

Unimolecular fragmentation kinetics by multiphoton ionization

D. PROCH*, D.M. RIDER and R.N. ZARE

Department of Chemistry, Stanford University, Stanford, CA 94305 (U.S.A.)

The multiphoton ionization spectra of aniline ($C_6H_5NH_2$) and its perdeutero analog were investigated as a function of laser wavelength (266 - 300 nm) using a time-of-flight mass spectrometer. The appearance of a broad asymmetrically distorted peak at $m/e = 66$ is interpreted to be the slow fragmentation of the parent ion



from which a unimolecular decomposition rate is estimated to be approximately $2 \times 10^6 \text{ s}^{-1}$.

This research was supported in part by the U.S. Air Force Office of Scientific Research under Grant AFOSR-81-0053 and by the U.S. Army Research Office under Grant DAAG-29-80-K-0097.

* Permanent address: Max-Planck-Institut für Quantenoptik, 8046 Garching, F.R.G.

Multiphoton ionization electron spectroscopy of organic molecules

Y. ACHIBA, K. SATO, K. SHOBATAKE and K. KIMURA

Institute for Molecular Science, Myodaiji, Okazaki 444 (Japan)

Information on kinetic energies of photoelectrons ejected by multiphoton ionization (MPI) is very important for understanding the mechanisms of formation of fragment ions. In this paper we report some results obtained from kinetic energy measurements of photoelectrons ejected from benzene by four-photon ionization. In the present experiment, an Nd-YAG-pumped dye laser (Quanta Ray DCR-1A, PDA-1) was used to ionize effusive benzene molecules through the resonant four-photon process via B_{2u} (e.g. 14_0^1 and $14_0^1 1_0^{(1)}$) intermediate states. Kinetic energy measurements on the photoelectrons were carried out with a time-of-flight (TOF) technique. From the TOF spectra thus obtained it was found that only one peak appears, which corresponds to the electron kinetic energy given by $E = 4h\nu - I$, where ν is the dye laser frequency used and I is the first adiabatic ionization energy of benzene. The present results therefore indicate that in the four-photon ionization of benzene $C_6H_6^+$ ions are first produced and

the subsequent photon absorption results in the production of fragment ions, as recently observed by Zandee and Bernstein [1]. The results are also consistent with those indicated from an MPI mass spectrometric study by Boesl *et al.* [2].

1 Zandee and Bernstein, *J. Chem. Phys.*, 71 (1979) 1359.

2 Boesl, Neusser and Schlag, *J. Chem. Phys.*, 72 (1980) 4327.

Two-photon excitation of H₂O, HCN and CS₂ with a KrF laser (248 nm)

R.J. DONOVAN, C. FOTAKIS, M. MARTIN and A. HOPKIRK

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh (Gt. Britain)

UV multiphoton excitation with intense laser sources allows access to *highly* excited (Rydberg) molecular states which can undergo dissociation to yield an interesting variety of excited state products. In the work presented, photofragment fluorescence after two-photon excitation of H₂O, HCN and CS₂ with a KrF laser (248 nm) is discussed. For H₂O it is shown that OH radicals are formed in the A ²Σ⁺ state and that a strong rotational population inversion is produced. Similar results for HCN and CS₂ are also presented. The results are compared with those for single-photon excitation in the vacuum UV region at 124 nm.

193 nm photodissociation of CS₂ and probing of the CS fragment

JAMES L. BUTLER

U.S. Naval Research Laboratory, Code 6110, Washington, DC 20375 (U.S.A.)

Single- and multiple-photon processes are identified in the 193 nm laser photolysis of CS₂. A partial internal energy distribution of the CS(X ¹Σ⁺) fragment was measured by dye-laser-induced fluorescence after the single-photon photolysis of CS₂. The 193 nm multiple-photon-induced emission of the CS(A ¹Σ⁺ → X ¹Σ⁺) system was studied using a narrow-bandwidth (about 0.1 Å) tunable ArF excimer laser. This unique spectroscopic probing allows the determination of the ground state of CS(X ¹Σ) over a 45 000 cm⁻¹ range of vibronic bands from $v'' = 0$ to $v'' = 45$.