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SPECTROSCOPY OF ATOMS AND MOLECULES

Near-Resonant Rovibronic Raman Scattering from 0_g^+ (*bb*) Valence State via the $D0_u^+$ Ion-Pair State in Iodine Molecule[1]

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Abstract—Near-resonant Raman scattering from the electronic excited $I_2(0_g^+(bb) \xrightarrow{h\nu} D0_u^+ \to X0_g^+)$ state via the intermediate ion-pair $D0_u^+$ state to the X one is observed for the first time. The Raman scattering follows a laser pulse. Its intensity I_R is inversely proportional to the squared value of detuning from the resonant D, 22, 51 ← $0_g^+(bb)$, 7, 52 transition, $(\Delta\nu_2)^2$, according to the theory of near-resonant Raman scattering. The ratio of Raman $D \to X$ scattering intensity to that of the $D0_u^+$, $\nu_D = 22$, $J_D = 51 \to X0_g^+$ luminescence, $I_R/I_{D-X} < 1.5 \times 10^{-4}$ for $\Delta\nu_2 > 0.5$ cm^{-1}. The Raman and luminescence spectra are found to be identical.

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INTRODUCTION

Many monographs, reviews, and papers are devoted to Raman spectroscopy involving electronic excited states in solids, liquids, and gases (see [1–3] and references). Raman spectroscopy has found wide application in fundamental investigations and applied science (see [4–9] and references).

Off-resonant [10, 11], resonant and near-resonant (discrete) Raman scattering [10–22], as well as Raman scattering via dissociative continuum from diatomic molecules [7, 9, 23–26], are objects of numerous experimental and theoretical studies. The $B0_u^+ - X0_g^+$ system of molecular iodine has been chosen for many studies [7–11, 16, 21, 22], since this transition belongs to the visible region, and the spectroscopic characteristics of both states are well known (see [27–29], e.g.). Emission to the X, $\nu_X = 1$–9, J_X vibrational levels was observed in resonant Raman scattering from the X, $\nu_X = 1$ state via the B, $\nu_B = 58$ intermediate one. In addition, the temporal behaviors of the reemission intensity at the Raman-shifted S branch of the $I_2(B, 43 \to X, 1)$ transition after excitation of iodine vapor by the single-mode Ar^+ laser $\lambda \approx 5145$ Å and at the B,43 ← X,0 R(15) transition for resonant and near-resonant excitation were measured [10] (see [22], also). The standard temporal behavior with a lifetime of ≈1 μs corresponding to the spontaneous B,43 → X,0 R(15) transition was recorded for resonant excitation. For near-resonant, $\Delta\nu = 1.2$ and 2.2 GHz, excitation, short-lifetime components that follow a 100-ns rectangular laser pulse have been observed as well. The short-lifetime component dominates at $\Delta\nu = 2.2$ GHz [10, 22]. One can suggest that short-lifetime $I_2(B, \nu_B \to X, \nu_X)$ transitions with spectra similar to B, $\nu_B \to X$, ν_X luminescence spectra have to occur at near-resonant excitation. However, to the best of our knowledge, no experimental data on similar transitions have been reported to date. Moreover, no data on Raman scattering from iodine molecule excited states via intermediate ion-pair states are available in the literature.

In the present paper, we report for the first time results of study of near-resonant Raman scattering from the $I_2(0_g^+(bb))$ state correlating with the third, $I(^2P_{1/2}) + I(^2P_{1/2})$, dissociation limit of valence states via the $D0_u^+$ ion-pair state, in which optical transition to the X state ($\lambda_{em} \approx 263$–330 nm) occurs. This effect was observed at the laser wavelength nearest to that of the $I_2(D,22,51 \xleftarrow{h\nu_2} 0_g^+(bb),7,52)$ transition ($\lambda_2 \approx 641$ nm). The $0_g^+(bb)$, $\nu_0 = 7$, $J_0 = 52$ rovibronic state

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