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K. C. Kim and G. M. Campbell

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The absorption spectrum of the PuF_6 photodissociation product in the visible wavelength region

K. C. Kim and G. M. Campbell Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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We report the first spectroscopic observation of the transient photodissociation product following the 248 nm (KrF excimer laser) photolysis of PuF_6 and present its low resolution absorption spectrum in the visible. Although this photoproduct was postulated as the primary reaction intermediate for some time, up to now it has not been detected in the gas phase because of its extreme reactivity and instability.

I. INTRODUCTION

It is generally known that a photon energy greater than 2.5 eV photodissociates PuF_6 molecules. However, very little is known about the product species and states. The difficulty arises because the primary photoproduct, presumably PuF_5 , is rather unstable and has not been observed in the gas phase. The stable photoproduct in bulk photodissociation experiments has been shown to be PuF_4 . A similar molecular system, UF_6 photodissociates at a higher photon energy to yield stable UF_5 and its molecular structure has been studied.¹⁻³ Other photodissociation experiments conducted in low temperature solid matrices showed infrared absorption bands which were attributed to PuF_5 .⁴

In this paper, we report the first gas-phase spectroscopic observation of the transient product species and its complete low resolution absorption spectrum in the visible. The parent molecule PuF_6 has rich absorption features in the visible due to the *f*-*f* transitions among the spin-orbit energy levels^{5,6} of the two 5*f* electrons in the central atom, but the absorptions are vibronically enabled^{7,8} and therefore generally very weak. We find that the photoproduct species has a much stronger, broader absorption features which help us interpret the electronic structure of the product species.

II. EXPERIMENTAL PROCEDURES

The absorption measurement was made by the technique of laser flash photolysis followed by transient absorption measurement of the product species.⁹ The photolysis was done in a static cell (27 cm path length) using the 248 nm (5.0 eV) radiation from a KrF excimer laser (Lumonics). The probe light beam source was a Xe arc. The probe beam and the photolysis beam were coaxial counterpropagating and made totally overlapped inside the cell using a dichroic optical element placed in front of the cell. The dichroic optics reflected the photolysis beam and transmitted the probe radiation. After passing through the cell, the probe beam was dispersed by a 1/4 m monochromator and analyzed by a Reticon diode array detector (Model RL 1728H).

The sweep time of the detector was about 2.0 ms in which time the absorption signal, monitored at a fixed wavelength as a function of time, decayed to a value approximately 50% of the initial signal size at t = 0. The detector signals

were averaged over ten laser pulses using a signal averaging computer (Tektronix Model 7612 Transient Digitizer).

For all measurements, N_2 was added to the photolysis mixture to rapidly cool the photoproducts and to slow down diffusion of the species in and out of the probe beam. The total pressure of the gas mixture was constant at 128 Torr. Partial pressures of PuF_6 were in the range of 0.4–0.8 Torr. The gas mixture was circulated during photolysis and the photolysis laser was operated at 1/4 Hz to allow a sufficient time for equilibration of the photolysis mixture between laser shots. The photolysis volume was small compared to the total volume so that the overall depletion of PuF₆ after ten laser pulses was insignificant. The full sweep of the detector array covered a spectral range of approximately 80 nm. The probe beam intensity varied significantly on both ends of the scan so that we used only the central portion of the detector and constructed the entire spectrum basically in point-bypoint measurement.

III. EXPERIMENTAL RESULTS

A. Transient depletion and absorption measurement

In the present experiment, two kinds of measurements were made. The first set consists of measuring the instantaneous depletion of the PuF_6 concentration with each laser pulse. This was done by setting the probe beam at wavelengths where PuF_6 absorbs. During the laser pulse duration (~20 ns), the transmitted light intensity of the probe beam increases momentarily corresponding to depletion of PuF_6 . Knowing the initial concentration and the absorbance value, the amount of PuF_6 molecules that has been photodissociated can then be calculated from the depletion signal. The photodissociation fraction ranged typically from 15% to 50% within the irradiated volume.

The second set of the experiments consists of measuring changes in the detector signal, a decrease in the transmitted light intensity, in the wavelength region where PuF_6 is transparent to the probe beam or very weakly absorbing. In order to characterize the absorption signal further, we conducted extensive measurements of the absorption signal as a function of the laser energy fluence, PuF_6 concentration, and the probe beam wavelength.

In both sets of the experiments, the signal rise time is fast

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FIG. 1. A low resolution absorption spectrum of the PuF_6 photodissociation product in the gas phase.

within a microsecond (limited by the detection system frequency response) and the signal decays within several tens of milliseconds to their original levels. The depletion signal usually persists much longer than the product absorption signal. This is because there are more reactive channels for the photoproduct which reduce its concentration within the probe beam. The diffusion rates for PuF_6 and PuF_5 should not be very different.

B. Photoproduct absorption spectrum

Figure 1 shows a composite spectrum constructed from the point-by-point measurements in the wavelength region between 500 and 820 nm. At wavelengths shorter than 500 nm the PuF_6 absorption interferes too much, while at wavelengths longer than 820 nm, we are limited by the insufficient detector sensitivity. The spectral resolution in this figure is poor but one observes several distinct absorption features with major peaks at around 680 nm, 720 nm, and possibly at wavelengths longer than 820 nm. Although we have not completed the absorption measurement at wavelengths shorter than 500 nm, our preliminary results indicated that the strong charge transfer bands nearly coincide with the PuF_6 absorption which also complicates the photoproduct absorption measurement.

The amount of the depleted PuF_6 concentration is equated to the initial concentration of the photoproduct. Based on the photodissociation fraction established by measurements of the instantaneous depletion and the laser fluence in the cell, one can estimate the absorption strengths of the product species. At the peak of the 720 nm feature, e.g., the absorption cross section is approximately 1.2 $\times 10^{-18}$ cm².

C. PuF₆ photodissociation in the presence of CF₃H

Identification of photodissociation intermediates can be achieved by studying their reactions with other reactants. Several studies^{10,11} of this kind have been reported on the photodissociation of UF_6 . The presence of hydrocarbons in the photolysis mixtures has been shown to increase the apparent quantum yields of UF_6 photodissociation.

The primary photodissociation reaction of PuF_6 is to



FIG. 2. The PuF_6 photodissociation product signal with (upper curve) and without (lower curve) CF_3H .

produce PuF₅ and F according to

$$PuF_6 \rightarrow PuF_5 + F.$$
 (1)

A host of post photolytic reactions among the primary products follow after reaction (1). Hydrogen-containing molecules react with the F atoms thus preventing the recombination of the primary products. The UF₅ absorption signal with CH₄, e.g., was shown to decay slower than without CH₄.¹⁰

In the case of PuF_6 photodissociation with CF_3H , we do observe the photoproduct absorption behavior as shown in Fig. 2. The following reaction sequence can be postulated:

$$CHF_3 + F \to CF_3 + HF, \qquad (2)$$

$$PuF_6 + CF_3 \rightarrow PuF_5 + CF_4.$$
(3)

The PuF_5 absorption signal with CF_3 H is greatly enhanced over that without CF_3 H. Apparently, reaction (3) accounts for a large fraction of the secondary formation of PuF_5 . The wavelength-dependent absorption features, the absorption signal with the known chemical species and the well established absorption-depletion spectroscopic diagnostic, all considered together, provide a strong support for the positive spectroscopic identification of the PuF_6 photodissociation product.

In summary, we present the experimental results which support the primary photochemical reaction of PuF_6 and report the first spectral information on the PuF_6 photoproduct in the gas phase which definitively identifies the product species.

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