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DEPOLARIZATION RATIOS OF I_2 RAMAN LINES IN THE RESONANCE REGION

Susumu MATSUZAKI and Shiro MAEDA
Research Laboratory of Resources Utilization
Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152

Depolarization ratio(ρ_ℓ) of I_2 Raman lines in the resonance region was observed in several solutions, and appreciable dependence of ρ_ℓ on exciting wavelengths was found out. The origin of the observed ρ_ℓ changes was discussed on the basis of the composite nature of the visible band.

The resonance Raman effect of iodine molecules has been studied quite intensively so far, and the depolarization ratio was reported to be $\rho_\ell=1/3$ in both vapor and solutions at 514.5 nm excitation.1) This ρ_ℓ value is in consistency with the interpretation of the visible I_2 absorption that it is mostly ascribable to a single nondegenerate transition $B_0{+}_u({}^3\Pi) \longleftarrow X_0{+}_g({}^1\Sigma)$. In the present investigation, however, we found out that the ρ_ℓ is not invariably equal to 1/3 but changes appreciably depending on exciting wavelength and the properties of solvents. This observation is considered to be closely related to the composite nature of the visible absorption, which was demonstrated in I_2 to be the case rather recently. That is, photofragment spectrum obtained by Oldman et al.,2) the detailed analysis of the absorption band by Tellinghuisen3) as well as the magnetic circular dichroism study by Brith et al.4) equally claimed that the visible I_2 band cannot be entirely attributable to the above $B \longleftarrow X$ transition but it includes a considerable contribution (ca. 20%)5) from $1u({}^1\Pi) \longleftarrow X_0{+}_g({}^1\Sigma)$ transition. It will be shown in the following that the ρ_ℓ behavior as mentioned above is reasonably interpretable by taking such a composite nature of the visible band into account.

Experimental

The measurements have been carried out for dilute I_2 solutions (ca. 10^{-2}mol/ℓ)

at exciting wavelengths of 632.8, 514.5, 501.7, 496.5, 488.0, 476.5 and 457.9 nm. The spectrum was recorded on a JEOL JRS S1 Raman spectrometer normally with the slit width of 6 cm^{-1} at 514.5 nm. A rotating cell was used for Ar^+ laser exciting lines.

Linear depolarization ratio $\rho_\ell = I_\perp / I_\parallel$ was determined by measuring the parallel and perpendicular components of scattered radiation at 90° geometry, using a pollaroid analyzer placed in front of the entrance slit. Although the spectrometer was equipped with a polarization scrambler, there still remained a slight polarization characteristic, so that the observed results were corrected by a calibration curve obtained with a standard lamp. Some solvent lines such as 1349cm^{-1}(C_6H_{12}), 1148cm^{-1}(CH_2Cl_2) and 1559cm^{-1}(C_6D_6), whose ρ_ℓ was precisely known, were appropriately used as internal standards.[6)]

Results and discussion

The plot of observed ρ_ℓ vs. exciting wavelengths of the fundamental and the 1-st overtone has been given in Fig.1 for three different solutions. Standard deviation may be estimated at about 10%.

In cyclohexane, probably the most inert solvent here, ρ_ℓ's of the fundamental and 1-st overtone are equal to 1/3 at 514.5 nm in agreement with the earlier result[1)] but they gradually decrease towards shorter wavelengths down to 1/5. Similar trend can be observed for the same lines in CH_2Cl_2 though less remarkably, but in C_6D_6 it seems to have collapsed to a constant lower value already near 500 nm.

The problem may be discussed on the basis of the usual expression for depolarization ratio:

$$\rho_\ell = \frac{3\,\beta^2}{45\,\bar{\alpha}^2 + 4\,\beta^2} \qquad \text{-----------} \; (1)$$

where, $\bar{\alpha} = (1/3)(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$

and $\beta^2 = (1/2)\,\{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\{\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2\}\}$.

According to the usual theory of Raman intensity, a scattering tensor element is composed of the terms carrying the factor $(M\rho)_i(M\sigma)_j$, where $(M\rho)_i$ is the transition moment from the ground to i-th excited electronic states and ρ and σ denote

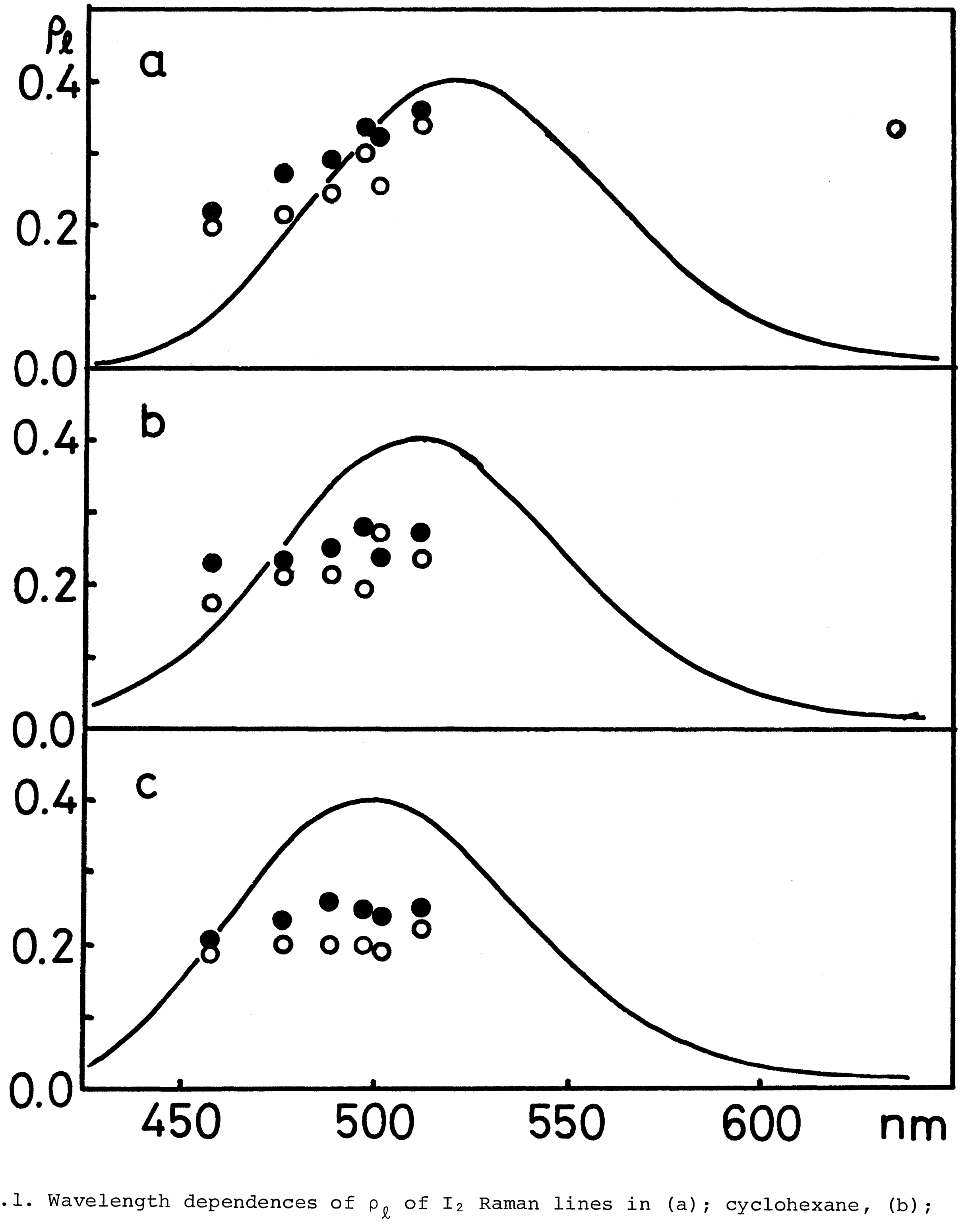

Fig.1. Wavelength dependences of ρ_{ℓ} of I_2 Raman lines in (a); cyclohexane, (b); dichloromethane and (c); benzene-d_6. (o): fundamental. (●): 1-st overtone. ————: absorption profile.

the coordinates fixed on a molecule. As for the present resonance scattering, we may confine our attention to the transitions mentioned before. The moments of $B_{0^+_u}(^3\Pi) \longleftarrow X_{0^+_g}(^1\Sigma)$ and $1u(^1\Pi) \longleftarrow X_{0^+_g}(^1\Sigma)$ transitions are parallel (z) and perpendicular (x,y) to the internuclear axis respectively. If we maintain the former view that the visible band is dominated by the single transition $B_{0^+_u}(^3\Pi) \longleftarrow X_{0^+_g}(^1\Sigma)$, then only a sigle element α_{zz} may have a dominant value in the resonance region so that ρ_ℓ be almost equal to 1/3. On the other hand, if another transition $1u(^1\Pi) \longleftarrow X_{0^+_g}(^1\Sigma)$ also absorbs appreciably in the same region, other components as α_{xx}, α_{yy}, $\alpha_{xz}=\alpha_{yz}$ may be significant so that the ρ_ℓ value may deviate from 1/3. It is obvious through the following transformation that the observed decline of ρ_ℓ from 1/3 is certainly due to the diagonal components α_{xx} and α_{yy} enhanced together with α_{zz}, whereas the off diagonal ones always serve to raise ρ_ℓ.

$$\rho_\ell=\frac{1}{3}+\frac{5}{3}\times\frac{6\alpha_{zx}{}^2-3\alpha_{xx}{}^2-6\alpha_{xx}\alpha_{zz}}{45\bar{\alpha}^2+4\beta^2} \qquad \text{---------}\ (2)$$

Therefore, we shall confine the following consideration to those diagonal elements.

Recently Jacon et al. derived an expression of Raman scattering tensor for the cases of resonance with either of discrete and continuous states.$^{7)}$ In the present case, the diagonal components $\alpha_{\rho\rho}$ may be mostly associated with the terms of Franck-Condon type, which correspond to the A-term by Albrecht.$^{8)}$ This is because the two excited states concerned, $B_{0^+_u}(^3\Pi)$ and $1u(^1\Sigma)$, give mutually perpendicular transition moments, and no other states can be found out to give appreciable influence on the diagonal components through vibronic mixing. Thus, we have for $B_{0^+_u}$ state:

$$\alpha_{zz}^{wv}(E_0)=\left|M_e\right|^2\{\pi i\langle w|E_0+E_v\rangle\langle E_0+E_v|v\rangle\rho(E_0+E_v)$$
$$+P\int_D^\infty\frac{\langle w|E\rangle\langle E|v\rangle}{E-E_v-E_0}\rho(E)dE+\sum_u\frac{\langle w|u\rangle\langle u|v\rangle}{E_u-E_v-E_0+i\gamma}\} \qquad \text{---------}\ (3)$$

where M_e; electronic transition dipole moment to $B_{0^+_u}$ state,

E_0; incident photon energy,

$\rho(E)$; density of continuous states,

w,v; initial and final vibrational states of the electronic ground state,

E_v; vibrational energy of electronic ground state,

D; dissociation energy of the excited state ($B_{0^+_u}$),

u; vibrational state of the excited state,

γ; damping factor,

P; principal value of the integral.

On the other hand, for the wholly dissociative $1u(^1\Pi)$ state we have,

$$\alpha^{wv}_{xx}(E_0) = \alpha^{wv}_{yy}(E_0) = |M_e'|^2\{\pi i\langle w|(E_0+E_v)\rangle\langle(E_0+E_v)|v\rangle\rho'(E_0+E_v) + P\int_{D'}^{\infty}\frac{\langle w|E\rangle\langle E|v\rangle}{E-E_v-E_0}\rho'(E)dE\}. \quad \text{---------} \ (4)$$

As seen in the above formulas, the continuous states differ from the discrete ones, as intermediate state of Raman scattering, in that they do not include γ. Therefore, if the γ value is increased, which may be effected by raising pressure for gaseous samples or by changing the solvent to the more active one in solutions, the scattering due to discrete levels may be considerably quenched while the contribution of continuous states be essentially unchanged. Such a circumstance suggests the following interpretation of the observed feature of depolarization ratio.

Considering the case in a relatively inert solvent cyclohexane, the γ of discrete levels may assume a rather small value so that the scattering tensor may be dominated by the $B_0+_u(^3\Pi)$ discrete level contribution, α_{zz}, in the longwave region, resulting in $\rho_\ell \simeq 1/3$. As the exciting wavelength travels to the shortwave side, the continuous level contribution may become more important while the discrete one grows weaker as surmised from Fig. 2b. Then, perpendicular components α_{xx} and α_{yy} associated with the $1u(^1\Pi) \longleftarrow X_0+_g(^1\Sigma)$ transition become relatively more important to exhibit descending ρ_ℓ value towards shortwave excitation. In a polar solvent dichloromethane, the ρ_ℓ is appreciably less than 1/3 already at 514.5 nm probably because of less pronounced discrete level scattering due to greater γ value than in cyclohexane. In benzene-d_6, presumably the more interacting one, the observed ρ_ℓ profile seems to indicate that the discrete level contribution has mostly colapsed due to an extremely great γ. This interpretation is also in consistency with the observed intensity profiles, which were found out to become considerably lower for more interacting solvents when compared in a standardized scale.9)

In view of above observations, $\rho_\ell \simeq 1/5$ obtained for all solvents at the shortwave edge may be looked as being determined mostly by the composition of continuous level scattering. As $B_0+_u(^3\Pi)$ and $1u(^1\Pi)$ states have fairly similar potential surfaces in the above region as seen in Fig. 2a, it may be a good practice to assume the frequency-dependent parts in the braces of Eqs. (3) and (4) to be approximately equal

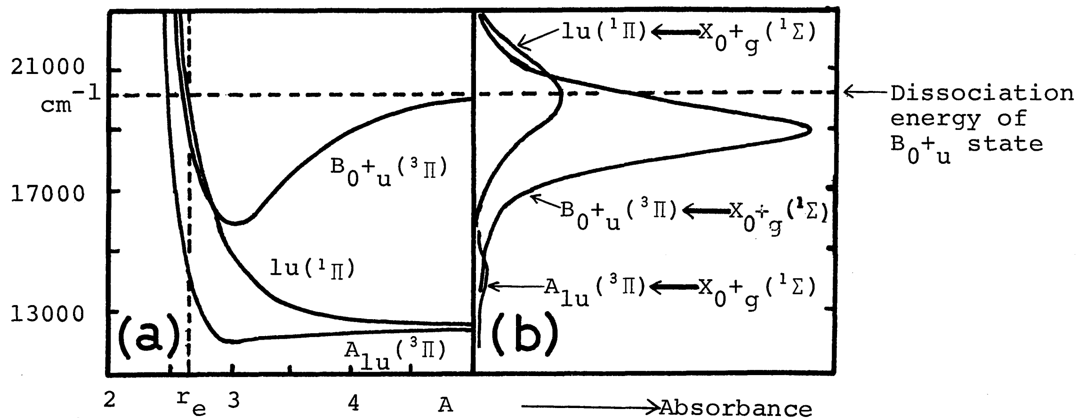

Fig.2. a; potential diagram showing relevant states of I_2 in the region of interest and b; absorption profiles of separate components (based on Ref.3). r_e; equilibrium nuclear distance of $X_{0^+g}(^1\Sigma)$ state.

in the region of question. Then we have,

$$\rho_\ell \simeq \frac{3(1-x)^2}{5(1+2x)^2 + 4(1-x)^2} \qquad \text{----------} \quad (5)$$

where $x = |M_e'|^2/|M_e|^2$. Equating the above expression to 1/5, it turns out that the $1u(^1\Pi) \longleftarrow X_{0^+g}(^1\Sigma)$ transition is responsible for 22% of the visible absorption band of I_2. This value is a rather rough estimate but it is fairly consistent with those based on other experiments. Incidentally, the low energy $A_{1u}(^3\Pi)$ state seems to be little effective for the Raman scattering, because the ρ_ℓ at 632.8 nm excitation is closely equal to 1/3 contrary to the expectation for the resonance of this doubly degenerate state.

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