The formation of chemically bonded argon via photoexcitation of Ar-I₂ van der Waals complex

Bogomolov A.S.,^{1,2*} Dozmorov N.V.,¹ Kochubei S.A.,³ Baklanov A.V.^{1,2}

*bogomolov.kinetic@gmail.com

¹ Voevodsky Institute of Chemical Kinetics and Combustion, Russia

² Novosibirsk State University, Russia,

³ Rzhanov Institute of Semiconductor Physics, Russia

Van der Waals complex Ar-I₂ is a model system for a study of the influence of weakly bonded molecular environment on the photochemistry and photophysics of molecules. Earlier studies of this complex reported in literature were focused only on processes including transition to the first excited states of iodine molecule. In the current work of the photo-induced processes following the excitation of the complex Ar-I₂ into high-lying Rydberg states and ion-pair states are investigated. The mechanism of the photodissociation of free iodine molecules excited to the high-lying Rydberg states ($E\approx 9.2 \text{ eV}$) has been studied earlier with the use of velocity map imaging technique.¹ It was shown that excitation of I₂ into high-lying Rydberg states is followed by the formation of ion pair state I₂(Ry) \rightarrow I⁺+I⁻ as well as of all energetically accessible Rydberg states of iodine atom I₂(Ry) \rightarrow I⁺H(Ry). Femtosecond dynamics of these processes was also investigated.² In present work we have been focused on the processes of excitation of iodine in van der Waals complex Ar-I₂ in the same spectral range. Ar-I₂ van der Waals complex has been generated in supersonic molecular beam. Ions Ar⁺ and ArI⁺ were observed in a mass-spectrum

at Ar-I₂ van der Waals complex photoexcitation by laser radiation with wavelength ~270 nm (hv≈4.6 eV). It should be noted that ionization potential of argon is 15.7 eV that requires four photons of radiation used. The four-photon ionization of free Ar atoms is not possible in our experimental condition (nanosecond laser with pulse energy about 1 mJ). Velocity map of Ar^+ (see fig. 1) have rings as in case of diatomic molecule dissociation. It means that Ar⁺ is formed from photodissociation of parent ArI⁺ ion where argon ion is covalently bound. The photon energy dependence of the channels giving rise to Ar⁺ ions with different kinetic energy has been also investigated. The mechanism of covalently bound Ar⁺ ions formation is suggested.³

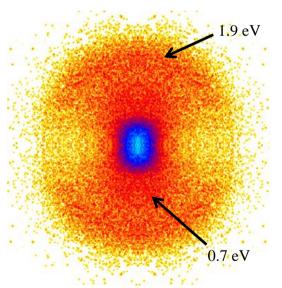


Figure 1: Velocity map image of Ar⁺ arising from complex

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