Supramolecular photoprocesses in van der Waals complexes of iodine X-I_2: A velocity map imaging investigation

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Appearance of a supramolecular intense absorption band was earlier observed in many iodine-containing media. The weakly bound complexes of the type X-I_2 were supposed to be responsible for this absorption which in turn was supposed to be governed by transition in a charge-transfer state of the complex [1]. In the presented work we investigate experimentally the nature of the excited electronic states of the complex X-I_2 responsible for supramolecular absorption band as well as a mechanism of photodissociation arising from this absorption. Our earlier studies of complexes of oxygen X-O_2 [2,3] showed that application of the technique of velocity map imaging provides very detailed information about the nature of elementary photoprocesses in van der Waals molecular complexes. In the presented work the photodissociation of several van der Waals complexes of iodine X-I_2 (X=I_2, C_2H_4, C_6H_6) in a molecular beam has been studied with the use of this technique. Examples of the images are presented in Fig. 1. Measured energy distribution and angular anisotropy of the channels observed together with the known structure of the complexes X-I_2 allow us to identify the nature of the excited states responsible for supramolecular band in these complexes. Resolved vibrational structure of the image allows us also to make conclusions about location of the "conical intersection" responsible for appearance of excited and translationally "hot" molecules of a complex.

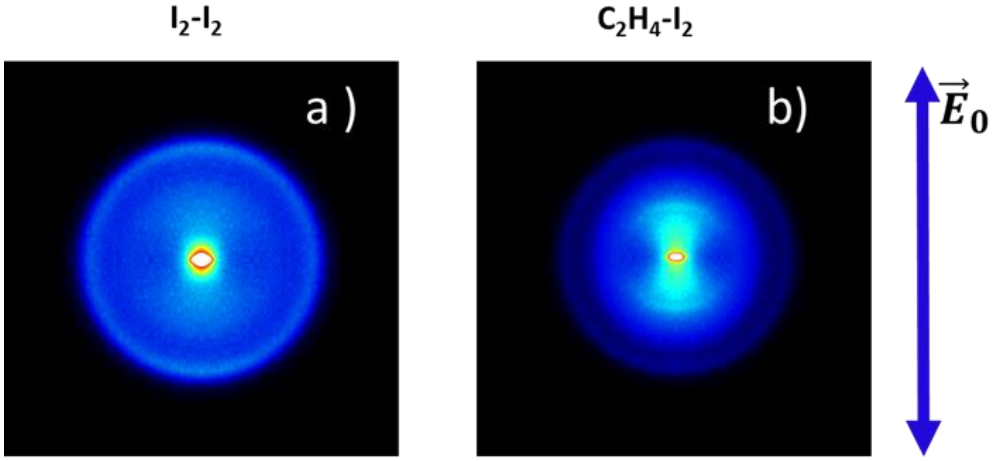

Figure 1. Velocity map images of I_2^+ ions provided by photoionization of I_2 molecules arising from UV-photodissociation of van der Waals complexes X-I_2 (X=I_2, C_2H_4). Double-sided arrow indicates direction of laser radiation polarization.

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