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Research paper

The HeI_2(ion-pair states) van der Waals complexes

V.V. Baturo, S.S. Lukashov, S.A. Poretsky, A.M. Pravilov *, A.I. Zhironkin

Department of Physics, Saint-Petersburg State University, SPbSU, 7/9 Universitetskaya nab., St. Petersburg 199034, Russia

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ABSTRACT

The *T*-shaped $HeI_2(E0_g^+)$ van der Waals complexes populated in the $HeI_2(E,v_E = 0–2,n_E = 0 \leftarrow B,19, n_B = 0 \leftarrow X,0,n_X)$ excitation pathway have been studied. Analysis of the luminescence excitation spectra as well as the $I_2(E0_g^+ \rightarrow B0_u^+, D0_u^+ \rightarrow X0_g^+$, and $D'2_g \rightarrow A'2_u)$ luminescence spectra themselves has been carried out. It has been shown that the $I_2(D \rightarrow X$, and $D' \rightarrow A')$ luminescence is due to $HeI_2(E \leftarrow B)$ transitions with subsequent electronic predissociation. We have determined dissociation energies of the $HeI_2(E,v_E = 0–2)$ complexes, vibrational populations of the *E*, *D* states and branching ratios of vibrational and electronic predissociations. One can suppose that luminescence of the $HeI_2(E,v_E = 0,n_E = 0)$ complexes occurs.

1. Introduction

Investigation of spectroscopic characteristics and dynamics of rare gas-diatomic halogen van der Waals (vdW) complexes, HeI_2 in particular, has a long history (see [1–15] and references) since pioneering work of R.E. Smalley, D.H. Levy and L. Wharton published in 1976 [16] and subsequent works [17,18]. These complexes have proven to be theoretically tractable model systems for understanding weakly-bound coupling in molecular species and unimolecular reaction dynamics. Dissociation energies, lifetimes, quantum yields of luminescence of vibrational predissociation products of the electronically excited valence state vdW complexes, as well as frequencies of vdW modes have been determined experimentally [1–3,5,6,9,11–13,15]. Detailed theoretical analysis of potential energy surfaces of the complexes and their dynamical behavior has been carried out, also (see [1,3,4–10,14] and references therein).

The HeI_2 is the simplest objects for *ab initio* calculations among the $RgHal_2$ complexes. Therefore, valence state $HeI_2(X0_g^+$ and $B0_u^+)$ complexes draw theoreticians (see [1,4,6–8,10,14]. The data obtained in these works have been compared with experimental data [6,13,16–18].

Meanwhile, ion-pair (IP) states of iodine molecules provide a more promising system for studies on dynamics in vdW complexes than the $I_2(B)$ one. It is due to the fact that IP states are arranged in four narrow manifolds (tiers), the $D'2_g$, $\beta 1_g$, $D0_u^+$, $E0_g^+$, $\gamma 1_u$, and $\delta 2_u$, in order of increasing T_e in the first tier, for example. Their similar potential energy curves form a very dense rovibronic structure [19]. Nevertheless, experimental data on the $HeI_2(E)$ have been presented in one work [6], only, and only one theoretical work has been devoted to studies on this state [20].

Very recently, we have studied the $ArI_2(E)$ vdW complexes [21]. We have observed the $I_2(E \rightarrow B)$ and $I_2(D \rightarrow X$, $\beta \rightarrow A1_u$ and $D' \rightarrow A'2_u)$ luminescence and shown that luminescence occurs due to transitions in the vdW complex, $ArI_2(E \leftarrow B)$. We have determined the ω_e, $\omega_e x_e$ spectroscopic constants for the stretching vdW mode, dissociation energy of the Ar + $I_2(E,v_E = 0–3)$ complexes and estimated their equilibrium Ar-$I_2(E)$ distance. And finally, we have determined vibrational population distributions of the $I_2(E, D, \beta, D')$ states.

In this letter, we report on the study of the $HeI_2(E)$ vdW complexes. We have observed the $I_2(E \rightarrow B)$, $I_2(D \rightarrow X)$ and $I_2(D' \rightarrow A')$ luminescence and shown that luminescence from the *D* and *D'* states occurs because of transitions in *T*-shaped vdW complexes, $HeI_2(E \leftarrow B)$. We have determined vibrational populations of the *E* and *D* states and branching ratios of the $HeI_2(E,v_E = 0–2,\ n_E = 0)$ vibrational and electronic predissociations (VP and EP, respectively). One can suppose that luminescence of the $HeI_2(E,v_E = 0, n_E = 0)$ complexes occurs.

2. Experimental

The experimental setup and procedure of measurements and calculations used have been described in [21] (see [22,23] and references, also). Briefly, a He (backing pressure, $p_{He} = 40$ atm, typically) was passed via bubbler packed with mixture of iodine crystals and Teflon facing heated up to 70 °C (iodine vapor pressure was ~6 Torr). The $HeI_2(X0_g^+)$ vdW complexes were formed in pulsed supersonic jet expansion in a molecular beam chamber.

* Corresponding author.
E-mail address: a.pravilov@spbu.ru (A.M. Pravilov).

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