

Laser photochemistry of UF_6

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Abstract. The photochemistry of volatile uranium compounds, in particular of UF_6 , is of great importance. Although conventional photochemistry is related to electronically excited states, it is now possible to investigate the ground state photochemistry with the advent of intense tunable IR lasers. The IR-multiphoton dissociation of UF_6 can be performed using a high power pulsed 16μ laser in the electronic ground state. Results of a theoretical estimate of rate constants $K_a(E\nu^*)$ for MPD of UF_6 using RRKM—unimolecular reaction rate theory will be presented. Calculations made on the basis of known spectroscopic parameters of UF_6 and those generated from group theoretical considerations for the activated complex UF_6^\ddagger are presented. It has been shown that an excess of 15 photons above the dissociation threshold is necessary to preserve the isotopic selectivity in 1 torr of UF_6 sample. This corresponds to the utilization of about 50 photons of 16μ laser per UF_6 molecule dissociated. This knowledge of the level of excitation is useful in defining the optimum laser fluence requirement in MPD experiments.

In the context of two-step photodissociation of UF_6 via the electronic excited states, photochemistry in the $\tilde{B}-\tilde{X}$ band has been studied at two different wave lengths— 2537\AA line of a low pressure Hg-lamp and the 3371\AA line of a pulsed N_2 -laser. Decomposition of UF_6 yielded a mixture of solid products, which have been identified as UF_4 and UF_3 . The quantum yield ratio for these products has also been determined. Implication of its photophysical parameters for dissociation efficiency in the $\tilde{A}-\tilde{X}$ band will also be considered.

1. Introduction

In view of the promising economic implications of laser isotope separation (LIS) schemes, the photochemistry of volatile uranium compounds, in particular of UF_6 , is of great importance. The chief advantages of UF_6 are its high vapour pressure (Ca. 100 torr at 25°C), known spectroscopy, thermal stability and the monoisotopy of fluorine. Although a corrosive gas, UF_6 handling is a known

and familiar art. In its 16μ IR absorption band, the ν_3 -mode of UF_6 has a marked isotope shift: $\sim 0.6\text{ cm}^{-1}$ at 625 cm^{-1} .

In the molecular approach schemes of LIS, selective excitation of the desired isotopic molecule can therefore be achieved by a suitable IR laser excitation in the 16μ -region. Of the various alternate methods of collecting the vibrationally excited molecule, two appear to be promising. The first approach is based on massive multiphoton excitation of UF_6 in its ground state so that the molecule absorbs sufficient energy to unimolecularly dissociate. In the second approach a limited vibrational excitation is followed by an electronic excitation by the absorption of a suitable UV/visible laser photon. The electronically excited molecule then decomposes.

The objective of either of these approaches is to maximise selective photodissociation of the desired isotopic species. The parameters which limit the selectivity, in addition to spectroscopic factors, are:

- 1) The unimolecular decomposition rates which are in competition with collisional energy exchange losses.
- 2) The photodecomposition rates and modes of the electronic excited state.

In this paper we will first consider how the unimolecular decomposition rate varies with the vibrational energy content of the UF_6 molecule. In a subsequent section, we will present some of our experimental data on the UF_6 -decomposition in its second, $\tilde{B}-\tilde{X}$ electronic state (cf Figure 1). During the course of this work, multiphoton dissociation (MPD) of UF_6 (Rabinowitz 1978) and its isotopic enrichment (Wittig 1978) have been reported. Its photochemistry in the $\tilde{A}-\tilde{X}$ band has also been studied by a few groups (Andreoni 1976, Wampler 1978, Dewitte 1977).

2. Experimental

Computer Calculations: A BESM-6 computer was used to compute the unimolecular reaction rates.

UF_6 Purification: UF_6 was purified from HF and other volatile impurities by a dynamic fractional condensation technique. UF_6 condensed in a cold trap at 196 K while the impurities were pumped out.

Irradiations: Photolysis at 2537 \AA was conducted in a photochemical reactor. The reactor consisted of a cylindrical array of sixteen low pressure Hg lamps, providing flux of 1.6×10^{16} photons $\text{cm}^{-2}\text{ sec}^{-1}$ at the sample position in the centre. The 1 cm-diameter, 21 cm long quartz sample cell was initially baked thoroughly under vacuum before filling with a mixture of 137 torr UF_6 and 240 torr H_2 .

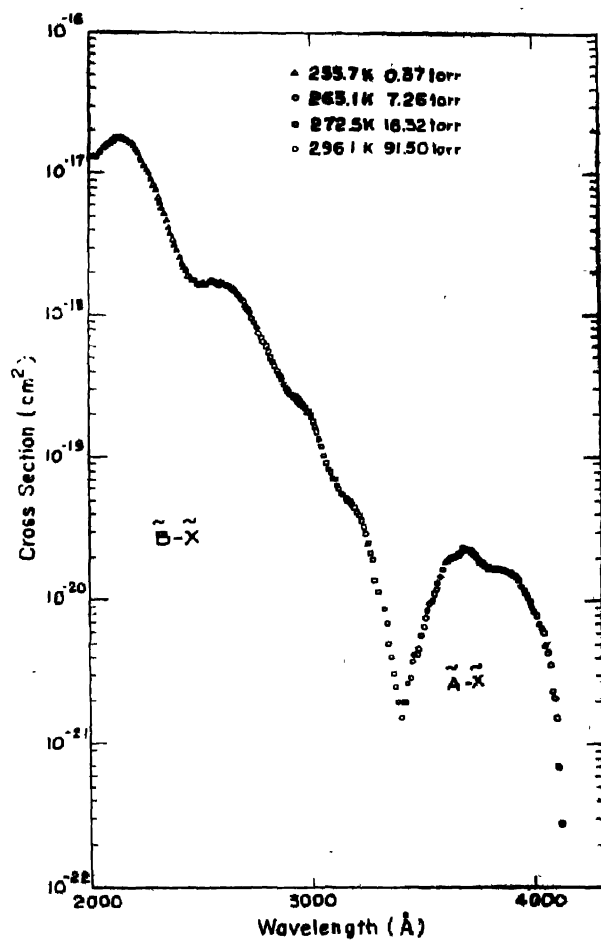


Figure 1. Composite Absorption Spectrum of UF_6 from data taken at different temp. [Depoorter 1976]. In the figure $\bar{A}-\bar{X}$ and $\bar{B}-\bar{X}$ band are indicated.

A Molelectron UV 400 pulsed N₂-laser was used for irradiations at 3371 Å. The pulse width of the laser was 10 ns and at a repetition rate of 10 Hz, its peak energy is 250 mJ/pulse. The sample cell for the laser irradiation was made of stainless steel, 21 cm long and fitted with CaF₂ end windows. The cell was passivated by BrF₃ at 60°C and thoroughly evacuated before filling with 105 torr UF₆ and 240 torr H₂.

Analysis: The green and white solid deposits obtained on photolysis at 2537 Å, were dissolved, in an inert atmosphere, in 4N-HCl containing some Boric acid. The resulting solution was then potentiometrically analysed for U(IV) and U(VI).

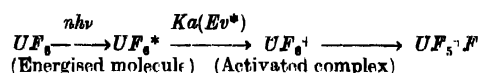
In the N₂-laser photolysis, UF₆-depletion was monitored periodically by its absorption at 3700 Å.

3. Results and discussions

Evaluation of Unimolecular decomposition rates

Extensive work on IR multiphoton dissociation (MPD) of polyatomic molecules, in particular SF₆, has indicated that the process is unimolecular. Although a full evaluation of the experimental results in terms of the existing unimolecular rate theories have not yet been done, it appears that RRKM theory generally explains the thermal as well as laser induced dissociation of SF₆. In this paper, we have utilised the RRKM theory to compute the UF₆-dissociation rates.

Following the RRKM theory (Robinson 1972), it is assumed that the multiphoton excitation energy of UF₆ molecule is rapidly randomised between all the vibrational modes of the molecule. The energised molecule, having more than sufficient energy for the dissociation process to occur, will then reorganise its internal degrees of freedom to become an activated complex, having the appropriate critical molecular configuration for the dissociation process to occur readily.



The conversion of the energised to activated complex occurs at a definite rate, $K_a(E_v^*)$, which is a function of the non-oxide energy, available for redistribution, with the molecule. The RRKM-expression for the unimolecular rate constant for the dissociation of the molecules with energy E_v^* , is given by:

$$K_a(E_v^*) = L^\ddagger \frac{Q_1^\ddagger}{Q_1} \frac{1}{hN^*(E_v^*)} \frac{E_0^\ddagger}{\sum_{E_v^\ddagger \geq 0} P(E_v^\ddagger)}$$

The internal energy of the activated complex is defined as :

$$E_v^\ddagger = E_v^* - E_0,$$

since an energy E_0 , equivalent to the energy barrier between the reactants and the products, becomes fixed in the formation of the activated complex. For UF_6 , E_0 is taken as the U-F bond dissociation energy 68 KCal mole⁻¹ (Hilderbrand 1977). Other parameters in the above expression are as follows :

L^\ddagger the statistical factor, is taken as 6 representing the number of equivalent paths by which the dissociation can occur.

Q_1^\ddagger and Q_1 are the rotational partition functions for the activated complex and the undistorted molecule respectively. Assuming one U-F bond length is doubled in forming the activated complex, $Q_1^\ddagger/Q_1 = 1.75$.

$N^*(E_v^*)$, the density of the vibrational states at energy E_v^* , is given by

$$N^*(E_v^*) = \frac{(E_v^* + aE_z)^{S-1}}{(S-1)! \prod_{i=1}^S h\nu_i} \left[1 - \beta \frac{dW(E')}{dE'} \right]$$

where ν_i 's are the fundamental vibrational frequencies of UF_6 and $E_z = \frac{1}{2} \sum_{i=1}^S h\nu_i$, the total zero-point vibrational energy for all $S = 15$ normal modes of UF_6 .

a is an empirical parameter which gives the best approximation to the direct count of the quantum states and is given by :

$$a = 1 - \beta W(E')$$

where $\beta = [(S-1)/S] < \nu^2 > / < \nu >^2$ in which $< \nu >$ and $< \nu^2 >$ are the mean and mean square frequencies of the molecule

Empirical function $W(E')$ is given by :

$$W = [5.00E' + 2.73E'^{0.7} + 3.51]^{-1} \quad \text{for } 0.1 < E' < 1.0$$

$$= \exp[-2.4191E'^{0.25}] \quad \text{for } E' > 1.0$$

where $E' = E_v^*/E_z$.

The above treatment known as Whitten-Rabinovitch approximation gives the vibrational state density $N^*(E_v^*)$ as a function of E_v^*

$P(E_v^+)$ is the number of vibrational quantum states in the activated complex

at energy E_v^+ , and the sum $\sum_{E_v^+=0}^{E_v^+} P(E_v^+)$ is the total number of vibrational states

in the activated complex upto E_v^+ which is given by

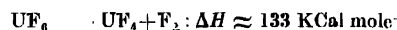
$$\sum_{E_v^+=0}^{E_v^+} P(E_v^+) = \frac{(E_v^+ + aE_z^+)^S}{S! \prod_{i=1}^S h\nu_i^+}, \quad S = 14 \text{ for } UF_6^+$$

UF_6 has the highly symmetrical O_h point group. The frequencies corresponding to the six fundamental vibrational modes are given in table 1. The evaluation of $\Sigma P(E_v^+)$ depends on what set of vibrational frequencies can be assigned to the activated complex, UF_6^\ddagger . For the primary decomposition channel of UF_6 as in $UF_6 \xrightarrow{h\nu} UF_6^\ddagger \rightarrow UF_5 + F$; $\Delta H \approx 68$ KCal mole $^{-1}$; the activated complex UF_6^\ddagger assumed to have the configuration where one U-F bond has been stretched and the bond length is doubled. Although other possible decomposition channel like molecular elimination of F_2

Table 1. $UF_6(O_h)$ point group) fundamental vibrational frequencies [Claassen 1970]

i	Γ_i	$\nu_i(\text{cm}^{-1})$	Assignments
1	A_{1g}	667.1	$\nu_{(U-F)}$
2	E_g	532.5	$\nu_{(F-U-F)}$
3	F_{1u}	624.0	$\nu_{(U-F)}$
4	F_{1u}	186.2	$\delta_{(F-U-F)}$
5	F_{2g}	202.0	$\delta_{(F-U-F)}$
6	F_{2u}	142.0	$\delta_{(F-U-F)}$

$$\begin{aligned} \langle \nu \rangle &= 346.3 \text{ cm}^{-1} \\ \langle \nu^2 \rangle^{1/2} &= 405.55 \text{ cm}^{-1} \\ \bar{\nu}_1 &= 285.98 \text{ cm}^{-1} \end{aligned}$$



exists; it is much more energetically prohibitive. Hence the decomposition may be expected to proceed through U-F bond dissociation as in the case of SF_6 (Grant 1977). The number of modes in the activated complex is reduced by one since the normal stretching mode of U-F' (which is now different from other F-atom) becomes the reaction co-ordinate. The vibrational frequencies of the activated complex were determined by first dividing the frequencies of UF_6 into two categories:

- those which are little affected and
- those most affected by extending the bond.

As one bond is stretched and that particular F atom is different from the rest, the symmetry point group for the activated complex changes from O_h to C_{4v} . From the correlation table of O_h point group to C_{4v} , it will be possible to assign UF_6^\ddagger frequencies (cf. Table 2). The frequencies which are least affected were taken to be 0.95 times the corresponding UF_6 -frequencies. The most affected mode frequencies are taken as 0.75 and 0.65 times those of UF_6 to allow adequate

range for defining the properties of the activated complex. Figure 2 shows the variation of vibrational state density $N^*(E_v^*)$ with E_v^* . Figure 3 shows the variation of $K_a(E_v^*)$ with energy in terms of excess photon for the above mentioned two cases. The predicted trends are similar and show that the unimolecular

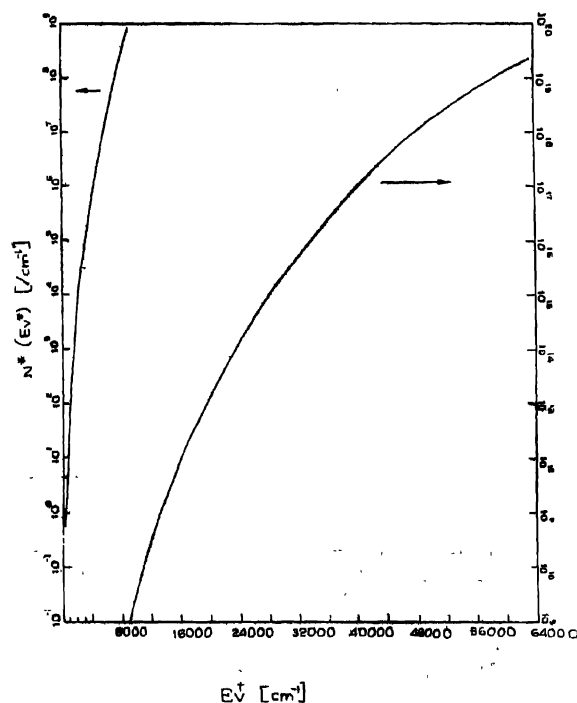


Figure 2. Variation of vibrational state density $N^*(E_v^*)$ with vibrational energy content of the molecules E_v^* for UF_6 using Whitten-Rabinovitch approximation with the parameters in table 1.

rate constant increases rapidly upto about seven photons excess. At higher energies, the dissociation rate increases slowly. It will be possible to define the vibrational frequencies of the activated complex more precisely by comparison

with thermal reaction rate data, if available. In the case of SF_6 , such a comparison had enabled Lyman (Lyman 1977) to conclude that the most affected SF_6^+ frequencies are 0.75 times those of SF_6 .

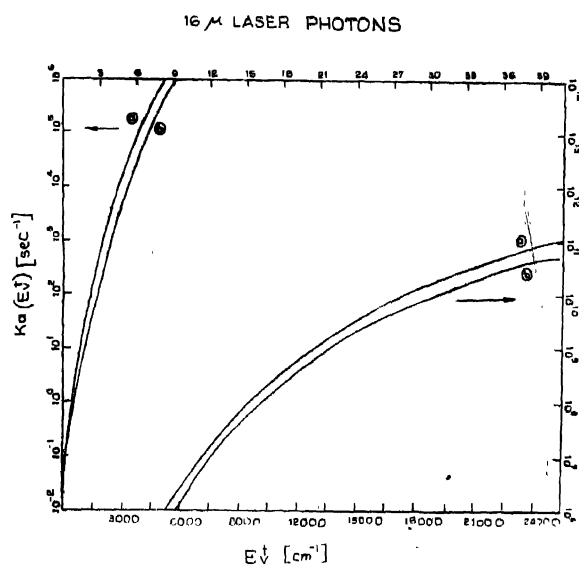


Figure 3. The unimolecular rate constant $K_a(E_0^\ddagger)$ versus internal energy content of activated complex E_0^\ddagger . Curve (a) is calculated with vibrational frequencies for UF_6^+ , 0.95 times (least affected) & 0.65 times (most affected) the corresponding frequencies of UF_6 . Curve (b) is calculated using the above factors as 0.95 and 0.75. The upper scale is E_0^\ddagger in terms of excess photons of 16μ laser [625 cm^{-1}] above the dissociation threshold.

From the point of view of isotopic selectivity, two parameters which are of interest are (1) What should be the optimum level of energisation for UF_6 molecule to dissociate without collisional energy-exchange and (2) What laser fluences are required to achieve this energisation. The mean collisional time for $^{235}\text{UF}_6$ collisions at 1 torr natural UF_6 is 285 ns. The random life time for an energised UF_6 molecule at 15 excess photons is 10–20 ns. Within a typical laser pulse of 200 ns, we can therefore expect $\sim 10\%$ loss of $^{235}\text{UF}_6$ excited at 13–15 excess photons i.e., about 56–16 μ laser photons (cf. Table 3).

Table 2. Activated complex (UF_6^\ddagger) fundamental vibrational frequencies

Γ_{UF_6}	$\Gamma_{UF_6^\ddagger}$	i	Assignment	$\nu_i^\ddagger(\text{cm}^{-1})$	
				(a) = $0.95\nu_{UF_6}$ (b) = $0.65\nu_{UF_6}$	(a) = $0.95\nu_{UF_6}$ (b) = $0.75\nu_{UF_6}$
A_{1g}	A_1	2	$\nu_{sym}(UF_4)$	633.75 ^a	633.75 ^a
E_g	A_1	3	$\delta_{sym}(UF_4)$ out of plane	346.13 ^b	399.37 ^b
	B_1	5	$\nu_{sym}(UF_4)$ out of phase	505.88 ^a	505.88 ^a
F_{2u}	A_1	1	$\nu_{(U-F)}$	405.6 ^b	468.0 ^b
	E	8	$\nu_{asym}(UF_4)$	592.8 ^a	592.8 ^a
F_{1u}	A_1	4	ν_{U-F}	Reaction Co-ordinate	
	E	9	$\delta(FUF_4)$ wagging	176.89 ^a	176.89 ^a
F_{2g}	B_2	7	$\delta_{sym}(UF_4)$ in plane scissoring	191.9 ^a	191.9 ^a
	E	10	$\delta_{asym}(UF_4)$ in plane	131.3 ^b	151.5 ^b
F_{3u}	B_1	6	$\delta_{asym}(UF_4)$ out of plane	92.3 ^b	106.5 ^b
	E	11	$\delta(FUF_4)UF_6$ rocking	134.9 ^a	134.9 ^a

$$\begin{aligned} \langle \nu^\ddagger \rangle &= 303.38 \text{ cm}^{-1} & \langle \nu^\ddagger \rangle &= 315.54 \text{ cm}^{-1} \\ \langle \nu^{\ddagger 2} \rangle &= 1360.9 \text{ cm}^{-2} & \langle \nu^{\ddagger 2} \rangle &= 371.48 \text{ cm}^{-2} \\ \bar{\nu}^\ddagger &= 244.59 \text{ cm}^{-1} & \bar{\nu}^\ddagger &= 257.47 \text{ cm}^{-1} \end{aligned}$$

Table 3.
0.75 case

Excess energy	$N^*(E_V^*)$	$\Sigma P(E_V^\ddagger)$	$K_a(E_V^*)\text{sec}^{-1}$	$\tau(ns)$	% loss of selectivity
5	6.2×10^{14}	1.8×10^7	9.15×10^9	109289	—
7	1.1×10^{15}	4.2×10^8	1.18×10^9	8774	96.7
9	1.85×10^{15}	4.4×10^8	8.56×10^8	1168	80.4
10	2.54×10^{15}	1.6×10^{10}	1.98×10^8	505	64.0
12	4.28×10^{15}	1.13×10^{11}	6.47×10^8	118	29.3
13	5.56×10^{15}	2.82×10^{11}	1.6×10^7	62.5	18.0
14	7.15×10^{15}	6.53×10^{11}	2.87×10^7	35	10.9
15	9.17×10^{15}	1.44×10^{12}	4.94×10^7	20	6.6

The laser fluence requirements for creating such massive multiphoton excitation are now being evaluated. Experimentally, Kaldor *et al* have found for UF_6 , MPD occurs with a threshold of 1J cm^{-2} . In general, it has been found that higher laser fluxes will populate higher and higher quantum states in polyatomic molecules within a limited energy spread.

UF_6 -Photolysis in the $\tilde{B}-\tilde{X}$ band

Irradiation of UF_6 alone or with H_2 at 2537 \AA produced extensive solid deposits, which on chemical analysis, were shown to be a mixture of UF_6 and UF_4 . The ratio of these two products was determined as 7 : 3. The fact that the dissociation product is a solid is of tremendous importance. It implies that the separation of enriched products from the feed material will be simple, as it involves only phase separation. Also, isotopic scrambling between enriched product and starting material is likely to be reduced.

Irradiation of UF_6 and H_2 at 3371 \AA by N_2 laser gave rise to fine white deposit on the window. The depletion of UF_6 on irradiation, as determined by spectrophotometry, corresponded to a quantum yield of UF_6 dissociation of 0.14.

The existing literature on UF_6 photolysis is confined to the $\tilde{A}-\tilde{X}$ band, which is also a weakly fluorescent excited state. Much of the reported work monitored the fluorescence to obtain the quenching rate with various additives, including self-quenching by UF_6 . At low pressures and in the absence of additives the life time of $\tilde{A}-\tilde{X}$ band excitation is about 400 ns at 30°C (Androni 1977), rather large to be useful for isotopic enrichment. The lifetimes also decrease very rapidly in the presence of additives, especially hydrocarbons (Wampler 1978), but it is not yet known whether the high quenching rates definitely involve chemical reactions which can be used as a means of collecting the selectively excited species. The only indication about the UF_6 photo decomposition in the $\tilde{A}-\tilde{X}$ band was that of Kaldor (Kaldor 1978) who reported quantum yields of about 0.1, comparable to what we have now obtained for excitation within the $\tilde{B}-\tilde{X}$ band.

3. Summary

1. We have discussed the various parameters for IR-MPD and two step photodissociation of UF_6 .
2. The optimum level of vibrational excitation for isotopically selective MPD has been estimated by applying RRKM theory.
3. We have studied the photo decomposition of UF_6 in the $\tilde{B}-\tilde{X}$ band which can be used as 2nd step of two step dissociation.

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