PHOTOFRAGMENTATION OF THE FLUORENE CATION: NEW EXPERIMENTAL PROCEDURE USING SEQUENTIAL MULTIPHOTON ABSORPTION AND ENERGY-DEPENDENT RATE CONSTANT FOR THE H-LOSS CHANNEL.

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The Polycyclic Aromatic Hydrocarbons (PAHs) could be responsible for the emission of the characteristic mid-infrared emission bands observed in the interstellar medium. In order to validate this conjecture, the competition between fragmentation and IR emission has to be studied in detail. This paper focusses more specifically on the dissociation mechanism of energetically photo-excited PAH cations.
We propose here a new experimental method capable to determine the evolution of the dissociation rate constant within a wide range of initial internal energy. The hydrogen-loss channel, induced by sequential multiphoton absorption, of the vapor phase fluorene cation was investigated using a pulsed supersonic molecular beam, a time-of-flight mass spectrometer and pulsed nanosecond lasers. The fluorene cation was prepared by resonantly enhanced two-photon ionization.
A particular attention was focused on the data analysis techniques. A model-free determination of the evolution of the dissociation rate constant in a wide energy range was obtained by solving numerically the adequate set of coupled differential kinetic equations. The free fit of these rate constants is close to the photo-thermo-dissociation statistical model, but shows a discrepancy with the Rice, Ramsperger and Kassel model mainly at high energy. The resulting activation energy is in agreement both with that deduced from the *ab initio* calculations and from a newly developed tight-binding potential energy surface.

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