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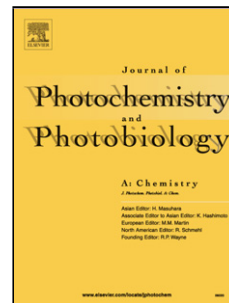
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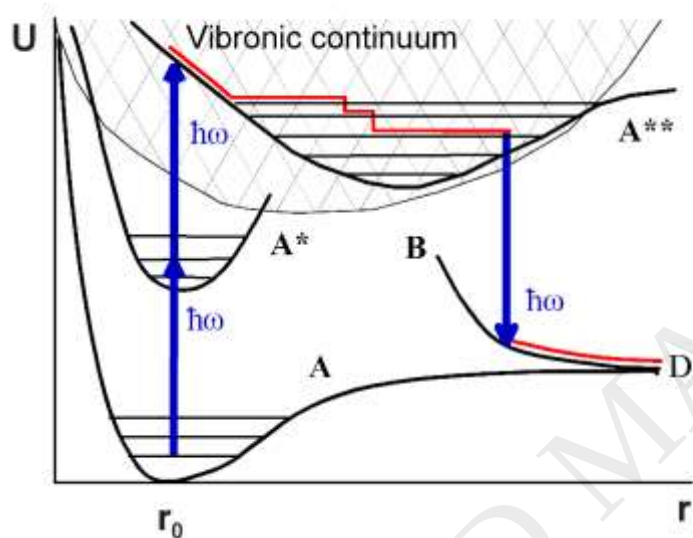
Photolysis of adsorbed benzene at 248 nm

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Graphical Abstract



Highlights

- Photolysis of adsorbates via electronic states at elongated bond lengths.
- Three dissociation channels were found in adsorbed benzene at 248 nm.
- One and the same three-photon excitation mechanism provided all fragmentations.
- No similarity was observed in adlayer and gas benzene photolysis.

Aromatics are widely detected in the interstellar media, although the origin of their photostability is not clear. Gaseous molecules should be decomposed by cosmic UV or VUV radiation and little is known about the photochemistry of adsorbed aromatics. In this study, the channels and mechanisms of KrF laser-induced dissociation of benzene condensed on cooled fused silica have been studied using mass spectrometry. The release of H atoms (along with C_6H_5), C_2H_2 , and C_2H_4 from the substrate surface indicates three dissociative pathways, including the last two as the aromatic ring opening. All these photoprocesses occurred to be controlled by interaction with three KrF laser photons ($\lambda=248$ nm). The general mechanism of UV photodissociation of adsorbed benzene includes its two-photon excitation into the vibronic continuum, followed by transitions into repulsive states using

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