NEAR-UV PHOTODISSOCIATION OF GASEOUS UF₆ IN THE PRESENCE OF H₂

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Mixtures of UF₆ and H₂ in different ratios have been irradiated at 360 and 400 nm by means of a filtered mercury lamp. A significant pressure drop has been observed at both excitation wavelengths due to the dissociation of UF₆ into UF₅ + F. A very high dissociation quantum yield has been found

1. Introduction

In view of possible laser isotope separation (LIS) schemes of uranium, the photophysical and photochemical properties of gaseous UF₆ have been the subject of experimental and theoretical investigations in the last few years, as recently reviewed by de Silvestri et al. [1]. In particular the fluorescence emission from UF₆ excited in the A-X band (340-410 nm) exhibits different time behaviour and quantum yield, depending on the excitation wavelength [2,3]. These experimental data can be explained in terms of a model involving two excited electronic states [3]. The fluorescence quantum yield is generally very low. For instance, at 10 Torr pressure, its value is $\approx 5 \times 10^{-4}$ at the long wavelength edge of the absorption spectrum and drops down to $\approx 10^{-6}$ at shorter wavelengths. A very efficient quenching mechanism must therefore be present. It could be both a redistribution of the excitation energy amongst the internal degrees of freedom of the molecule and a dissociative process The latter, followed by a chemical or physical removal of the photo-products, would be useful for LIS No experimental data, however, are available in the literature to evaluate the relative efficiency of the two processes.

In this paper we report results on the photodissociation of gaseous UF_6 under excitation at 360 and 400 nm in the presence of H_2 .

2. Experimental

The reaction cell (3.5 cm diameter and 20 cm long) and the vacuum line were all in monel and quartz with indium O-rings. The rotary and the diffusion pump both employed special fluorinated oils (Fomblin Y25/5 and Fomblin 18/8 respectively) compatible with UF₆ and having very low vapor pressure. The highly purified UF₆ was supplied by CNEN. Research-grade H₂ was used. The pressure in the cell was measured by an MKS Baratron model 310 AHS-100, whose analog output was sent to a chart recorder. The gas mixture was fully irradiated by an Osram HBO mercury lamp (200 W). The two excitation wavelengths at 360 and 400 nm were selected by interference filters with 6 nm bandwidth. The incident power was measured to be 60 mW and 100 mW, respectively.

3. Results and discussion

It is well known that UF_5 has negligible vapor pressure at room temperature. Thus a pressure decrease in the reaction cell would be expected as a consequence of the UF_6 photodissociation into $UF_5 + F$. In our experiment, no appreciable decrease in the cell pressure was observed when irradiating 10 Torr of UF_6 alone at both wavelengths In our opinion, this is due to the $UF_5 + F \rightarrow UF_6$ recombination process. This process has recently been shown to be very efficient in the kinetics following the photolysis of pure UF_6 [4]. In order to prevent this recombination, H_2 has been added as a scavenger of

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the fluorine atoms No pressure decrease was observed when UF₆ and H₂ were mixed in the cell in the absence of irradiating light. On the other hand, a definite pressure drop was observed when the gas mixture was irradiated by both 360 and 400 nm light. The corresponding time evolution of the overall pressure in the cell is shown in fig 1 (curves (a) and (b), respectively) for 10 Torr initial pressure. The two wavelengths were chosen in order to excite preferentially one or the other electronic states, which contribute to the A- \tilde{X} absorption band of UF₆ [5] The stoichiometry of the reaction that we expect to occur is

$$2UF_6 + H_2 \rightarrow 2UF_5(\text{solid}) + 2HF. \tag{1}$$

Thus, if the UF_6 H_2 initial pressure ratio is stoichiometric (i e 2.1), a pressure drop to a final value of 2/3 of the initial one is expected This is in fact the case with curves (a) and (b) in fig 1, which tend towards an asymptotic value slightly lower than that expected (i.e. 6.6 Torr). Curve (c) in fig.1 refers to a 1.1 mixture and tends towards an asymptotic value that is still slightly lower than that expected from (1) which, in this case, should be 3/4 of the initial pressure These results enable us to rule out the possibility of UF₆ decomposition into UF₄, which would lead to a final pressure higher than that expected from (1)



Fig 1 Total pressure of UF₆ H₂ mixtures as a function of the irradiation time Curves (a) and (b) 2 1 ratio under excitation at 360 and 400 nm, respectively, curve (c) 1 1 ratio under excitation at 360 nm

The experimental time behaviour of the overall pressure could be intepreted in terms of the following reaction mechanism

$$UF_6 \xrightarrow{h\nu} UF_5 + F,$$
 (2)

$$F + H_{\gamma} \rightarrow HF + H. \tag{3}$$

$$H + UF_6 \rightarrow UF_5 + HF.$$
 (4)

$$H + H + M \rightarrow H_{2} + M, \tag{5}$$

$$F + UF_5 \to UF_6, \tag{6}$$

in which M represents all possible collisional partners. However, according to reaction (1), reaction (6) is not likely to occur when the initial pressure of $H_2(p_{H_2}^0)$ is at least half of the initial pressure of $UF_6(p_{UF_6}^0)$. This case only is discussed in the following. Assuming the rate of reactions (2)--(5) to be fast on the time scale of our observation, the time evolution of the UF₆ pressure (p_{UF_6}) in the linear absorption regime can be described as follows

$$dp_{\rm UF_6}/dt = -(I_0 \sigma \phi/h\nu) p_{\rm UF_6}$$
(7)

where I_0 is the intensity of the incident light, σ is absorption cross section at frequency ν , and ϕ is the number of UF₆ molecules that disappear per photon absorbed. Once the above scheme of reactions is assumed, ϕ also represents the number of UF₅ molecules produced per photon absorbed. The value of ϕ depends both on the quantum yield of photodissociation of the excited UF₆ (reaction (2)) and on the competition between reactions (4) and (5). On the basis of cq. (7), the time evolution of the total pressure p turns out to be

$$p = p_{H_2} + p_{HF} + p_{UF_6}$$

= $p_{H_2}^0 + \frac{1}{2} p_{UF_6}^0 \{1 + \exp[-(I_0 \sigma \phi/h\nu)t]\}.$ (8)

Thus the overall pressure p is expected to decay exponentially towards the value $p_{H_2}^0 + \frac{1}{2}p_{UF_6}^0$. Fig. 2 shows a logarithmic plot of curves (a) and (b) in fig. 1, once the experimental asymptotic pressure values were subtracted. The corresponding time decay constants turned out to be $\tau_a = 33.95$ min and $\tau_b = 63.40$ min, respectively. The same value for the decay time constant at 360 nm was obtained from curve (c) in fig. 1 in the case of a 1 1 mixture. From eq. (8) and from the absorption spectrum of UF₆ [6], then, the ϕ values are $\phi_a =$



Fig 2. Logarithmic plot of the curves (a) and (b) of fig 1, once their asymptotic pressure values have been subtracted

1.97 and $\phi_b = 1.42$. The fact that ϕ_a is almost 2 indicates that: (1) UF₆ molecules excited at 360 nm dissociate with a yield that is almost 1; (1) H atoms produced by reaction (3) undergo reaction (4) rather than (5). Reaction (4) was not observed by Parker and Pimentel [7] on a microsecond time scale after flash photolysis of UF₆ in the presence of H₂. Our result can be explained by assuming reaction (4) to occur on a much slower time scale. The competing reaction (5), in fact, is known to be very slow [8]. On the basis of this discussion, from the value of ϕ_b we can conclude that the photodissociation quantum yield after excitation at 400 nm is $\approx \phi_b/2$ = 0.71. No simple explanation has been found for the difference between the experimental asymptotic values of the pressures and those expected from reaction (1).

4. Conclusions

A pressure drop has been observed when irradiating a UF₆ \cdot H₂ mixture both at 360 and at 400 nm. This is an indication that UF₆ dissociates, producing UF₅ and not UF₄. The photodissociation yield turned out to be very high The two excited electronic states of the A- \tilde{X} band have been shown to have different values of this yield.

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