



Mixing of the DO_u^+ and $\delta 2_u$ ion-pair states of iodine molecule



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ABSTRACT

Optical population of the $I_2(\delta 2_u)$ state by three-step laser excitation from the ground state XO_g^+ via the valence BO_u^+ and $O_g^+(bb)$ states correlating with the $I(^2P_{3/2})+I(^2P_{1/2})$ and the $I(^2P_{1/2})+I(^2P_{1/2})$ dissociation limits, respectively, has been observed for the first time. It has been shown that luminescence from the $I_2(\delta 2_u)$ state becomes observable due to interaction between the rovibronic levels of the DO_u^+ and $\delta 2_u$ states described by the nonadiabatic operator V_n of the heterogeneous interaction taken in the second order of the perturbation theory where the main intermediate state contribution is provided by the $\gamma 1_u$ state.

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1. Introduction

Various types of spectroscopic perturbation and electronic predissociation in diatomic molecules were the subject of numerous studies since the beginning of the XX century (see, e.g. [1–3] and references therein). The perturbations lead to the mixing of molecular adiabatic wave functions and to shifts of the corresponding rovibronic levels. They can be roughly divided into three groups: homogeneous perturbations, heterogeneous perturbations, and hyperfine interactions.

The homogeneous perturbations occur between rovibronic states satisfying the following selection rules [1,3]:

$$\Delta A = 0, \Delta S = 0 (\Delta \Omega = 0 \text{ for Hund } c \text{ case}), \Delta J = 0, + \leftrightarrow +, - \rightarrow - \text{ and } u \leftrightarrow u, g \leftrightarrow g \text{ for homonuclear molecules,} \quad (1)$$

where J is a molecular total angular momentum, A and Ω are the projections of electron orbital angular momentum and electron total angular momentum onto the molecular axis, respectively, S is a total molecular electronic spin, u, g and $+, -$ are molecular parities. The homogeneous perturbation matrix elements do not depend on J .

The heterogeneous perturbations occur between rovibronic states satisfying the selection rules [1,3]:

$$\Delta A = \pm 1, \Delta S = 0 (\Delta \Omega = \pm 1 \text{ for Hund } c \text{ case}), \Delta J = 0, + \leftrightarrow +, - \rightarrow - \text{ and } u \leftrightarrow u, g \leftrightarrow g \text{ for homonuclear molecules.} \quad (2)$$

The heterogeneous perturbation matrix elements are proportional to J in the high- J limit.

The hyperfine interactions can be of the magnetic-dipole (MD) or electric-quadrupole (EQ) types and can mix the molecular wave functions with different u and g parities. The following selection rules:

$$|\Delta A| \leq 1 (|\Delta \Omega| \leq 1 \text{ for Hund } c \text{ case}), |\Delta J| \leq 1 \quad (3)$$

$$|\Delta A| \leq 2 (|\Delta \Omega| \leq 2 \text{ for Hund } c \text{ case}), |\Delta J| \leq 2 \quad (4)$$

are valid for the MD and EQ hyperfine interactions, respectively [4–6].

The ion-pair (IP) states in molecular iodine form four tears (manifolds) containing the electronic states with different g/u and $+/-$ parities and very similar close-lying potential energy curves. These features make them very attractive as model system for studying of the heterogeneous perturbations and hyperfine interactions.

The first tier correlates with the $I^+(^3P_2)+I(^1S_0)$ dissociation limit and consists of six states: $D'2_g, \beta 1_g, DO_u^+, EO_g^+, \gamma 1_u,$ and $\delta 2_u$, presented here in the order of increasing of a term value, T_e [7,8]. The equilibrium distances and spectroscopic constants of IP states within each tier only slightly differ from each other. The rovibronic levels of each IP state are shifted with respect to those of other states of the same tier, and accidental resonances between the levels may occur. The state PECs can cross or approach each other, and the Franck–Condon factors (FCFs) between vibronic levels of

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