Mechanism of Resonant Two-photon Transitions *via* Repulsive Intermediate States. Experimental and Theoretical Studies on I_2 Vapor

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Mechanisms of resonant two-photon transitions *via* repulsive intermediate states are experimentally and theoretically studied. Polarization ratios, $\Omega=\sigma_{\circlearrowright\circlearrowright}/\sigma_{\uparrow\uparrow}$ (where $\sigma_{\circlearrowright\circlearrowright}$ and $\sigma_{\uparrow\uparrow}$ are the cross section of the two-photon transitions obtained by the circularly polarized light and that by the linearly polarized light, respectively) of the two-photon excitation of iodine vapor have been measured in the wavelength range of 420—510 nm. An expression for the polarization ratio for the two-photon absorption in which both simultaneous and sequential processes take place has been presented. The polarization ratios calculated by using the δ-function approximation for the repulsive intermediate states as a function of the laser frequency for the iodine molecule system explain qualitatively the experimental result. This indicates that both the simultaneous and the sequential process take place in the frequency region measured.

Multi-photon spectroscopy has made a great contribution to clarifying structures of electronically excited states of molecules and the dynamical processes taking place in these states.[1] Most of papers so far reported were concerned with resonant multi-photon transitions *via* bound intermediate states. Resonant multi-photon transitions *via* repulsive intermediate states such as bound-free-bound or bound-free-free transition can be induced with production of fragments. These types of the multi-photon transition can be observed in iodine and halogen substituted compounds *etc.*[2,3] At present mechanisms of the multi-photon transitions involving repulsive intermediate states are not well known. It is interesting to investigate which is dominant, simultaneous or sequential process. The latter is induced by elastic collisions between molecules and perturbers.

One of the methods for identifying the mechanisms of the multi-photon transitions is to measure the polarization ratio Ω defined by ratio of the transition probability obtained by using circularly polarized light to that obtained by using parallel linearly polarized light. Kasatani *et al.*[4] have observed two- and three-photon transitions of I_2 *via* the repulsive intermediate states in gases. From the polarization measurement of the fluorescence excitation spectra, they have found that even though the I_2 molecule excited in the energy region beyond the attractive potential of the B state, the photon absorption proceeds *via* the real repulsive intermediate states. Another method is to analyze the vibronic structure appearing in the spectra.

The purpose of this paper is to investigate the mechanisms of resonant two-photon transitions *via* repulsive intermediate states from both experimental and theoretical points of view. We first report polarization ratios of two-photon fluorescence excitation spectra of gaseous I_2 in the laser wavelength range of 420—510 nm. Secondly effects of the repulsive intermediate states on the resonant two-photon absorption (TPA) probability are theoretically studied. Neglecting effects of molecular rotations, and assuming the molecules to be randomly oriented, we derive expressions for the transition probabilities of the simultaneous and sequential TPA processes. In the Born-Oppenheimer and Condon approximations, these expressions are divided into two terms. One involves electronic transition matrix elements relevant to the two-photon transitions with laser intensity. This term depends on the polarization of photon for the simultaneous TPA process. The other term is a line shape function which characterizes the vibronic intensity distribution. Expressions for the line shape functions for the simultaneous process and sequential one are derived by using the δ-function approximation to the repulsive intermediate states and the displaced harmonic oscillator approximation to the initial and final states. In deriving the expressions for the line shape functions, two cases can be considered, depending on the dimensionless potential displacement Δ between the initial and final states: one is the weak coupling case in which $\Delta \lesssim 1$, and the other is the strong coupling case which is characterized by a large potential displacement. Ion pair states in I_2 can be taken as belonging to the latter case. In this paper, we derive an expression for the line shape function of the TPA process of I_2 in the strong coupling case. Finally the frequency dependence of the polarization ratio is evaluated and is compared with that observed for the gaseous I_2 molecule.

Experimental

The Polarization Measurements of I_2 Vapor. Iodine vapor in a quartz cell at 90 °C was excited by visible light from an N_2 laser pumped dye laser (Molectron UV-24 and DL-14) in the wavelength range of 420—510 nm. The laser intensity was $\lesssim$1 mj/pulse of a few nanoseconds. The

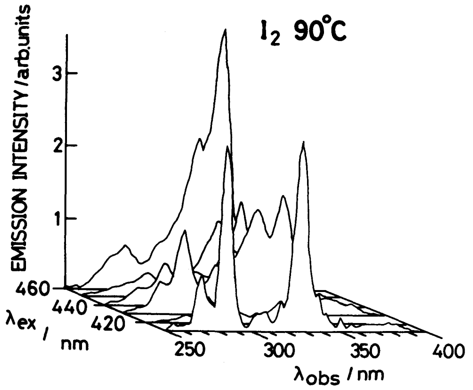

Fig. 1. Fluorescence spectra taken at various excitation wavelengths of I_2 vapor at 90 °C.

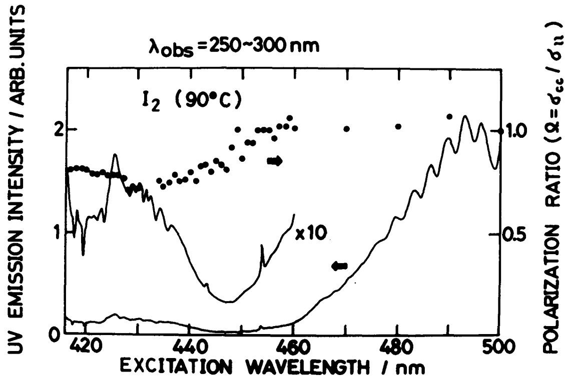

Fig. 2. Fluorescence excitation spectra (solid curves) and polarization ratios (points) of I_2 vapor at 90 °C.

band width was around 0.4 cm^{-1}. The ultraviolet emission from iodine molecules was observed at right angles to the focused laser beam with a monochromator (or a filter), a telescope and a photomultiplier (Hamamatsu Photonics R-166 UH or 1P28). In order to measure the effect of the polarization of laser light on the two-photon absorptivity, the laser beam was passed through a rotatable double Fresnel rhomb followed by a single Fresnel rhomb. This optical arrangement provides linearly or circularly polarized light without changing the optical pass and intensity of the laser beam. At the lower vapor pressure, the polarization ratio could not be quantitatively measured because of low S/N ratios.

By the excitation of iodine vapor at $\lambda_{ex} \geq 498.9$ nm *i.e.*, below the dissociation limit of the B (0_u^+) state, the UV emission was observed at 385, 342, 320, 287, and 270 nm as reported previously.[4] When the energy of laser light was above the dissociation limit $\lambda_{ex} < 498.9$ nm, the UV emission was still observed at various wavelengths as shown in Fig. 1. When the UV emission intensity was measured as a function of excitation wavelength, the intensity decreased drastically at $\lambda_{ex} < 498.9$ nm with unfocused laser light. The excitation spectra were detected for two UV wavelength regions, one with an interference filter centered at 320 nm, and the other with a broad band pass filter (240—330 nm). UV excitation spectra taken by these two methods were essentially the same. The decrease in UV intensity is caused by the decrease in the number density of the intermediate B 0_u^+ state for two-photon absorption process,

$$I_2 + \hbar\omega_R \longrightarrow I_2^*(B\,0_u^+),$$

$$I_2^*(B\,0_u^+) + \hbar\omega_R \longrightarrow I_2^{**}.$$

Same sharp decrease in the excitation spectra at $\lambda_{ex} < 498.9$ nm has been reported when iodine vapor was irradiated by the visible laser light from a flash lamp pumped dye laser, the peak power of which was weaker than the N_2 laser pumped dye laser by a factor of ≈ 200. This drastic intensity change at $\lambda < 498.9$ nm, however, was not observed when the laser light was focused by a lens (f=30 mm). This is probably because the pumping rate to the upper state(s) by the focused laser light is comparable to the dissociation rate of the intermediate state.

The influence of the incident light polarization (circular or linear) on the rate of the photon absorption process was investigated at various laser wavelengths. The results for benzene were in good agreement with those obtained by Friedrich and McClain.[5] The polarization ratios for iodine vapor were measured by observing the UV emission with the UV band pass filter as shown in Fig. 2. They were found to be essentially unity in the laser wavelength range of 450—510 nm where iodine molecules absorb visible light in the transition from the ground states to the dissociative states B (0_u^+) and 1_u. Below 450 nm, one-photon absorption diminishes. When the laser wavelength became less than 450 nm, the transition probabilities or UV emission decreased and the polarization ratios began to deviate from unity as shown in Fig. 2. This deviation indicates that the contribution of two-photon absorption *via* the real dissociative state becomes less important and that *via* virtual states becomes important. The interaction time between photons and dissociative state becomes shorter with increasing the photon energy because the dissociative lifetime is classically a function of the incident photon energy. At the shorter wavelength region observed the polarization ratio became less than 1.0. This transition corresponds to $\Delta\Omega=0$, or 0_g^+–$X0_g^+$ two-photon transition *via* virtual states.[6] In the following sections we shall discuss theoretically both two-photon transition probabilities through a dissociative state and polarization ratios in more detail.

Theoretical

Transition Probabilities of Resonant TPA via *Repulsive Intermediate States.* We consider a resonant two-photon absorption (TPA) *via* repulsive intermediate states as shown in Fig. 3. The two-photon transition probability from vibronic state a to n, $W_{a\rightarrow n}(\omega_R)$ can be approximately expressed in terms of the simultaneous transition probability $W_{a\rightarrow n}^{\text{sim}}(\omega_R)$ and the sequential one $W_{a\rightarrow m}^{\text{seq}}(\omega_R)$ as

$$W_{a\rightarrow n}(\omega_R) \simeq W_{a\rightarrow n}^{\text{sim}}(\omega_R) + W_{a\rightarrow n}^{\text{seq}}(\omega_R), \tag{1}$$

where we have assumed that molecules absorb identical two-photons with frequency ω_R and polarization vector $\vec{\lambda}$, and mixed terms have been omitted though these may make a significant contribution

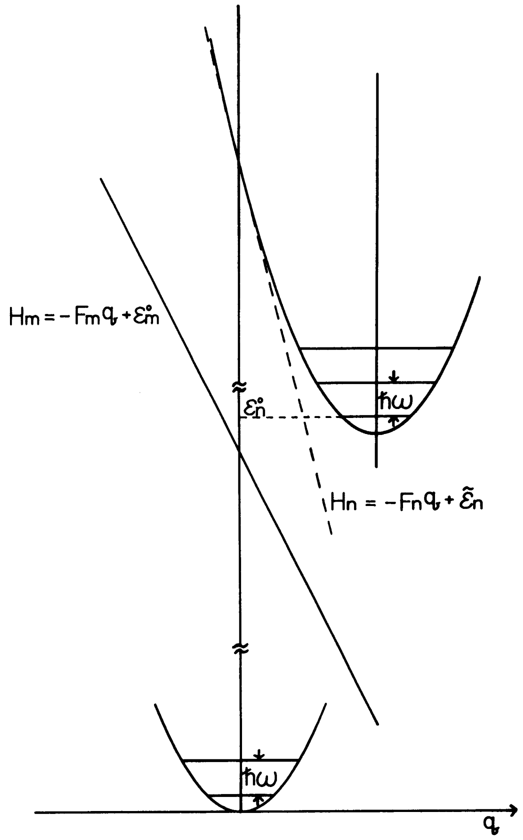

Fig. 3. Model potentials for TPA in the strong coupling case. Potentials of the initial and final states are expressed in terms of displaced harmonic ones with frequency ω and a large displacement Δ. Potential of the intermediate state is approximated by a linear one.

in some cases.[7] General forms for the transition probabilities have already been given elsewhere.[7] In the Born-Oppenheimer approximation in which wave functions can be expressed as a product of electronic (Φ) and vibrational (θ) ones, and in the Condon approximation, we can separate the simultaneous transition probability into two terms, a polarization dependent term P_λ and a line shape function $L(\omega_R)$:[8–12]

$$W_{a\to n}^{\mathrm{sim}}(\omega_\mathrm{R}) = P_\lambda^{\mathrm{sim}} L^{\mathrm{sim}}(\omega_\mathrm{R}), \tag{2}$$

where

$$P_\lambda^{\mathrm{sim}} = \langle\!\langle |\vec{H}'_{nm}\cdot\vec{\lambda}\,\vec{H}'_{ma}\cdot\vec{\lambda}|^2 \rangle\!\rangle, \tag{3}$$

$$L^{\mathrm{sim}}(\omega_\mathrm{R}) = \frac{2}{\hbar^4}\mathrm{Re}\sum_a\sum_n \frac{\rho_{aa}}{\mathrm{i}\omega_{na}+\Gamma_{na}} \times \left|\int \mathrm{d}\omega_m \frac{\langle\theta_n|\theta_m\rangle\langle\theta_m|\theta_a\rangle}{\mathrm{i}\omega_{ma}+\Gamma_{ma}}\right|^2, \tag{4}$$

where summations are carried out over the vibronic states of the a and n electronic states. In Eq. 3, double bracket $\langle\!\langle\cdots\rangle\!\rangle$ denotes averaging over orientations of the molecules, and $\vec{H}'_{nm} = \langle\Phi_n^0|\vec{H}'|\Phi_m^0\rangle$ is the matrix element of the molecule-photon interaction Hamiltonian. In Eq. 4, ρ_{aa} represents the population in the initial state, $\omega_{na}=\omega_n-\omega_a-2\omega_R$, $\omega_{ma}=\omega_m-\omega_a-\omega_R$ in which ω_n, ω_m, and ω_a denote molecular eigenfrequencies of the relevant states, and Γ, dephasing constant between two states, for example, is given by

$$\Gamma_{ma} = \frac{1}{2}(\Gamma_{mm}+\Gamma_{aa})+\Gamma_{ma}^{(\mathrm{d})}, \tag{5}$$

in which Γ_{mm} is the population decay constant of state m, and $\Gamma_{ma}^{(\mathrm{d})}$ the pure dephasing constant.[7,13,14]

Assuming the sequential process to be induced by intermolecular interactions between molecules and heat bath, we can express the two-photon transition probability in the similar way,

$$W_{a\to n}^{\mathrm{seq}}(\omega_\mathrm{R}) = P^{\mathrm{seq}} L^{\mathrm{seq}}(\omega_\mathrm{R}), \tag{6}$$

where

$$P^{\mathrm{seq}} = \langle\!\langle |\vec{H}'_{nm}\cdot\vec{\lambda}|^2 \rangle\!\rangle \langle\!\langle |\vec{H}'_{ma}\cdot\vec{\lambda}|^2 \rangle\!\rangle \propto |\vec{H}'_{nm}|^2 |\vec{H}'_{ma}|^2, \tag{7}$$

which is independent of polarization, and $L^{\mathrm{seq}}(\omega_\mathrm{R})$, the line shape function for the sequential TPA is given as

$$L^{\mathrm{seq}}(\Omega_\mathrm{R}) = \frac{2}{\hbar^4}\mathrm{Re}\sum_a\rho_{aa}\sum_n\int\mathrm{d}\omega_m\int\mathrm{d}\omega_k(\Gamma_{ma}-\Gamma_{mk}+\Gamma_{ak}) \times \frac{\langle\theta_a|\theta_m\rangle\langle\theta_m|\theta_n\rangle\langle\theta_n|\theta_k\rangle\langle\theta_k|\theta_a\rangle}{(\mathrm{i}\omega_{mn}+\Gamma_{mn})(\mathrm{i}\omega_{ak}+\Gamma_{ak})(\mathrm{i}\omega_{ma}+\Gamma_{ma})(\mathrm{i}\omega_{mk}+\Gamma_{mk})}. \tag{8}$$

In order to evaluate ω_R-dependence of the transition probability of resonant TPA *via* repulsive intermediate states, we now derive expressions for the line shape functions $L^{\mathrm{sim}}(\omega_\mathrm{R})$ and $L^{\mathrm{seq}}(\omega_\mathrm{R})$ by using one dimensional model shown in Fig. 3.

Nuclear potentials of the initial a and final n electronic states are assumed to be characterized by displaced harmonic potentials with displacement Δ: The corresponding Hamiltonians $\hat{H}_a$ and $\hat{H}_n$ are expressed in the forms,

$$\hat{H}_a = \frac{\hbar\omega}{2}(\hat{p}^2+q^2), \tag{9a}$$

and

$$\hat{H}_n = \frac{\hbar\omega}{2}\{\hat{p}^2+(q-\Delta)^2\} + \varepsilon_n^0, \tag{9b}$$

where q and $\hat{p}$ are the dimensionless nuclear coordinate and the conjugated momentum, respectively. ω represents the frequency of the vibrational mode.

Vibronic Hamiltonian of repulsive intermediate states is assumed to be given by

$$\hat{H}_m = \frac{\hbar\omega}{2}\hat{p}^2 - F_m q + \varepsilon_m^0, \tag{10}$$

with $F_m>0$. We shall consider the line shape function of the simultaneous TPA *via* repulsive intermediate states in the strong coupling case.

a) Simultaneous TPA: Applying the generating function method[15] to Eq. 4, we obtain

$$L^{\mathrm{sim}}(\omega_{\mathrm{R}}) = \frac{2}{\hbar^4}\int_{-\infty}^{\infty}\mathrm{d}t\int_0^{\infty}\mathrm{d}\tau\int_0^{\infty}\mathrm{d}\tau'\exp\,[-\Gamma_{na}|t| -\Gamma_{ma}(\tau+\tau')-2i\omega_{\mathrm{R}}t-i\omega_{\mathrm{R}}(\tau'-\tau)]G(\tau,\,\tau',\,t), \tag{11}$$

where $G(\tau,\tau',t)$, generating function for the simultaneous TPA, is given as

$$\begin{aligned} G(\tau,\,\tau',\,t) = \sum_a\langle\theta_a|\rho_{aa}&\exp\,[-\mathrm{i}\hat{H}_a(t+\tau'-\tau)/\hbar] \\ &\times\exp\,[\mathrm{i}\hat{H}_m\tau'/\hbar]\exp\,[\mathrm{i}\hat{H}_n t/\hbar] \\ &\times\exp\,[-\mathrm{i}\hat{H}_m\tau/\hbar]|\theta_a\rangle. \end{aligned} \tag{12}$$

For simplicity we assume the vibrational mode of molecules to be in the low temperature limit. A temperature dependent line shape function can be derived by using the Boson operator technique.[16] In order to derive an expression for the line shape function within the δ-function approximation, we neglect the nuclear kinetic energy in the Hamiltonian for the repulsive intermediate states. In this approximation we obtain a line shape function as

$$\begin{aligned} L^{\mathrm{sim}}(\omega_{\mathrm{R}}) = \frac{2}{\hbar^4}\int_{-\infty}^{\infty}\mathrm{d}t\int_0^{\infty}\mathrm{d}\tau\int_0^{\infty}\mathrm{d}\tau'&\exp\,[\mathrm{i}(\tilde{\varepsilon}_n/\hbar-\omega/2-2\omega_{\mathrm{R}})t \\ &-\Gamma_{na}|t|-(F_m\tau'-F_m\tau+F_n t)^2/4\hbar^2 \\ &+\mathrm{i}(\varepsilon_m^0/\hbar-\omega/2-\omega_{\mathrm{R}})\tau'-\mathrm{i}(\varepsilon_m^0/\hbar-\omega/2-\omega_{\mathrm{R}})\tau \\ &-(\tau+\tau')\Gamma_{ma}], \end{aligned} \tag{13}$$

where quantum number dependences of Γ have been neglected. A brief derivation of Eq. 13 is given in Appendix A. In the case in which condition $\hbar\Gamma_{na}<F_n$ is satisfied, we can neglect effects of the dephasing constant Γ_{na} in Eq. 13. In this case after integration over t in Eq. 13 we obtain

$$\begin{aligned} L^{\mathrm{sim}}(\omega_{\mathrm{R}}) = \frac{4\sqrt{\pi}}{\hbar^3F_n}&\exp\left[-\left(\frac{\tilde{\varepsilon}_n-\hbar\omega/2-2\hbar\omega_{\mathrm{R}}}{F_n}\right)^2\right] \\ &\times\left|\int_0^{\infty}\mathrm{d}\tau\exp\left[-\mathrm{i}\left\{\varepsilon_m^0/\hbar-\omega/2-\omega_{\mathrm{R}}\right.\right.\right. \\ &\left.\left.\left.-(\tilde{\varepsilon}_n/\hbar-\omega/2-2\omega_{\mathrm{R}})\frac{F_m}{F_n}\right\}-\Gamma_{ma}\tau\right]\right|^2. \end{aligned} \tag{14}$$

Integration over τ in Eq. 14 yields an analytical expression for the simultaneous TPA in the strong coupling case as,

$$L^{\mathrm{sim}}(\omega_{\mathrm{R}}) = \frac{4\sqrt{\pi}}{\hbar^3F_n}\exp\left[-\left(\frac{\tilde{\varepsilon}_n-\hbar\omega/2-2\hbar\omega_{\mathrm{R}}}{F_n}\right)^2\right] \times\frac{r^2}{\{\tilde{\varepsilon}_n/\hbar-\omega/2-r(\varepsilon_m^0-\omega/2)-(2-r)\omega_{\mathrm{R}}\}^2+r^2\Gamma_{ma}^2}, \tag{15}$$

with $r=F_n/F_m$. The first term in Eq. 15 is equivalent to the band shape function for the one-photon bound-free transition with optical frequency $2\omega_{\mathrm{R}}$. In the usual case in which $F_n>\Gamma_{ma}r/|2-r|$, the band shape for the simultaneous TPA process is dominated by the second term in Eq. 15. This indicates that the maximum of the band locates at $\{\tilde{\varepsilon}_n/\hbar-\omega/2-r(\varepsilon_m^0-\omega/2)\}/(2-r)$ with the effective width $\Gamma_{ma}r/|2-r|$. The same expression for the line shape function as Eq. 15 can be derived if the vibronic Hamiltonian of the final state is assumed to be expressed in terms of a linear potential, $\hat{H}_n=-F_nq+\tilde{\varepsilon}_n$, in stead of using the approximation expansion Eq. A. 9.

b) Sequential TPA: The line shape function for the sequential TPA in the strong coupling case takes the form

$$L^{\mathrm{seq}}(\omega_{\mathrm{R}}) = \frac{2}{\hbar^4}\mathrm{Re}\sum_a\rho_{aa}\int\mathrm{d}\omega_n\int\mathrm{d}\omega_m\int\mathrm{d}\omega_k(\Gamma_{ma}-\Gamma_{mk}+\Gamma_{ak}) \times\frac{\langle\theta_a|\theta_m\rangle\langle\theta_m|\theta_n\rangle\langle\theta_n|\theta_k\rangle\langle\theta_k|\theta_a\rangle}{(\mathrm{i}\omega_{mn}+\Gamma_{mn})(\mathrm{i}\omega_{ak}+\Gamma_{ak})(\mathrm{i}\omega_{ma}+\Gamma_{ma})(\mathrm{i}\omega_{mk}+\Gamma_{mk})}. \tag{16}$$

For the strong coupling case, the linear potential approximation can be adopted both to the intermediate and final state potentials, and the overlap integral between the two states can be expressed as

$$\langle\theta_m|\theta_n\rangle = (F_nF_m)^{-1/2}\delta(q_m-q_n). \tag{17}$$

Applying Eq. 17 into Eq. 16 and integrating over the frequencies ω_n and ω_k, we obtain

$$\begin{aligned} L^{\mathrm{seq}}(\omega_{\mathrm{R}}) = \frac{2}{\hbar^4}\int_{-\infty}^{\infty}\mathrm{d}q_m&\frac{(2\Gamma_{ma}-\Gamma_{mm})\Gamma_{mn}}{\Gamma_{mm}} \\ &\times\frac{1}{[\{(\tilde{\varepsilon}_n-F_nq_m)/\hbar-(\varepsilon_m^0-F_mq_m)/\hbar-\omega_{\mathrm{R}}\}^2+\Gamma_{mn}^2]} \\ &\times\frac{|\theta_a(q_m)|^2}{[\{(\varepsilon_m^0-F_mq_m-\hbar\omega/2)/\hbar-\omega_{\mathrm{R}}\}^2+\Gamma_{ma}^2]}, \end{aligned} \tag{18}$$

where we have restricted ourselves to the TPA in the low temperature limit. In the case in which $F_m\gg\hbar\Gamma_{ma}$ is satisfied, the integrand in Eq. 18 involves the δ-function in the limit $\hbar\Gamma_{ma}/F_m\rightarrow0$. In this case the integration over q_m can be performed as

$$L^{\mathrm{seq}}(\omega_{\mathrm{R}}) = \frac{2\pi}{\hbar^3}\,\frac{(2\Gamma_{ma}-\Gamma_{mm})\Gamma_{mn}}{F_m\Gamma_{mm}\Gamma_{ma}} \times\frac{\exp\left[-\left(\dfrac{\varepsilon_m^0-\hbar\omega/2-\hbar\omega_{\mathrm{R}}}{F_m}\right)^2\right]}{\{\varepsilon_n^0/\hbar-\omega/2-2\omega_{\mathrm{R}}-r(\tilde{\varepsilon}_n/\hbar-\omega/2-\omega_{\mathrm{R}})\}^2+\Gamma_{mn}^2}. \tag{19}$$

From Eq. 19, we can see that the peak of the band for the sequential TPA process locates at the same frequency as that for the simultaneous process, and its effective width is given by $\Gamma_{mn}/|2-r|$.

Polarization Ratio of the Resonant TPA of I_2 Vapor. We consider the polarization ratio for the TPA in the presence of both simultaneous and sequential processes at the same time. In this case, the polarization ratio $\Omega(\omega_{\mathrm{R}})$ can be defined as

$$\Omega(\omega_{\mathrm{R}}) = \frac{W_{a\to n}^{\rightleftarrows}(\omega_{\mathrm{R}})}{W_{a\to n}^{\uparrow\uparrow}(\omega_{\mathrm{R}})} = \frac{P_{\rightleftarrows}^{\mathrm{sim}}L^{\mathrm{sim}}(\omega_{\mathrm{R}})+P^{\mathrm{seq}}L^{\mathrm{seq}}(\omega_{\mathrm{R}})}{P_{\uparrow\uparrow}^{\mathrm{sim}}L^{\mathrm{sim}}(\omega_{\mathrm{R}})+P^{\mathrm{seq}}L^{\mathrm{seq}}(\omega_{\mathrm{R}})}. \tag{20}$$

The polarization dependence of the simultaneous TPA has been studied by McClain,[10] Monson and McClain,[9] Nascimento,[11] and Bray and Hochstrasser[12] included rotational effects. In order to calculate the polarization ratio, the values of $P_{\lambda}^{\mathrm{sim}}/P^{\mathrm{seq}}$ must be determined. Averaging the $P_{\lambda}^{\mathrm{sim}}$ of Eq. 3 over the orientation of the molecule, we obtain

$$\begin{aligned} P_{\uparrow\uparrow}^{\mathrm{sim}} = \frac{1}{15}[3\{(M_{na}^{xx})^2+(M_{na}^{yy})^2+(M_{na}^{zz})^2\} \\ + 4\{(M_{na}^{xy})^2+(M_{na}^{xz})^2+(M_{na}^{yz})^2\} \\ + 2\{M_{na}^{xx}M_{na}^{yy}+M_{na}^{xx}M_{na}^{zz}+M_{na}^{yy}M_{na}^{zz}\}], \end{aligned} \tag{21}$$

for the linearly polarized light, and

$$\begin{aligned} P_{\circlearrowleft\circlearrowright}^{\mathrm{sim}} = \frac{1}{30}[4\{(M_{na}^{xx})^2+(M_{na}^{yy})^2+(M_{na}^{zz})^2\} \\ + 12\{(M_{na}^{xy})^2+(M_{na}^{xz})^2+(M_{na}^{yz})^2\} \\ - 4\{M_{na}^{xx}M_{na}^{yy}+M_{na}^{xx}M_{na}^{zz}+M_{na}^{yy}M_{na}^{zz}\}], \end{aligned} \tag{22}$$

for the circularly polarized light, where M_{na} the two-photon electronic transition matrix element, for example, is given by

$$M_{na}^{xy} = \langle \Phi_n^0|x|\Phi_m^0\rangle\langle\Phi_m^0|y|\Phi_a^0\rangle. \tag{23}$$

In the similar way the P^{seq} given by Eq. 7 is written as

$$\begin{aligned} P^{\mathrm{seq}} = \frac{1}{9}\{(H_{nm}^{x})^2+(H_{nm}^{y})^2+(H_{nm}^{z})^2\} \\ \times\{(H_{ma}^{x})^2+(H_{ma}^{y})^2+(H_{ma}^{z})^2\}, \end{aligned} \tag{24}$$

where, for example,

$$H_{nm}^{x} = \langle\Phi_n^0|x|\Phi_m^0\rangle. \tag{25}$$

From Eq. 24 we can see that the two-photon transition matrix element of the sequential process is independent of the polarization of light.

For the resonance TPA of I_2, the final state which is dipole allowed belongs to a Σ_g^+ or Π_g state in the optical frequency range reported in this paper. We consider the following two cases.

$$\text{(i)}\quad \Sigma_g^+ \text{ or } \Pi_{0g} \xleftarrow{x,\,y} \Pi_{1u} \xleftarrow{x,\,y} \Sigma_g^+.$$

By using $M_{na}^{xx}=M_{na}^{yy}$ in Eqs. 21 and 22, we obtain $P_{\uparrow\uparrow}^{\mathrm{sim}}=(8/15)(M_{na}^{xx})^2$ and $P_{\circlearrowleft\circlearrowright}^{\mathrm{sim}}=(2/15)(M_{na}^{xx})^2$. Similary from Eq. 24 we obtain $P^{\mathrm{seq}}=(4/9)(M_{na}^{xx})^2$. Using these expressions for the electronic matrix elements, we can express Eq. 20 in terms of the line shape functions as

$$\Omega(\omega_{\mathrm{R}}) = \frac{3L^{\mathrm{sim}}(\omega_{\mathrm{R}})+10L^{\mathrm{seq}}(\omega_{\mathrm{R}})}{12L^{\mathrm{sim}}(\omega_{\mathrm{R}})+10L^{\mathrm{seq}}(\omega_{\mathrm{R}})}. \tag{26}$$

It should be noted that the polarization ratio $\Omega(\omega_{\mathrm{R}})$ is dependent only on the value of $L^{\mathrm{sim}}(\omega_{\mathrm{R}})/L^{\mathrm{seq}}(\omega_{\mathrm{R}})$ and independent of the position of the peak of the line shape functions for the simultaneous and sequential processes. In cases in which effects of elastic collisions can be neglected, and the simultaneous process dominates the TPA process, the polarization ratio is then independent of laser frequency ω_{R} and $\Omega(\omega_{\mathrm{R}})=0.25$. In other extreme cases in which sequential process is dominant, we obtain $\Omega(\omega_{\mathrm{R}})=1$.

$$\text{(ii)}\quad \Pi_{1g} \text{ or } \Pi_{2g} \xleftarrow{z} \Pi_{1u} \xleftarrow{x,\,y} \Sigma_g^+.$$

Substituting $M_{na}^{xz}=M_{na}^{yz}$ into Eqs. 21 and 22, we obtain $P_{\uparrow\uparrow}^{\mathrm{sim}}=(8/15)(M_{na}^{xz})^2$ and $P_{\circlearrowleft\circlearrowright}^{\mathrm{sim}}=(12/15)(M_{na}^{xz})^2$. Similary we obtain $P^{\mathrm{seq}}=2/9(M_{na}^{xz})^2$. From these relations, the polarization ratio is expressed as

$$\Omega(\omega_{\mathrm{R}}) = \frac{18L^{\mathrm{sim}}(\omega_{\mathrm{R}})+5L^{\mathrm{seq}}(\omega_{\mathrm{R}})}{12L^{\mathrm{sim}}(\omega_{\mathrm{R}})+5L^{\mathrm{seq}}(\omega_{\mathrm{R}})}. \tag{27}$$

In cases in which effects of elastic collisions can be neglected, we obtain $\Omega(\omega_{\mathrm{R}})=1.5$. In other extreme cases in which sequential process is dominant, on the other hand, we obtain $\Omega(\omega_{\mathrm{R}})=1$. In the real system in which collisional dephasings take place and both simultaneous and sequential processes make a contribution to the TPA, we can see that the polarization ratio depends on the laser frequency used.

Discussion

It has experimentally been shown that the two-photon absorption process above the dissociation limit of the B state may occur before the excited iodines dissociate or during the dissociation process,

$$I_2 \xrightarrow{\hbar\omega_{\mathrm{R}}} I_2{}^* \xrightarrow{\hbar\omega_{\mathrm{R}}} I_2{}^{**}.$$

The dissociation rate is estimated to be faster than $10^{-12}\,\mathrm{s}^{-1}$ from the results of photofragment spectroscopy,[17] and the pumping rate to $I_2{}^{**}$ from the dissociative state must be comparable to it. Concerning the pumping process above the dissociation limit of the B state, the following recombination mechanism is another plausible one,

$$I_2 + \hbar\omega_{\mathrm{R}}\ (<498.9\ \mathrm{nm}) \longrightarrow 2I,$$

$$I + I \xrightarrow{M} I_2{}^*\ (\mathrm{B}\ 0_u^+),$$

$$I_2{}^*\ (\mathrm{B}\ 0_u^+) + \hbar\omega_{\mathrm{R}} \longrightarrow I_2{}^{**},$$

where M is an iodine parent molecule as a third body. If this is the case, both UV emission intensity and VIS emission intensity originating from bound levels of the B state increase with the pressure of the third body, M. When the pressure of I_2 increased from 0.2 Torr to 27 Torr (1 Torr=133.322 Pa) by changing the cell temperature from 20 °C to 90 °C, the VIS emission was still undetectable but the UV emission intensity increased ten-fold for irradiation at $\lambda_{\mathrm{ex}}<498.9\ \mathrm{nm}$.

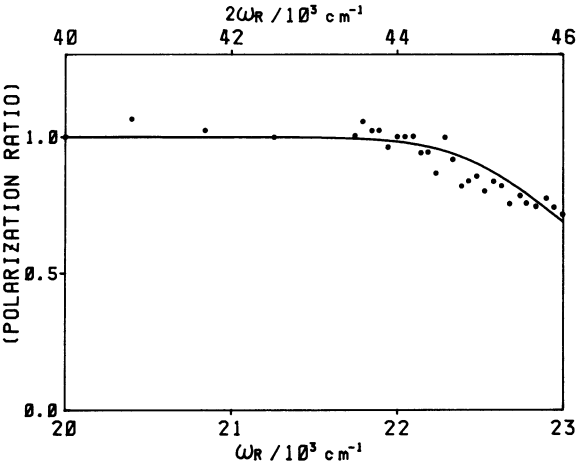

Fig. 4 The calculated polarization ratios for I_2 vapor. Points represent the experimental results (see Fig. 2). The molecular parameters used are $\omega=215\,\mathrm{cm}^{-1}$, $\varepsilon_m^0/\hbar=20300\,\mathrm{cm}^{-1}$, $\tilde{\varepsilon}_n/\hbar=48000\,\mathrm{cm}^{-1}$, $\Gamma_{ma}=5\,\mathrm{cm}^{-1}$, $\Gamma_{mn}=3\,\mathrm{cm}^{-1}$, $\Gamma_{mm}=4\,\mathrm{cm}^{-1}$, $F_m/\hbar=3200\,\mathrm{cm}^{-1}$, and $F_n/\hbar=2000\,\mathrm{cm}^{-1}$.

Thus, the recombination mechanism should be excluded from the two-photon absorption process.

Expressions for the transition probabilities and the polarization ratio of TPA *via* repulsive intermediate states have been derived within the Born-Oppenheimer adiabatic approximation and the Condon approximation. It has been shown that abilities of the simultaneous and sequential TPA processes are dominated by two factors. One is the electronic transition matrix elements with polarization of photons. For the simultaneous process, this factor depends on the polarization of photons, and for the sequential process, on the other hand, it is independent of the polarization. The other factor is a line shape function representing the vibronic intensity distribution of the TPA spectra.

We are now in a position to calculate the polarization ratio for the resonant TPA of I_2. The nuclear potential of the ground state is assumed to be harmonic with a frequency $\omega=215\,\mathrm{cm}^{-1}$; its equilibrium point is located at 2.66 Å. Analytical forms of the repulsive potential energy curve of the $^1\Pi_{1u}$ state have been proposed by Tellinghuisen,[18] and Williams *et al.*[19] In this calculation, we adopt $\varepsilon_m(q)=-3200q+20300$ (in cm^{-1} units), which is very close to the expression derived to reproduce the potential energy and its slope at the equilibrium nuclear position in the ground state.[14] The nuclear potential of the final state is not well known to our knowledge. A large equibibrium nuclear distance compared with that of the ground state is predicted. It will, therefore, be a good approximation to regard the TPA of the I_2 system as the strong coupling case. In Fig. 4 the Σ_g^+or $\Pi_{0g}\leftarrow\Pi_{1u}\leftarrow\Sigma_g^+$ transition is considered; the polarization ratios calculated by using Eq. 22 are shown. The parameter used are $\tilde{\varepsilon}_n/\hbar=48000\,\mathrm{cm}^{-1}$, $\Gamma_{ma}=5\,\mathrm{cm}^{-1}$, $\Gamma_{mn}=3\,\mathrm{cm}^{-1}$ and $\Gamma_{mm}=4\,\mathrm{cm}^{-1}$. These dephasing and damping constants have been assumed to be independent of ω_R, which should be valid in a restricted frequency range near the resonant region. Figure 4 shows that the polarization ratio is a decrease function with a constant value near the resonance as increasing the laser frequency. This indicates that the simultaneous process increases in its contribution to the resonant TPA process. For the comparison, the observed ratios are indicated by points. We can see that there is a good correlation between the observed and calculated polarization ratios. Thus, the polarization behavior measured can qualitatively be explained in terms of the gradual increase in the contribution of the simultaneous process.

In this paper it is assumed that the sequential process is induced by an elastic interaction between the molecules and heat bath from the basis of the pressure effect appeared in the UV emission intensity obtained by the puming process above the dissociation limit of the B state though the quantitative investigation of the pressure effect has not been reported. Dissociation processes of I_2 play an important role in the resonant multiphoton transition especially *via* the repulsive Franck-Condon state because in this state the magnitude of the dissociation rate constant is in the ps order which is much larger than that of the pure dephasing constant.[20] The dissociation rate constant is a function of the laser frequency. As the laser frequency increases, the rate constant increases with its magnitude comparable to that of the pure dephasing constant which is reflected in the pressure effect observed above the dissociation threshold.

We have neglected rotation of I_2 in the analysis of the polarization ratio for the resonant TPA. Polarization is destroyed by *M*-changing collisions when time of rotation is comparable or faster than the interaction time between photons and molecule. In this case rotational effects on the polarization dependence of the TPA have to be taken into account.[12] For the TPA *via* the dissociative intermediate states, the rotational effects can safely be neglected because the interaction time between photons and the dissociative state is much shorter than time of the rotation.

Finally it would be worth to mention that the theoretical treatment developed in this paper can be easily applied to resonance Raman scattering from molecules with repulsive resonant states.[21] The expression for the cross section for the resonance Raman scattering is obtained from that of the transition probability of the simultaneous TPA process by specifying both incident and emitted photons and by letting $\Delta\rightarrow 0$.

To summarize, experimental and theoretical studies have been carried out in order to clarify the mechanism of the resonant two-photon transition involving repulsive intermediate states. It has been shown from the polarization ratios measurement of the gaseous I_2 molecules that the sequential process makes a significant contribution even in a laser frequency range belonging to the repulsive states. Both simultaneous and sequential two-photon transitions take place below the wavelength around 450 nm, which has qualitatively been explained by using the expression for the polarization ratio derived though the expression has been derived by using a simple model.

Appendix A. Derivation of Eq. 13

In this Appendix, we shall present a derivation of Eq. 13 on the basis of the Boson operator algebra. From Eq. 12, the generating function in the low temperature limits can be expressed as

$$G(\tau, \tau', t) = \langle 0|\exp(\mathrm{i}\hat{H}_m\tau'/\hbar)\exp(\mathrm{i}\hat{H}_n t/\hbar)\exp(\mathrm{i}\hat{H}_m\tau/\hbar) \times \exp[-\mathrm{i}\hat{H}_a(t-\tau+\tau')/\hbar]|0\rangle, \qquad (\mathrm{A.}\ 1)$$

where $|0>$ denotes the vibrational eigenket in the zeroth state of the ground electronic state. In terms of the Boson operators $\hat{b}$, $\hat{b}^{\dagger}$ which satisfy $[\hat{b}, \hat{b}^{\dagger}]=1$, the vibronic Hamiltonians related to TPA are given as

$$\hat{H}_a = \hbar\omega\left(\hat{b}^{\dagger}\hat{b}+\frac{1}{2}\right), \qquad (\mathrm{A.}\ 2)$$

$$\hat{H}_m = -\frac{F_m}{\sqrt{2}}(\hat{b}+\hat{b}^{\dagger}) + \varepsilon_m^0, \qquad (\mathrm{A.}\ 3)$$

and

$$\hat{H}_n = \hat{H}_a - \hbar\omega\varDelta(\hat{b}+\hat{b}^{\dagger}) + \frac{\hbar\omega\varDelta^2}{2} + \varepsilon_n^0. \qquad (\mathrm{A.}\ 4)$$

In deriving Eq. A.3, the nuclear kinetic energy term has been omitted. This is equivalent to the delta function approximation for the repulsive state.

Using the expression,

$$\exp(\mathrm{i}\hat{H}_n t/\hbar) = \exp[\mathrm{i}\varepsilon_n^0 t/\hbar+\frac{\varDelta^2}{2}\{\exp(\mathrm{i}\omega t)-1\}] \times\exp(\mathrm{i}\hat{H}_a t/\hbar)\exp[-\lambda(t)\hat{b}^{\dagger}]\exp[\lambda^*(t)\hat{b}], \qquad (\mathrm{A.}\ 5)$$

where $\lambda(t)=(\varDelta/\sqrt{2})[1-\exp(-\mathrm{i}\omega t)]$, Eq. A.1 is rewritten as

$$G(\tau, \tau', t) = \exp[\mathrm{i}\varepsilon_n^0 t/\hbar+\frac{\varDelta^2}{2}\{\exp(\mathrm{i}\omega t)-1\} + \mathrm{i}\tau'(\varepsilon_a^0-\hbar\omega/2)/\hbar-\mathrm{i}\tau(\varepsilon_a^0-\hbar\omega/2)/\hbar]U(\tau, \tau', t), \qquad (\mathrm{A.}\ 6)$$

where

$$U(\tau, \tau', t) = \langle 0|\exp[-\mathrm{i}\tau' F_m(\hat{b}+\hat{b}^{\dagger})/\sqrt{2}\hbar]\exp[\mathrm{i}t\omega\hat{b}^{\dagger}\hat{b}] \times\exp[-\lambda(t)\hat{b}]\exp[\lambda^*(t)\hat{b}]\exp[\mathrm{i}\tau F_m(\hat{b}+\hat{b}^{\dagger})/\hbar]. \qquad (\mathrm{A.}\ 7)$$

Utilizing the Boson operator algebra, Eq. A.7 is expressed as

$$U(\tau, \tau', t) = \exp[-F_m^2(\tau^2+\tau'^2)/4\hbar^2+F_m^2\tau\tau'\exp(\mathrm{i}t\omega)/2\hbar^2 -\mathrm{i}F_m\tau'\lambda^*(t)/\sqrt{2}\hbar+\mathrm{i}F_m\tau\lambda^*(t)/\sqrt{2}\hbar]. \qquad (\mathrm{A.}\ 8)$$

We expand $(\varDelta/\sqrt{2})\exp(\mathrm{i}\omega t)$ in Eq. A.6 to second order of t:

$$\frac{\varDelta}{\sqrt{2}}\exp(\mathrm{i}\omega t) \simeq \frac{\varDelta}{\sqrt{2}}\left(1+\mathrm{i}\omega t-\frac{\omega^2 t^2}{2}\right). \qquad (\mathrm{A.}\ 9)$$

Substitution of Eqs. A.8 and A.9 into Eq. A.6 results in

$$G(\tau, \tau', t) = \exp[\mathrm{i}(\tilde{\varepsilon}/\hbar-\omega/2)t+\mathrm{i}(\varepsilon_m^0/\hbar-\omega/2)\tau' -\mathrm{i}(\varepsilon_m^0/\hbar-\omega/2)\tau-(F_m\tau'-F_m\tau+F_n t)^2/4\hbar^2], \qquad (\mathrm{A.}\ 10)$$

where $\tilde{\varepsilon}_n=\varepsilon_n^0+\hbar\omega\varDelta^2/2$, and $F_n=\varDelta\omega$. Substituting Eq. A.10 into 11, we obtain the desired expression:

$$L^{\mathrm{sim}}(\omega_{\mathrm{R}}) = \frac{2}{\hbar^4}\int_{-\infty}^{\infty}\mathrm{d}t\int_0^{\infty}\mathrm{d}\tau\int_0^{\infty}\mathrm{d}\tau'\exp[\mathrm{i}(\tilde{\varepsilon}_n/\hbar-\omega/2-2\omega_{\mathrm{R}})t -\Gamma_{na}|t|-(F_m\tau'-F_m\tau+F_n t)^2/4\hbar^2 +\mathrm{i}(\varepsilon_m^0/\hbar-\omega/2-\omega_{\mathrm{R}})\tau'-\mathrm{i}(\varepsilon_m^0/\hbar-\omega/2-\omega_{\mathrm{R}})\tau -(\tau+\tau')\Gamma_{ma}]. \qquad (\mathrm{A.}\ 11)$$

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between the dissociative and bound states of I_2 has not been reported. The magnitude of the dephasing constant between the bound ($B^3\Pi_{0^+u}$) and bound ($^1\Sigma_g^+$) states has been measured by Brewer and Kano (R. G. Brewer and S. S. Kano, "Laser-Induced Processes in Molecules," ed by K. L. Kompa and S. D. Smith, Springer-Verlag, Berlin, (1979) p. 54). From the view point of the large potential energy change between the dissociative and bound states it is deduced that the magnitude of the pure dephasing constant relevant to the transition between the dissociative and bound states is larger than that reported by Brewer and Kano. See also Ref. 14.

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