

Laser Chem.
Volume 1(1), October 1982, pp. 1-7
0278-6273/82/0101-0001\$6.50/0
© 1982 harwood academic publishers gmbh
Printed in the United States of America

COMMUNICATIONS

“Single Shot” Laser Multiphoton Ionization Detection of UF₅ Following the 266 nm Photodissociation of UF₆^a

J. S. CHOU, D. SUMIDA, M. STUKE^b and C. WITTIG^c

University of Southern California, SSC 404, Mail Stop 0483, Los Angeles, California 90089 USA

(Received May 25, 1982; in final form June 11, 1982)

By using laser multiphoton ionization and a time-of-flight mass filter, we have detected nascent UF₅ from the 266 nm laser photodissociation of UF₆, following a single laser firing. The method can be used to monitor these species under conditions wherein isotopically selective excitation is responsible for the dissociation of UF₆.

INTRODUCTION

The detection of free radicals by laser multiphoton ionization (MPI) is an attractive application of this technique, particularly under collision free conditions, since the method is extremely sensitive and is often state specific. It is also possible to detect species which absorb radiation but do not fluoresce, since the absorption can define a signature which is then manifest in the production of ions.^{1,2} In this communication, we report the results of experiments which address these issues for the technologically important case of UF₅. Despite its significance in laser isotope separation

^aResearch supported by the U.S. Department of Energy.

^bPermanent Address: Max-Planck-Institut für biophysikalische Chemie, Postfach 968, 3400 Göttingen, Federal Republic of Germany.

^cPerson to whom correspondence should be addressed.

schemes, the diagnostics available for monitoring the nascent UF_5 which derives from the photodissociation of UF_6 are primitive,^{3,4} with the exception of the recently devised method involving surface ionization of UF_5 in the presence of UF_6 .⁵ In a previous publication, we demonstrated that UF_5 could be ionized via MPI in the presence of large backgrounds of UF_6 , and we pointed out that this method of detection allows the isotopic composition of the UF_5 to be determined.⁶ We also pointed out that by using a time-of-flight (TOF) mass filter, it would be possible to obtain such information very rapidly, allowing important parameters to be monitored continuously during experiments. We have now extended our experiments to include a TOF mass filter, and the use of tunable dye laser radiation for MPI of the nascent UF_5 photofragments, following the 266 nm photodissociation of UF_6 . The sensitivity is improved by at least two orders of magnitude over our previous results, and the entire MPI mass spectrum can be obtained following a single laser firing. Signal averaging will produce very high signal to noise ratio (S/N) in just a few seconds. This is the most promising diagnostic for monitoring UF_6 dissociation in an isotopically selective environment that has been developed to date.

EXPERIMENTAL

The experimental arrangement is straightforward, and will be described in detail in a future publication. Both photodissociation and MPI are done with radiations which derive from a Quanta Ray Nd:YAG laser system. In the present experiments, we use the 266 nm 4th harmonic from the Nd:YAG laser to prepare nascent species which are then acted on with the dye laser radiation. The lasers overlap in an interaction region located between mesh electrodes, and positive ions are accelerated toward a 2 mm dia. hole which is the entrance to the field free region of the TOF mass filter. The mesh electrode system consists of two regions in series. One region is 0.95 cm long and the potential difference between meshes is 700 V, and in the other region the meshes are 1.0 cm apart and the potential difference is 4000 V. The ions are formed in the region of low electric field, and pass through the region of higher electric field on the way to the drift tube. The counterpropagating 266 nm and dye laser radiations are both focused, with 50 and 30 cm focal length lenses respectively, in order to prevent radiation from striking surfaces near the accelerating grids. The 266 nm radiation is attenuated ($\sim 50 \text{ mJ cm}^{-2}$) in order that no more than

a few percent of the UF_6 molecules are dissociated, as in our previous report.⁶ An optical delay of 20 ns between the 266 nm and dye laser pulses insures that the action of these two pulses is sequential, and that multiphoton processes involving the simultaneous annihilation of 266 nm and dye laser photons do not occur.

Ions which enter the field free region travel 1 m and are then detected with a tandem microchannel plate array (Varian). Signals from the plates are amplified, digitized (Biomation 8100), and either stored or averaged, depending on the experiment. The TOF/detection region is pumped separately from the sample chamber, and is maintained at $\sim 10^{-7}$ Torr during experiments.

RESULTS

Using the arrangement described above, it was possible to reproduce the results of ref. 6, but under experimental conditions which seriously compromised the performance of the microchannel plate detectors. These detectors are adversely affected by high pressures of UF_6 vapor (10^{-5} Torr), and the ionization efficiency at 532 nm is quite low, therefore requiring more differential pumping than was possible with our arrangement. Even with 100 mJ of 532 nm radiation, MPI signals were small and required uncomfortable amounts of UF_6 vapor in the sample chamber. We were thus led to peruse shorter wavelengths for MPI, while trying to maintain the same high discrimination against undesirable MPI of UF_6 which we achieved in our earlier work.⁶ All of the results reported below were obtained using low energy tunable dye laser radiation (2-3 mJ, 433-474 nm), which proved quite superior to 532 nm radiation for ionizing the nascent photofragments. We estimate that the ionization efficiency at the shorter wavelengths exceeds that at 532 nm by approximately two orders of magnitude.

Typical experimental results are shown in Figure 1 for "single shot" as well as averaged mass spectra, taken with 3 mJ of 450 nm ionizing radiation. Averaging 256 signals requires less than half a minute, and produces very high S/N spectra. In Figure 1, the resolution is 3 amu, and this is not acceptable for monitoring ^{235}U in the presence of large concentrations of ^{238}U . However, we have recently improved the resolution in our instrument by 50%, and others have reported resolution of 200:1 at the 10% peak height points,^{7a} and 3500 with a mass reflectron TOF spectrometer.^{7b}

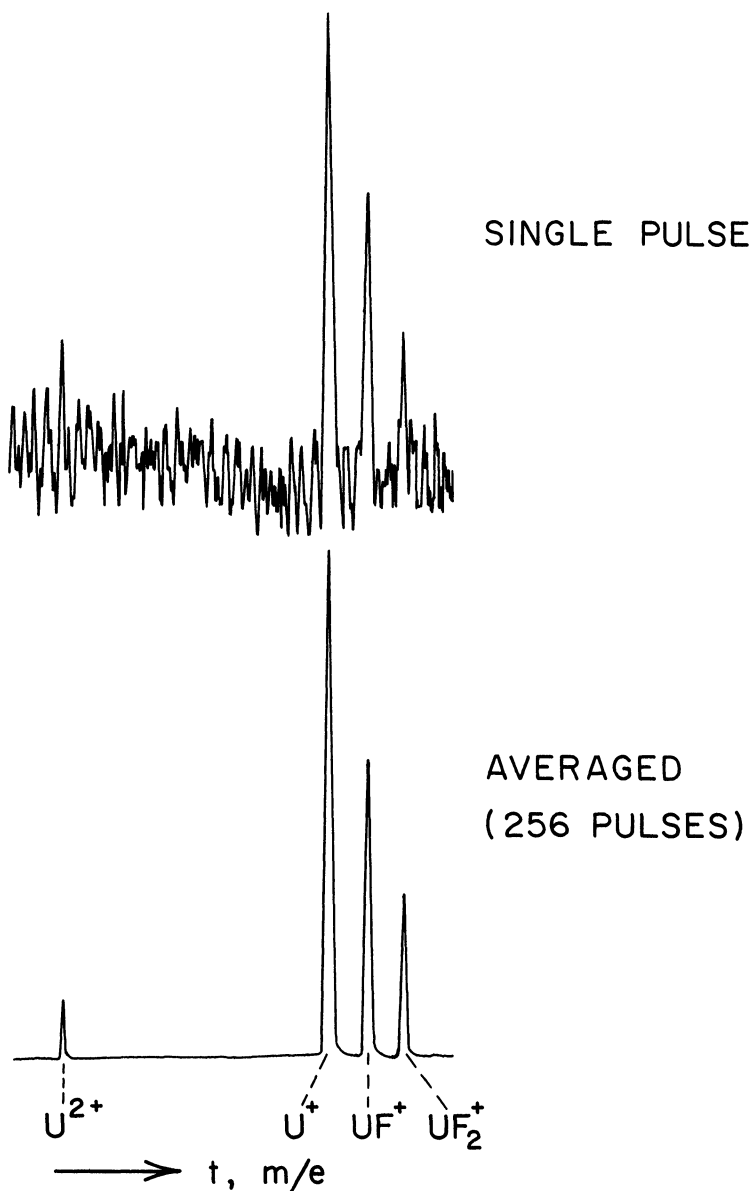


FIGURE 1 TOF mass spectra following MPI of the nascent photofragments from the 266 nm photodissociation of UF_6 . There is no detectable signal with either laser blocked, and there is a 20 ns delay between the onsets of the 266 and 450 nm pulses. The pressure in the sample chamber is 10^{-5} Torr, and the laser energies at 450 and 266 nm are 3 and <0.5 mJ respectively.

Therefore we believe that $^{235}\text{UF}_n^+$ can certainly be monitored in the presence of $^{238}\text{UF}_n^+$ with enriched samples, and in the case of in situ computer analysis as well as calibration samples, unenriched samples should also be possible. The mass spectra reported here are quite similar, but not identical, to those reported earlier. Since the cracking patterns for MPI excitation depend on the wavelength and intensity of the ionizing radiation, this behavior is to be expected.⁸ Although the (S/N) for a single laser firing was not particularly high in the present experiments, we are confident that modest technological changes can improve this markedly. We estimate that only $\sim 10^{-3}$ of the nascent photofragments are ionized via MPI under the present experimental conditions,⁹ and this can be improved by using higher energy laser pulses. The laser energy used for MPI can be increased until parent ionization begins, at which point further increases in the intensity of the ionizing radiation are pointless for diagnostic purposes. The use of a pulsed supersonic expansion nozzle operating synchronously with the lasers enables high densities to be achieved under collision free conditions, and we hope to include this in our apparatus in the future. Also, another stage of differential pumping would be beneficial to the detection system.

The nascent UF_5 photofragments produced by the 266 nm photodissociation of UF_6 can contain as much as 1.5 eV of vibrational energy, and there is no simple way to measure this vibrational energy directly. The present work is concerned with obtaining an ion signal, *regardless of the ionic species*, which derives from nascent UF_5 , and therefore UF_2^+ is as useful as UF_5^+ insofar as their UF_5 parentage is concerned. The UF_n^+ ($n \leq 2$) which we observe is produced by ionization, and also by fragmentation processes which involve neutrals and/or ions, and determining the precise pathways which lead to UF_n^+ ($n \leq 2$) is an arduous task.

Data which were qualitatively similar to those shown in Figure 1 were also obtained using 433 and 474 nm ionizing radiation. In all cases, the ionizing radiation was < 3 mJ, and the signals increased markedly with the intensity of the ionizing radiation. As before, there was no detectable signal with either the 266 nm or ionizing radiation blocked, showing that ions formed by the direct dye laser MPI of UF_6 are negligible.

With larger 266 nm fluences, it was possible to produce ions in addition to neutrals, and to further act on this ensemble of neutral and ionic species with dye laser radiation. A typical result from such an experiment, under single shot conditions, is shown in Figure 2 for the case of 433 nm dye laser radiation. As before, there is no MPI using 433 nm radiation alone.

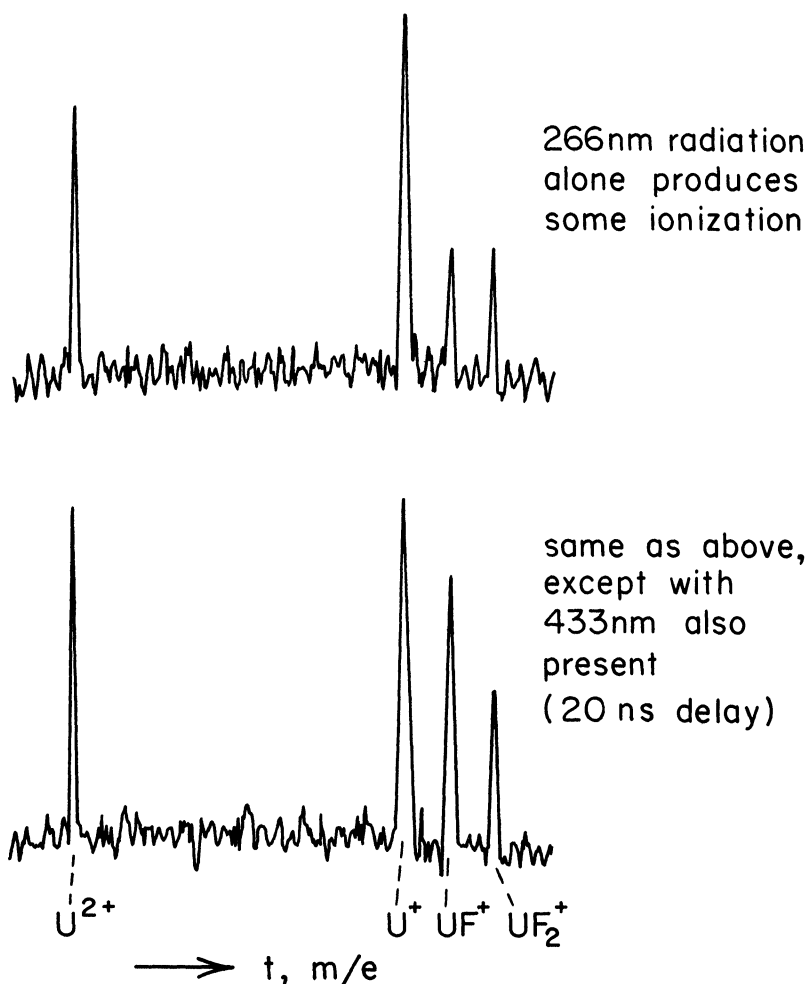


FIGURE 2 TOF mass spectra for the case when the 266 nm fluence is high enough to produce some ionization in the absence of the dye laser radiation. The 433 nm radiation may now fragment the ions as well as ionize the neutrals (see text for details).

Clearly, there are ions formed by MPI at both 266 and 433 nm. The ion distribution following 433 nm irradiation is the result of ionization and fragmentation at both 266 and 433 nm, and it is difficult to determine unambiguously the respective roles of 433 nm MPI of neutrals, and 433 nm fragmentation of the ions already present. This difficulty can be over-

come by delaying the 433 nm radiation with respect to the 266 nm radiation. With suitable delay, the ions deriving from 266 nm MPI will have been swept out of the interaction region before the 433 nm radiation arrives, thereby ionizing the remaining neutrals.¹⁰ A convenient, adjustable delay between the two groups of ions (e.g. 500 ns) will separate species in the TOF spectrum and allow the separate groups of ions to be determined without resort to messy manipulations of the data. Such experiments will be carried out in the future in our laboratory.

Acknowledgment

The authors acknowledge useful discussions with D. Cox and Y. Haas, and the expert technical assistance of E. Dietl and H. Lloyd.

References

1. a) P. M. Johnson, M. R. Berman, and D. Zakheim, *J. Chem. Phys.* **62**, 2500 (1975). b) *ibid.*, **64**, 4683 (1976). c) *ibid.*, **68**, 3644 (1978).
2. C. H. Chen, G. S. Hurst, and M. G. Payne, *Chem. Phys. Lett.* **75**, 473 (1980), and references cited therein.
3. E. Borsella, F. Catoni, and G. Freddi, *J. Chem. Phys.* **73**, 316 (1980).
4. K. C. Kim, R. Fleming, D. Seitz, and M. Reisfeld, *Chem. Phys. Lett.* **62**, 61 (1979).
5. P. Rabinowitz, private communication.
6. M. Stuke, H. Reisler, and C. Wittig, *Appl. Phys. Lett.* **39**, 201 (1981).
7. a) D. Proch, D. M. Rider, and R. N. Zare, *Chem. Phys. Lett.* **81**, 430 (1981). b) B. A. Mamyrin, V. I. Karataev, D. V. Shmikk, and V. A. Zagulin, *Sov. Phys. JETP* **37**, 45 (1973).
8. a) R. B. Bernstein, *J. Phys. Chem.* **86**, 1178 (1982). b) U. Boesl, H. J. Neusser, and E. W. Schlag, *J. Chem. Phys.* **72**, 3034 (1980). c) T. E. Carney and T. Baer, *J. Chem. Phys.* **75**, 4422 (1981).
9. G. L. DePoorter and C. K. Rofer-DePoorter, *Spectrosc. Lett.* **8**, 521 (1975).
10. R. S. Pandolfi, D. A. Gobeli, and M. A. El-Sayed, *J. Phys. Chem.* **85**, 1779 (1981).