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The ArI_2(ion-pair states) van der Waals complexes

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ABSTRACT

The $ArI_2(E0_g^+)$ van der Waals complexes have been observed and studied for the first time. Analysis of the luminescence excitation spectra as well as luminescence spectra themselves in the spectral ranges, where the $I_2(E0_g^+ \rightarrow B0_u^+$, $D0_u^+ \rightarrow X0_g^+$, $\beta 1_g \rightarrow A1_u$ and $D'2_g \rightarrow A'2_u)$ transitions can occur, has been carried out. It has been shown that the $I_2(D \rightarrow X, \beta \rightarrow A$ and $D' \rightarrow A')$ luminescence is due to $ArI_2(E \leftarrow B)$ transitions with subsequent predissociation. We have determined the spectroscopic parameters of the $ArI_2(E,\nu_E = 0–3)$ complexes.

It has been shown that rate of vibrational predissociation is ~10 times less than total rate of the $ArI_2(E,\nu_E = 0–3) \rightarrow Ar + I_2(D, \beta, D')$ electronic predissociation.

1. Introduction

Spectroscopic characteristics and dynamics of rare gas-diatomic halogen van der Waals (vdW) complexes have been studied in numerous experimental and theoretical works (see [1–12] and references therein) since pioneering work of Smalley et al. [13] (see [14] and references therein, also). This is largely because the 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 homonuclear halogen vdW complexes, $RgHal_2$, and RgICl valence state vdW complexes, as well as frequencies of vdW modes, have been determined experimentally (see [1–17] and references therein). Detailed theoretical analysis of potential energy surfaces (PESs) of the complexes and their dynamical behavior have been carried out, also (see [5,7,18] and references therein).

The $RgHal_2$ valence state complexes undergo fast vibrational and electronic predissociation (VP and EP, respectively), so, *e.g.*, lifetime of the $ArI_2(B0_u^+, \nu_B)$ vdW complexes, $\tau < 80$ ps (see [5] and references), is much less than its radiative lifetime (~1 μs), if one suppose that it is close to that of free (isolated) $I_2(B)$ molecule (here and further a subscript in ν_B *etc.* means to which state this vibronic level belongs). To the best of our knowledge, the only exception is $NeICl(A^3\Pi_1,\nu_A = 12–15)$ complex, $\tau = 3 \pm 2$ ns for $\nu_A = 14$ [19]. Therefore, nobody observed luminescence of the $RgHal_2$ valence state complexes. Luminescence of products of vibrational predissociation ($Hal_2(B,\nu_B)$, $\nu'_B < \nu_B$) has been observed, only.

Meanwhile, ion-pair (IP) states of halogen molecules, especially iodine, provide a more promising system for studies dynamics in vdW complexes than those in the valence states, correlating with the second dissociation limit, $I_2(B)$, for example. It is due to the fact that IP states are arranged in four narrow manifolds (tiers) nested by similar potential energy curves that form a very dense rovibronic structure (see [20] and references therein). The first IP tier consists of six states of distinct symmetries, namely, $D'2_g$, $\beta 1_g$, $D0_u^+$, $E0_g^+$, $\gamma 1_u$, and $\delta 2_u$, in order of increasing T_e.

To populate the complexes of the IP states, one can utilize usual pump-probe technique (see [3,6,11] and references). There are only several papers devoted to these complexes. The $HeI_2(E)$ complex has been observed in [7]. Luminescence in the $\lambda_{lum} = 338–345$ nm spectral range, where $I_2(\beta 1_g \rightarrow A1_u$ and $D'2_g \rightarrow A'2_u)$ transitions should be observed, was detected, whereas the probe radiation was corresponded to the $HeI_2(E,\nu_E = 1 \leftarrow B,\nu_B = 23)$ spectral range. The origin of the $I_2(\beta \rightarrow A$ and $D' \rightarrow A')$ luminescence was not discussed. Signals were extremely low due to low lifetime of the $HeI_2(B)$ state (see above). The $NeICl(E0^+, \beta 1$ and $D'2)$ complexes have been also observed and studied in transitions from long-lived $NeICl(A,\nu_A = 12–15)$ complex [21,22].

In this letter, we report on the first observation of $ArI_2(E)$ vdW complexes.

We have observed the $I_2(E \rightarrow B)$ and $I_2(D \rightarrow X, \beta \rightarrow A$ and $D' \rightarrow A')$ luminescence and shown that luminescence from the D, β and D' states occurs due to transitions in vdW complex, $ArI_2(E \leftarrow B)$. At some excitation bands, we have observed the $I_2(E \rightarrow B)$ luminescence, which origin is optical transitions in vdW ArI_2 complexes, also. Analysis of the excitation spectra has allowed us to assign

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