# Heterogeneous and hyperfine interactions between valence states of molecular iodine correlating with the $I(^2P_{1/2}) + I(^2P_{1/2})$ dissociation limit

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Detailed analysis of interactions between all $0_g^+$, $1_u$, and $0_u^-$ weakly bound states of iodine molecule correlating with the $I(^2P_{1/2}) + I(^2P_{1/2})$ $(bb)$ dissociation limit has been performed. For this purpose, the $0_u^-$ $(bb)$ state has been described using analysis of rotationally resolved excitation spectra of luminescence from the $g0_g^-$ state populated in a three-step three-color perturbation facilitated excitation scheme via the $0_u^-$ state. Energies of 41 rovibrational levels, molecular constants, and potential energy curve have been determined. Energy gaps between closest rovibrational levels of the $0_u^-$ and $0_g^+$, $1_u$ $(bb)$ states are found to be large, ~6 $cm^{-1}$. However, interaction of all three $0_g^+$, $1_u$, and $0_u^-$ $(bb)$ states has been observed. It has been found that the $0_u^-$ and $1_u$ electronic states are mixed by heterogeneous interactions, while their mixing with the $0_g^+$ one is due to hyperfine interactions predominantly. Admixture coefficients and electronic matrix elements of the coupling between the $0_g^+$ ~$1_u$, $0_g^+$ ~ $0_u^-$, and $0_u^-$ ~$1_u$ states have been estimated. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4948630]

## I. INTRODUCTION

Perturbations in electronic states of diatomic molecules are the subject of numerous studies for several decades (see, e.g., Refs. 1–4 and references therein). One of the practical applications of the perturbations between states is perturbation facilitated optical-optical double resonance spectroscopy[5–9] in which mixed intermediate states are used as gates to excited states of various symmetry. This method allows to investigate "dark" excited states that are inaccessible in direct excitation from a ground state or in a commonly used optical-optical double resonance scheme.

Some scientific groups utilized mixed valence states of iodine molecule as an intermediate ones to populate ion-pair (IP) states of the tiers, correlating with four dissociation limits of atomic ions, $I^-(^1S) + I^+(^3P, ^1D, ^1S)$. These states draw sufficient attention of researchers because they provide a very convenient system for understanding collisional nonadiabatic energy transfer processes,[10,11] molecular perturbations,[6,7,12,13] and development of theoretical models.[14,15]

A hyperfine interaction of the iodine molecule $B\ 0_u^+$ and $c1_g$ states, correlating with the second $I(^2P_{3/2}) + I(^2P_{1/2})$ $(ab)$ dissociation limit, was used for the $\gamma 1_u$,[5] $H1_u$,[6] and F $0_u^+$[8] IP state optical population. The $B\ 0_u^+ \sim 0_g^-$ $(ab)$ hyperfine coupling allowed to describe the $h\ 0_u^-(^3P_1)$ ion-pair state,[6] and the $g\ 0_g^-(^3P_1)$ state was excited via the $B\ 0_u^+ \sim (3)0_u^-$ coupled state.[9]

Theoretical description of the hyperfine interaction of the $B\ 0_u^+$ state with different valence states was given by Vigue *et al.*[16] and Pique *et al.*[1] Vigue *et al.* estimated the electronic matrix elements of two major terms of hyperfine Hamiltonian corresponding to magnetic dipole and electric quadrupole interactions as ~0.3 $cm^{-1}$ and 0.1 $cm^{-1}$, respectively.[16] Similar results were reported by Pique *et al.*[1] Experimental studies gave the coupling matrix element value of about 0.01 $cm^{-1}$ similar to the theoretical estimations taking into account the Frank-Condon factor (*FCF*) of about 0.1.[7,8,17–20]

Recently, we have realized an effective population of IP states using the three-step three-color excitation scheme via the $B0_u^+$ and $0_g^+$ states, correlating with the second $(ab)$ and the third, $I(^2P_{1/2}) + I(^2P_{1/2})$ $(bb)$, dissociation limits, respectively. We have shown that the perturbation of the $0_g^+$ $(bb)$ and other two, $1_u$ and $0_u^-$, $(bb)$ states allows to populate both *gerade* and *ungerade* IP states[21–23]

$$IP \xleftarrow{h\nu_2} 0_g^+, 0_u^-, 1_u(bb) \xleftarrow{h\nu_f^i} B, v_B, J_B \xleftarrow{h\nu_1} X, v_X, J_X. \quad (1)$$

All three $(bb)$ states have been observed in condensed-phase emission studies[24] for the first time. In gas phase, Exton and Balla[25] observed very weak luminescence near 750 nm, following the 193 nm ArF laser excitation of the $D\ 0_u^+$ IP state, which can be assigned apparently to the $D0_u^+ \rightarrow 0_g^+$ $(bb)$ transition. Ridley *et al.*[5] described the $0_g^+$ and $1_u$ $(bb)$ states in analysis of the vibrationally resolved IP → $(bb)$ luminescence spectra.

In our previous work,[26] we observed population of $\beta 1_g$ and $D0_u^+$ IP states from the $1_u$ and $0_g^+$ $(bb)$ intermediate states, respectively, in a three-step excitation scheme in the $I_2 + Rg$, Rg = He, Ar, Kr, Xe mixture. We have observed luminescence spectra and energy loss *approximately* 400 $cm^{-1}$ in the excitation process. It has been proposed that there is optical excitation of $RgI_2$ van der Waals complexes with the

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