Spectroscopic constants and potential energy curves of some iodine valence ungerade weakly bound states

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Abstract

Luminescence spectra corresponding to transitions from $\beta 1_g$, $G1_g$, $D'2_g$, and $g0_g^-$ ion-pair states of an iodine molecule to weakly bound valence states $1_u$, $2_u$, and $0_u^-$, correlating with the $I(2P_{\frac{3}{2}})+I(2P_{\frac{3}{2}})(ab)$ and $I(2P_{\frac{1}{2}})+I(2P_{\frac{1}{2}})(bb)$ dissociation limits, respectively, have been observed and analyzed. Energies of vibrational levels, spectroscopic constants, and potential energy curves of the valence states have been determined. The $0_u^-$ state is shown to be bound by 488(2) cm$^{-1}$ and placed lower than $1_u(bb)$ and $0_u^-(bb)$, unlike ab initio estimations.

Keywords: diatomic molecules, valence states, weakly bound states, hyperfine coupling

(Some figures may appear in colour only in the online journal)

1. Introduction

The iodine molecule has 23 valence states that are grouped by correlation with three dissociation limits: $I(2P_{\frac{3}{2}})+I(2P_{\frac{3}{2}})(aa)$, $I(2P_{\frac{3}{2}})+I(2P_{\frac{1}{2}})(ab)$, and $I(2P_{\frac{1}{2}})+I(2P_{\frac{1}{2}})(bb)$. Though valence states of $I_2$ have been widely investigated (see [1–17] and references therein), only four deeply bound (dissociation energy exceeds 1000 cm$^{-1}$) states are well described: $X0_g^+(aa)$, $A2_g^-(aa)$, $A1_u^-(aa)$, and $B0_u^-(ab)$. Spectroscopic constants and potential energy curves (PECs) of these states have been determined with high precision from analysis of experimental data [4–10]. The remaining nineteen states are weakly bound and characterized less precisely or not defined at all in some cases. Some spectroscopic characteristics of weakly bound $B'0_u^-(aa)$, $a1_g^-(aa)$, $B'1_u^-(aa)$, $a'0_g^+(aa)$, $c1_g(ab)$, $b'2_g(ab)$, $b'0_b(ab)$, $0_g^-(ab)$, and $2_g(ab)$ states are presented in [1–3, 15–18].

Most of the spectroscopic characteristics of the weakly bound valence states have been determined from analysis of luminescence in transitions from the ion-pair (IP) to valence states (see [7, 15–17, 19–21] and references). For example, optical transitions to the $2_g(aa)$, $0_g^-(ab)$, $1_g(ab)$, $1_u(ab)$, and $2_g(ab)$ states from the IP states were observed and used for the determination of their PECs (see [19–21] and references).

Until recently, there were only two works on experimental analysis of three $0_g^-(bb)$, $1_u(bb)$, and $0_u^-(bb)$ states correlating with the third, $bb$, dissociation limit, both published by Ridley et al. [20, 21]. Vibrationally resolved emission spectra from $D0_u^-(bb)$, $F0_u^-(bb)$, and $1_u(1D_2)$ IP states rovibronic levels to the $0_g^-(bb)$ and $1_u(bb)$ states were measured and successfully simulated, and some spectroscopic parameters ($T_e$, $D_e$, $\omega_v$, $R_e$, and $R_v$) of $0_g^-(bb)$ and $1_u(bb)$ states were obtained. Very recently, we also reported [22, 23] on Dunham coefficients ($Y_0$) of these (bb) states determined with higher accuracy as result of analysis of the $DO_u^-(bb)$ and $\beta 1_g^-\rightarrow 1_u(bb)$ transitions. The $DO_u^-(bb)$ and $\beta 1_g^-\rightarrow 1_u(bb)$ states were populated using a three-step three-color $IP\rightarrow (bb)\leftarrow B0_u^-(bb)$ laser excitation scheme in these studies. Rotational as well as rovibronical energy transfer processes in the (bb) states induced by collisions with He and Ar atoms were used for population of a wide range of rovibronic levels. In such a way, we were able to observe more than 300 transitions in spectra and successfully determined molecular parameters of the lower valence states. As to the $0_u^-(bb)$ state, no experimental