taken, or the ratio of a pair of pulses could be taken and the average of several ratios calculated. The desired results were stored on a magnetic disc for later retrieval and data processing. On completion of both the spectrophone scans and the diode scans a suitable computer program calculated a table of values of normalized extinction coefficients as a function of the laser wavelength and made minor corrections for the experimentally determined wavelength calibration of the dye laser.

The dye laser wavelength was calibrated to within 0.01 Å by superimposing the laser line on a hollow cathode iron lamp spectrum in a Spex 1 m monochromator.

### 3. Results

The opto-acoustic response (OR) was observed to have the same dependence on the light intensity and the  $\text{UF}_6$  concentration as the photons per second absorbed in the cell, *i.e.*

$$\text{OR} \propto I_{\text{abs}} = I_0(1 - 10^{-\epsilon c_0 l})$$

where  $\epsilon$  is the molar absorptivity in liters per mole per centimeter,  $c_0$  is the  $\text{UF}_6$  concentration in moles per liter and  $l$  is the cell length. This dependence of the signal amplitude on the  $\text{UF}_6$  pressure, however, represents only that part associated with the absorption of photons in the cell. The relaxation rate of the excess energy to the thermal bath as well as the microphone damping rate depend on the  $\text{UF}_6$  pressure and therefore modify the signal amplitude. The response is also sensitive to geometric factors such as the degree to which the beam is focused and the location of this focal point with respect to the microphone, but we centered the focal point of the beam in the cell and kept the beam waist at a diameter at full width at half maximum of about 0.25 mm.

The complete spectrum for the A band was constructed from several segments obtained with different dyes, since no single dye gave useful power output over more than 10 - 20 nm. The dyes found to give the greatest power output in their respective lasing bands are listed in Table 1. The spectral scans or segments were joined to form a complete spectrum by matching signal intensities through the use of scale factors at some wavelength in the middle of each range of overlap between adjacent dyes. These scale factors were required because it was not possible to position exactly the laser beam in the cell at precisely the same point from one dye scan to the next. The signal amplitude was very sensitive to the position of the beam within the

TABLE 1  
Efficient dyes for opto-acoustic spectroscopy

Dye <sup>a</sup>	Solvent	Useful range (nm)
Normal PBD	1:1 Ethanol-toluene	362 - 385
BBQ	1:1 Ethanol-toluene	385 - 388
PBBO	Cyclohexane	388 - 398
PBBO	1:1 Ethanol-toluene	398 - 408
POPOP	Cyclohexane	408 - 418
POPOP	Dioxane	418 - 425

<sup>a</sup>PBD, 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole;  
BBQ, 4,4''-bis(2-butyloctyloxy)-*p*-quaterphenyl;  
PBBO, 2-(4'-biphenyl)-6-phenylbenzoxazole;  
POPOP, *p*-bis-[2-(5-phenyloxazolyl)]-benzene.

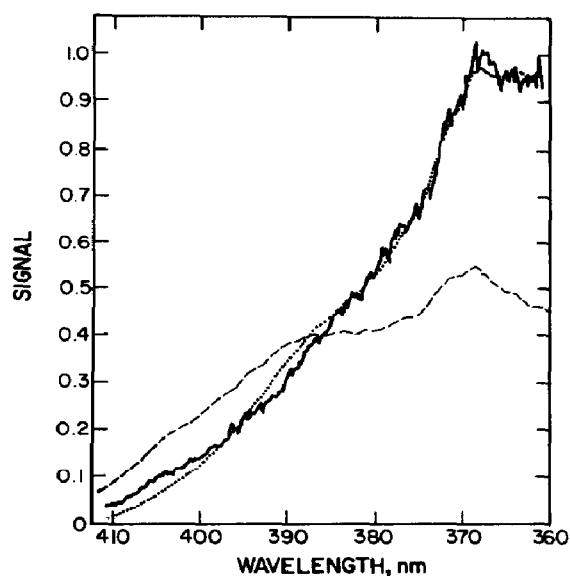


Fig. 1. Opto-acoustic spectrum of  $\text{UF}_6$  at 295 K:  $P_{\text{UF}_6} = 18$  Torr; - - -, molar absorptivity of  $\text{UF}_6$  from ref. 4; —, opto-acoustic spectrum; . . ., calculated opto-acoustic spectrum from the molar absorptivity of  $\text{UF}_6$  multiplied by  $h(\nu - \nu_0)$  and a scale factor.

cell, even with the use of irises within the cell. Exceptional care was also taken to reduce fluorescence, since near the edge of the useful range of each dye it could amount to a significant fraction of the total power output, and give a signal intensity which is averaged over a broad wavelength range.

The resulting spectrum for pure  $\text{UF}_6$  is shown in Fig. 1. Using the molar optical absorptivity data of ref. 4, it was possible to fit the experimental data rather well by simply multiplying the molar absorptivity data by the factor  $h(\nu - \nu_0)$  and an arbitrary scale factor, where  $h\nu$  is the photon energy at  $\lambda = c/\nu$  and  $h\nu_0$  is the energy of dissociation for the reaction

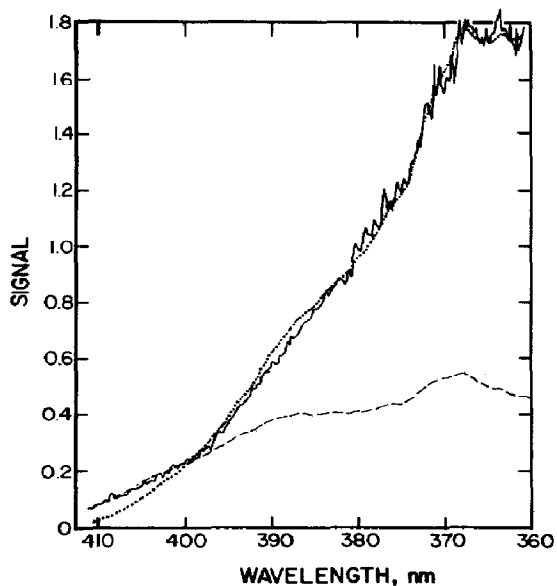


Fig. 2. Opto-acoustic spectrum of a  $\text{UF}_6\text{-H}_2$  mixture at 295 K:  $P_{\text{UF}_6} = 18$  Torr;  $P_{\text{H}_2} = 2$  Torr; ---, molar absorptivity of  $\text{UF}_6$  from ref. 4; —, opto-acoustic spectrum; ..., calculated opto-acoustic spectrum from the molar absorptivity of  $\text{UF}_6$  multiplied by  $h(\nu - \nu_0)$  and a scale factor.

$\text{UF}_6 \rightarrow \text{UF}_5(\text{g}) + \text{F}$ . The spectrum reconstruction procedure was carried out on the PDP-11/40 data acquisition system by using a non-linear least-squares curve fitting program and allowing  $h\nu_0$  and the scale factor to vary. The dotted curve in Fig. 1 is seen to give a good reproduction of the observed data (solid curve) within experimental error. The optimum value of  $h\nu_0$  was found to correspond to  $68.8 \text{ kcal mol}^{-1}$ , which is in good agreement with the average of the three independent values reported by Hildenbrand [3].

Inert gases such as nitrogen, helium and argon have a similar effect on the opto-acoustic response. At pressures less than that of  $\text{UF}_6$  their effect is negligible, but at higher pressures they reduce the response by damping the microphone diaphragm. Mixtures of  $\text{UF}_6$  and  $\text{WF}_6$  with the same total pressure exhibit responses that are directly proportional to the  $\text{UF}_6$  pressure and hence to the photons absorbed by the mixture.

Since the presence of a fluorine atom scavenger [5] such as  $\text{H}_2$  [6] leads to even greater thermal energy release when  $\text{UF}_6$  is photolyzed, opto-acoustic spectra were also run with a mixture containing 2 Torr  $\text{H}_2$  with 18 Torr  $\text{UF}_6$ . Figure 2 shows the spectra obtained with  $\text{H}_2$  present. It was found that  $\text{H}_2$  modifies the spectrum by increasing its intensity relative to  $\text{UF}_6$  with  $\text{N}_2$  instead of  $\text{H}_2$  by a factor of 1.8 at all wavelengths. A least-squares fit of the spectrum for a mixture of  $\text{UF}_6$  and  $\text{H}_2$  is shown in Fig. 2 and gave a value of  $68.8 \text{ kcal mol}^{-1}$  for the dissociation energy, or essentially the same result as that found for pure  $\text{UF}_6$ .

The effect of  $\text{D}_2$  on the signal intensity at 368 nm was also determined in order to detect a possible direct mass effect on the relaxation rate by com-

parison with helium. Whilst the effect of helium was no different from that of  $N_2$ ,  $D_2$  gave an intensity ratio of 2.1, or slightly greater than that of  $H_2$ .

#### 4. Discussion

The close agreement between the dissociation energy of  $UF_6$  determined here and the values listed by Hildenbrand [3] is indicative of the relative slowness of reactions (4) - (11) compared with reactions (2) - (3). If reactions (4) and (5), for example, had proceeded to the extent of 5% towards completion before the shock wave departed from the photolysis zone, 2 kcal mol<sup>-1</sup> of energy would have been released. That amount of thermal energy would have been detected and would have resulted in an apparent low energy of dissociation of  $UF_6$ .

With the kinetic model described previously [2], but omitting the terms in the differential equations appropriate for gas flow and continuous illumination, it was found that about 5% polymerization of  $UF_5$  can be expected to occur in about 0.1  $\mu s$  and 5% recombination should occur in about 0.5  $\mu s$ . These times are so short that only a small number of collisions between  $UF_5^*$  and  $UF_6$  or the scavenger molecules  $H_2$  or  $D_2$  could take place. The hard sphere collision frequencies between  $UF_5^*$  and other molecules of interest in these experiments are estimated at room temperature to be

$UF_6$	37 $\mu s^{-1}$
$H_2$	64 $\mu s^{-1}$
$D_2$	45 $\mu s^{-1}$

However, the hard sphere approximation may give a result for the  $UF_6$ - $UF_5^*$  collision frequency which is too small. No allowance has been made for the possibility that  $UF_5^*$  may not polymerize until relaxed to a near-thermal distribution of vibrational states nor for the time it takes for the energy of polymerization to appear as thermal energy. In any case it is evident that collisions between  $UF_5^*$  and  $UF_6$ ,  $WF_6$ ,  $H_2$  or  $D_2$  are very efficient at relaxing  $UF_5^*$ . It has been suggested that the relaxation proceeds in this case via the rotational levels of  $H_2$  and  $D_2$  or the rovibrational levels of  $UF_6$  [7], but the problem of accounting for the subsequent transfer of energy from such states to translational states remains. Such a mechanism at least would be consistent with the slightly more intense opto-acoustic signal observed in  $UF_6$ - $D_2$  mixtures relative to  $UF_6$ - $H_2$  as well as with the significantly more intense signal in  $UF_6$ - $D_2$  mixtures compared with  $UF_6$ -He mixtures.

#### 5. Conclusions

Opto-acoustic spectroscopy of  $UF_6$  with a tunable pulsed dye laser in the region of its weakest absorption band has been observed. Since  $UF_6$  is photodissociated with essentially a quantum yield of unity throughout this band, most of the photon energy is consumed in the dissociation process.

The excess energy, which very rapidly appears as thermal energy, creates a cylindrical shock wave following the laser pulse which sets up both acoustic mode oscillations and microphone diaphragm mode oscillations that are readily detectable as opto-acoustic signals. When geometric factors and the total pressure are held constant, the intensity of the opto-acoustic signal varies with the wavelength according to the number of einsteins per second of photons absorbed in the photolysis region and with the excess energy of the photons over that required to dissociate  $\text{UF}_6$  into the primary product species  $\text{UF}_5$  and fluorine atoms. The latter energy is found to be  $69 \pm 1$  kcal  $\text{mol}^{-1}$ , in very good agreement with the values reported previously [3].

From the close agreement between our value for the dissociation energy and those in the literature, it is concluded that no significant post-photolysis chemistry has occurred before the opto-acoustic shock wave leaves the perimeter of the photolysis zone. From estimates of the polymerization and recombination rates after photolysis, it can be inferred that the excess energy appears in the form of thermal energy within approximately  $0.1 \mu\text{s}$ . In view of the collision frequency of the  $\text{UF}_5$  product with  $\text{UF}_6$  molecules, only a small number of collisions are required to transfer the bulk of the excess energy to the thermal bath.

The fluorine atom scavengers  $\text{H}_2$  and  $\text{D}_2$  were added in an attempt to detect energy released from other post-photolysis reactions. Both  $\text{H}_2$  and  $\text{D}_2$  result in an increased signal intensity but this is attributed solely to an increased relaxation rate for the transfer of the excess energy to the thermal bath.

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