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Non-adiabatic transitions between first tier ion-pair states of I_2 induced by collisions with Ar atoms

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ABSTRACT

Non-adiabatic transitions from the $I_2(E0_g^+, D0_u^+, \beta 1_g$ and $D'2_g)$ states to first tier ion-pair (IP) states induced by collisions with Ar atoms have been investigated. The stepwise laser excitation schemes have been used for selective population of close-lying vibronic states: E, $v_E = 13$, D, $v_D = 18$, β, $v_\beta = 19$ and $D'2_g$, $v_{D'} = 23$. Rate constants of population of the first tier ion-pair states from the optically populated rovibronic states as well as rate constants of depopulation of the states have been determined. Analysis of the mechanism of the transitions has been carried out.

We find that the $\lambda_{lum}^{max} \approx 3410$ Å luminescence band in the case of optical population of the D and β states cannot be described assuming the collision-induced non-adiabatic transitions only. We conclude that there is an additional radiative channel for population of the states, probably, due to the formation of the ArI_2(IP) van der Waals complexes.

1. Introduction

Spontaneous and collision-induced non-adiabatic transitions in gas phase, in particular, are general phenomena (see [1–8] and references therein). These transitions play a fundamental role in a kinetic behavior of excited states of diatomic and polyatomic molecules and van der Waals (vdW) complexes since they occur in various physical and chemical systems including clusters, liquids, solids and biomolecules. These processes are responsible for energy exchange in the atmosphere, laser media, plasma, and many other media where excited states are involved. Therefore, they have fundamental and practical importance.

The *collision-induced* non-adiabatic transitions (CINATs) are least studied. The most noteworthy are studies in which both the initial and final rovibronic states of the molecule are monitored. However, up to beginning of XXI century, these studies had been limited in number and mainly focused on light diatomic systems with sparse energy levels such as CO^+, CN, NO, N_2, N_2^+, and SiCl [2]. Many features of these processes were challenging to analyze. Detailed, systematic, and state-of-the-art experimental and theoretical investigations are required for complete understanding of CINAT dynamics and mechanisms.

The ion-pair (IP) states of iodine molecules provide a very convenient system for understanding the principal features of the CINATs and studies of vdW complexes. These states are arranged in the four narrow manifolds (tiers) nested by similar potential energy curves (PECs) that form a very dense rovibronic structure [4,9]. The first IP tier correlates to the $I^+(^3P_2) + I^-(^1S_0)$ asymptote and consists of six states, $D'2_g$, $\beta 1_g$, $D0_u^+$, $E0_g^+$, $\gamma 1_u$ and $\delta 2_u$, in order of increasing term values, T_e. Significant experimental and theoretical attention has been paid to the non-adiabatic transitions between *gerade* $E0_g^+$ and *ungerade* $D0_u^+$ states induced by collisions with variety of atomic and molecular partners M. CINATs between these states are very efficient due to huge dipole moment of the $E0_g^+ \leftrightarrow D0_u^+$ optical transition (see [4,10–19] and references therein). Strong luminescence bands, $\lambda_{lum}^{max} \approx 3410$ Å, were observed in presence of M = Ar, Kr, Xe, N_2, CO_2, CF_4, SF_6 [13,14,16–18]. They can be assigned to transitions from the $I_2(D', \beta$ and $\delta)$ states. It was supposed that short-range coupling, non-selective with respect to final IP states, connects the optically populated $E0_g^+$ or $D0_u^+$ states with others [4,13,16,18]. No data on CINATs from other, D', β, γ and δ, IP states of the first tier are available. As an alternative explanation of $\lambda_{lum}^{max} \approx 3410$ Å origin, one can suppose that $I_2(D', \beta$, γ and $\delta)$ states are populated due to optical transitions in the MI_2 vdW complexes accompanied by their dissociation and/or predissociation which produce $M + I_2(D', \beta, \gamma$ and $\delta)$. Besides, luminescence of the MI_2 vdW complexes themselves can occur in this wavelength range (see [14,17] and references therein).

In our recent papers [20–26], we reported on optical population of free iodine molecule *gerade* $I_2(\beta 1_g, D'2_g)$ and *ungerade* $I_2(D0_u^+, \gamma 1_u)$ IP states via the valence $B0_u^+$ and $0_g^+, 1_u$ states correlating with the $I(^2P_{3/2}) + I(^2P_{1/2})$ $(I_2(ab))$ and $I(^2P_{1/2}) + I(^2P_{1/2})$ $(I_2(bb))$

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