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

$$C_6H_7N^+ \rightarrow C_5H_6^+ + HCN$$

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

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