Predissociation of High-Lying Rydberg States of Molecular Iodine via Ion-Pair States

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The photodissociation of the two-photon excited molecular iodine in the energy range 73500-74500 cm^{-1} covering the bands of high-lying *gerade* Rydberg states $[^2\Pi_{1/2}]_c6d;0_g^+$ and $[^2\Pi_{1/2}]_c6d;2_g$ has been studied with velocity map imaging technique. The ion signal was dominated by the atomic fragment ion I^+. Up to 5 dissociation channels yielding I^+ ions with different kinetic energy were observed when the I_2 molecule was excited within discrete peaks of Rydberg states and their satellites in this region. One of these channels gives rise to images of I^+ and I^- ions with equal kinetic energy indicating predissociation of I_2 via ion-pair states. The contribution of this channel was up to about 50% of the total I^+ signal. The four other channels correspond to predissociation via lower lying Rydberg states giving rise to excited iodine atoms providing I^+ ions by subsequent one-photon ionization by the same laser pulse. The ratio of these channels varied from peak to peak in the spectrum but their total ionic signal was always much higher than the signal of (2+1) REMPI of I_2, which was previously considered to be the origin of ionic signal in this spectral range. The first-tier $E0_g^+$ and $D'2_g$ ion-pair states are concluded to be responsible for predissociation of Rydberg states $[^2\Pi_{1/2}]_c6d;0_g^+$ and $[^2\Pi_{1/2}]_c6d;2_g$, respectively. Further predissociation of these ion-pair states via lower lying Rydberg states gives rise to excited $I(5s^25p^46s^1)$ atoms responsible for major part of ion signal. The isotropic angular distribution of the photofragment recoil directions observed for all channels indicates that the studied Rydberg states are long-lived compared with the rotational period of the I_2 molecule.

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