Measurements of dissociation rates of naphthalene and azulene cations close to threshold energy.

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There is broad consensus that some midinfrared fluorescence emissions observed in the photodissociation regions (PDRs) of interstellar clouds originate from polycyclic aromatic hydrocarbons (PAH). In PDRs, molecules are ionized and energized by intense radiation fields emitted from nearby stars. Astrophysical models describing PAH evolution require precise evaluation of the competition between dissociation and radiative stabilization as a function of internal energy. Depending on internal energy, isomerization may also play a key role in both the nature of dissociation processes and their lifetimes. Most recent studies [1] rely on statistical models that require input parameters such as dissociation energy, transition state energy, and the preexponential factor, which are often poorly constrained for complex PAHs. In the present work, we performed measurements of the dissociation rates of the naphthalene and azulene cations at internal energy. They were produced at a temperature close to ambient, stored in the Mini-Ring electrostatic storage ring [2], and irradiated with an OPO laser at various near-UV wavelengths. Two-photon absorption is needed to dissociate these molecular ions at ambient temperature and in this photon energy range (3.3 to 4.6 eV). Three-photon absorption could be excluded as the subsequent dissociation would be too fast. Therefore, after two photon absorption, the internal energy distribution was expected to peak close to two-photon energy, leading to exponential decay from which it would be easy to extract dissociation rates. However, as shown in Figure 1, the observed decay contained several contributions (up to four) that could be attributed to the presence of both naphthalene and azulene isomers in the stored beam and to fast radiative cooling by recurrent fluorescence (RF) that can shift the internal energy by a fixed amount. By scanning the photon energy, we could measure dissociation rates k_d as a function of internal energy and compare these $k_d(E)$ curves with statistical models (RRKM or Arrhenius) over a 2.5 eV energy range starting from ~6.6 eV. The results show a good agreement at high energy, while an observed deviation at low energy is attributed to RF. RF is found to be competitive and to quench dissociation at internal energy below ~7.2 eV.

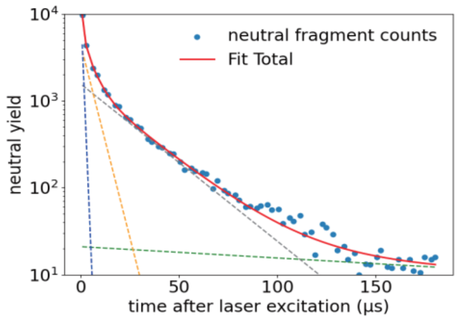

Figure 1. dots: Neutral yield resulting from two photon (340 nm) absorption in naphthalene cations stored in Mini-Ring. full line: Fit by a sum of four exponential decays.

[1] Lee Jason W. L. et al., *J. Chem. Phys.* 158 174305 (2023)
[2] Martin S et al., *Phys. Rev. Lett.* 110 063003 (2013)
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