Near threshold statistical dissociation of quinoline cations using action spectroscopy in cryogenic storage

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Synopsis Quinoline, a polycyclic aromatic nitrogen heterocycle (PANH), is of interest in astrophysical chemistry due to its potential role in the formation of complex organic molecules. This study explores the photodissociation dynamics of quinoline cations through experiments conducted at the cryogenic ion storage ring DESIREE, Stockholm University. The observed wavelength-dependent decay rates, possible two-photon processes, and signatures of recurrent fluorescence challenge established interpretations and raise fundamental questions about conventional RRKM theory and the underlying dissociation mechanisms.

Polycyclic aromatic nitrogen heterocycles (PANHs), and quinoline in particular, represent very important type of aromatics in astrophysical chemistry. The detection of Aromatic Infrared Bands (AIBs), attributed to polycyclic aromatic hydrocarbons (PAHs) and their clusters, together with the confirmed identification of nitrogen-containing aromatics including benzonitrile, cyanonaphthalene, cyanopyrene, and cyanocoronene, demonstrates their abundance and widespread distribution throughout the interstellar medium (ISM). Current hypotheses on the origin of these cyclic species highlight a combined association and dissociation processes as central mechanisms. A critical stage in chemical evolution involves the rapid fragmentation of molecules, generating reactive intermediates that drive subsequent pathways. Protoplanetary discs provide a key example: energetic radiation—ultraviolet, X-rays, and cosmic rays—penetrates to varying depths depending on opacity and radiation type, initiating complex chemistry. Likewise, high-energy charged particles and solar UV radiation catalyze reactions in planetary atmospheres, such as Titan, ultimately leading to the formation of complex organics.

Given the astronomical relevance of PANHs, their statistical dissociation dynamics warrant detailed investigation. Quinoline has therefore been the subject of PEPICO/VMI studies over the past five years, with particular attention to dissociation channels involving the loss of HCN, HNC, C_2H_2, and $HCNH$—species that play crucial roles in the evolution of larger organics in astrophysical environments [1, 2]. Structural calculations combined with RRKM modeling have been employed to complement these experiments. However, the substantial kinetic shift inherent to conventional approaches hindered validation of RRKM predictions. To address this, experiments on quinoline cations were conducted at cryogenic double ion storage ring DESIREE at Stockholm University, designed to minimize kinetic-shift effects and probe statistical decay near threshold.

Unexpectedly, the results diverged sharply from expectations and established understanding. First, the observed decay rates as a function of excitation wavelength directly challenge several well-established findings. Second, if the decay proceeds via two-photon processes, this implies highly specific and complex excited-state dynamics in quinoline cations. Third, the evolution of decay rates across laser shot sequences revealed signatures of recurrent fluorescence. Consequently, an experiment originally intended to confirm the applicability of conventional RRKM theory now raises fundamental questions about the established mechanisms of quinoline ion photodissociation.

References

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