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The Intensity in the Resonance Raman Effect. I. The Diatomic Molecule in the Harmonic Potential Approximation

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The formulas for the Raman intensities of fundamental and n-th overtones were investigated theoretically, starting from the Kramers-Heisenberg dispersion formula and referring to a diatomic molecule in a harmonic potential approximation. The derived formulas were then applied to fifteen overtone bands of iodine, which have been observed in gas, and to the exciting frequency dependence of the fundamental and the first overtone intensities of iodine in a $CHCl_3$ solution. It was shown that the formulas quantitatively explain the trend of the observed data well.

With the advent of various laser light sources, the resonance Raman effect has come to be investigated extensively in recent years. It has been observed that higher overtones appear in a spectrum with considerable intensities as the exciting light frequency approaches an electronic absorption band. For example, the fifteen overtones of iodine have been obtained in gas using the argon ion laser at 4880 Å by Holzer *et al.*[1]

The origin of the resonance Raman effect has been investigated theoretically by several authors. Peticolas *et al.*[2,3] have derived the formula of the n-th overtone Raman intensity using the technique of the time-ordered diagram and have then applied this equation to the experimental data on iodine in gas. The quantitative agreement with the observed data has been poor for higher overtones. Verlan[4] has investigated the formula of the resonance Raman intensity based on the generalized perturbation theory of Heitler,[5] and has formulated a rather complicated expression.

We obtained a simple expression of the Raman intensity starting from the Kramers-Heisenberg dispersion equation and using the idea of the effective transition frequency.[6] The vibrational frequency difference between the ground and the excited electronic states was taken into account. The formulas were then applied to the observed data on iodine; reasonable results were obtained.

Method

The intensity of the Raman scattering associated with the $m \rightarrow n$ vibrational transition in the electronic ground state, $|g\rangle$, is given,[7] after averaging the overall orientation of the molecule, by:

$$I_{mn} = (2^7\pi^5/(3^2c^4))I_0(\nu_0+\nu_{mn})^4 \sum_{\rho,\sigma} (\alpha_{\rho\sigma})^2{}_{mn} \tag{1}$$

where ν_0 and I_0 are the frequency and the intensity of the incident light. The ρ,σ (=x, y, z) component of the scattering associated with the transition is expressed by:

$$(\alpha_{\rho\sigma})_{mn} = (1/h) \sum_{e,v} (M_\rho)_{ev,gn}(M_\sigma)_{gm,ev}/(\nu_{ev,gn}-\nu_0+i\gamma_e)$$
$$+ (M_\rho)_{gm,ev}(M_\sigma)_{ev,gn}/(\nu_{ev,gn} + \nu_0 + i\gamma_e) \tag{2}$$

in accordance with the Kramers-Heisenberg dispersion theory. Verlan has shown that Eq. (2) is applicable in the case of the resonance Raman effect. The summation is taken over all the electronic excited states, $|e\rangle$, and the vibrational states, $|v\rangle$, accompanying them. The γ is the damping constant of the electronic state $|e\rangle$.[4,7]

The vibronic transition moment, $(M_\rho)_{ev,gn}$, can be expanded in the nuclear coordinate, Q, of a diatomic molecule assuming adiabatic approximation by:

$$(M_\rho)_{ev,gn} = (M_\rho)^0_{ge}\langle ev|gn\rangle + (M_\rho)'_{ge}\langle ev|Q|gn\rangle \tag{3}$$

where $(M_\rho)_{ge}{}^0$ is the component of the pure electronic transition moment at the equilibrium configuration in the $|g\rangle$ state. $(M_\rho)_{ge}{}'$ is the derivative of the electronic transition moment with respect to the nuclear coordinate, Q, $(M_\rho)_{ge}{}'=\{\partial(M_\rho)_{ge}/\partial Q\}_0$. The $\langle ev|gn\rangle$ and $\langle ev|Q|gn\rangle$ give integrals in the nuclear coordinate between the vibrational-state functions of $|e\rangle$ and $|g\rangle$ states.

Following Albrecht,[7,9] Eq. (2) is given by the representation:

$$(\alpha_{\rho\sigma})_{mn} = A_{mn} + B_{mn} + B'_{mn} \tag{4}$$

$$A_{mn} = (1/h) \sum_{e,v} (M_\rho)^0_{ge}M_\sigma)^0_{ge}\langle gm|ev\rangle\langle ev|gn\rangle$$
$$\times\{(\nu_{ev,gm}-\nu_0+i\gamma_e)^{-1} + (\nu_{ev,gn}+\nu_0+i\gamma_e)^{-1}\} \tag{4a}$$

$$B_{mn} = (1/h) \sum_{e,v} (\nu_{ev,gm}-\nu_0+i\gamma_e)^{-1}$$
$$\times\{(M_\rho)^0_{ge}(M_\sigma)'_{ge}\langle gm|Q|ev\rangle\langle ev|gn\rangle$$
$$+(M_\rho)'_{ge}(M_\sigma)^0_{ge}\langle gm|ev\rangle\langle ev|Q|gn\rangle\} \tag{4b}$$

$$\mathrm{B}'_{\mathrm{mn}} = (1/h) \sum_{e,v} (\nu_{ev,gn}+\nu_0+i\gamma_e)^{-1}$$
$$\times\{(M_\rho)^0_{ge}(M_\sigma)'_{ge}\langle gm|ev\rangle\langle ev|Q|gn\rangle$$
$$+ (M_\rho)'_{ge}(M_\sigma)^0_{ge}\langle gm|Q|ev\rangle\langle ev|gn\rangle\} \tag{4c}$$

The A_{mn} term, which does not depend on the vibronic interaction, $(M_\rho)'_{ge}$, contributes to the Raman intensity

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[1] W. Holzer, W. F. Murphy, and H. J. Bernstein, *J. Chem. Phys.*, **52**, 399 (1970).

[2] L. A. Nafie, P. Stein and W. L. Peticolas, *Chem. Phys. Lett.*, **12**, 131 (1971).

[3] W. L. Peticolas, L. Nafie, P. Stein, and B. Fanconi, *J. Chem. Phys.*, **52**, 1576 (1970).

[4] E. M. Verlan, *Opt. Spectry.*, **20**, 557 (1966).

[5] W. Heitler, "The Quantum Theory of Radiation," Oxford University Press, London (1954).

[6] J. Behringer, "Raman Spectroscopy," Vol. 1, ed. by H. A. Szymanski, Plenum Press, New York (1967), Chapt. 6.

[7] J. Tang and A. C. Albrecht, "Raman Spectroscopy," Vol. 2, ed. by H. A. Szymanski, Plenum Press, New York (1970), Chapt. 2.

[8] J. Behringer, *Z. Elektrochem.*, **62**, 906 (1958).

[9] A. C. Albrecht, *J. Chem. Phys.*, **34**, 1476 (1961).

only when the electronic ground and excited states have the potential curves displaced or distorted in relation to each other.[10] The B_{mn} and B'_{mn} terms depend on the vibronic interaction, $(M_\rho)'_{\mathrm{ge}}$, and have been extensively investigated by Albrecht in the case of the ordinary Raman effect. For practical use, we must further simplify these expressions of the scattering tensor.

A_{mn} Term. First, let us investigate the A_{mn} term. For the sake of simplicity, we will consider the vibration of a diatomic molecule assuming a harmonic oscillator. The vibrational ground state, $|\mathrm{g}0\rangle$, is taken as the initial state, $|\mathrm{g}m\rangle$. Then, the frequency corresponding to the vibronic transitions concerned may be expressed as:

$$\nu_{\mathrm{e}v,\mathrm{g}0} = \nu_{\mathrm{e}0,\mathrm{g}0} + v\nu_{\mathrm{e}} \tag{5}$$

where $\nu_{\mathrm{e}0,\mathrm{g}0}$ is the 0–0 transition frequency between $|\mathrm{g}\rangle$ and $|\mathrm{e}\rangle$ electronic states, and where ν_{e} is the vibrational frequency in the $|\mathrm{e}\rangle$ state. The substitution of the above expression into Eq. (4a) leads to:

$$A_{0n} = \sum_{\mathrm{e}} \{(M_\rho)^0_{\mathrm{ge}}(M_\sigma)^0_{\mathrm{ge}}/(h\nu_{\mathrm{e}})\} \sum_{v} \langle \mathrm{g}0|\mathrm{e}v\rangle\langle \mathrm{e}v|\mathrm{g}n\rangle \times\{(\mathrm{c}_1+v)^{-1}+(\mathrm{c}_2+v)\}^{-1} \tag{6}$$

where:

$$\begin{aligned} \mathrm{c}_1 &= (\nu_{\mathrm{e}0,\mathrm{g}0}-\nu_0+i\gamma_{\mathrm{e}})/\nu_{\mathrm{e}} \\ \mathrm{c}_2 &= (\nu_{\mathrm{e}0,\mathrm{g}n}+\nu_0+i\gamma_{\mathrm{e}})/\nu_{\mathrm{e}}. \end{aligned} \tag{6a}$$

It is generally difficult to carry out the summation over v because the $|\mathrm{e}\rangle$ state gives a different equilibrium internuclear distance, $r_{\mathrm{e}}{}^0$, and different fundamental vibrational frequency, ν_{e}, from the corresponding quantities in the ground state, $r_{\mathrm{g}}{}^0$ and ν_{g}. Therefore we will first consider a somewhat specialized case where $\nu_{\mathrm{e}}=\nu_{\mathrm{g}}$ but where $r_{\mathrm{e}}{}^0=r_{\mathrm{g}}{}^0$.

Now using the expression of the Franck-Condon overlap integrals given by Hutchinson,[11,12] we obtain for $\nu_{\mathrm{e}}=\nu_{\mathrm{g}}$:

$$\langle \mathrm{g}m|\mathrm{e}v\rangle = \exp(-\delta_{\mathrm{e}}^2/4)/\sqrt{(m!v!)/(2^{m+v})}\,\delta_{\mathrm{e}}^m \times \sum_{k=0} ((-1)^{m-k}2^k\delta_{\mathrm{e}}^{v-2k})/(k!(m-k)!(v-k)!) \tag{7}$$

and, consequently:

$$\sum_{v} \langle \mathrm{g}0|\mathrm{e}v\rangle\langle \mathrm{e}v|\mathrm{g}n\rangle/(c+v) = \sqrt{n!/2^n}(-\delta_{\mathrm{e}})^n\exp(-\delta_{\mathrm{e}}^2/2) \times\sum_{k=0} (-1)^k/(k!(n-k)!) \sum_{v} (\delta_{\mathrm{e}}^2/2)^{v-k}/(c+v)(v-k)!) \tag{8}$$

where:

$$\delta_{\mathrm{e}} = \alpha_{\mathrm{e}}(r_{\mathrm{g}}^0-r_{\mathrm{e}}^0) \tag{9}$$

$$\alpha_{\mathrm{e}} = 4\pi^2\mu\nu_{\mathrm{e}}/h;\ \mu;\ \text{reduced mass} \tag{9a}$$

The dimensionless quantity, δ_{e}, is the difference in the equilibrium internuclear distance between the $|\mathrm{g}\rangle$ and $|\mathrm{e}\rangle$ states in the unit of the classical vibrational amplitude, $1/\alpha_{\mathrm{e}}$, of the vibrational ground state.

The summation over v on the right-hand side of Eq. (8) can be approximately written as:

$$\sum_{v} (\delta_{\mathrm{e}}^2/2)^{v-k}/((c+v)(v-k)!) \doteqdot \exp(\delta_{\mathrm{e}}^2/2)/(c+\delta_{\mathrm{e}}^2/2+k) \tag{10}$$

It can easily be seen that the above relation applies fairly well for $c=1$ for all values of δ_{e} and when $\delta_{\mathrm{e}}<1$ for a wide range of c.

Then, using the formula:

$$\sum_{k=0}^{n} (-1)^k n!/((c+k)(n-k)!k!) = n!/\{c(c+1)\cdots\cdots(c+n)\} \tag{11}$$

Equation 8 can be written as:

$$\sum_{v} \langle \mathrm{g}0|\mathrm{e}v\rangle\langle \mathrm{e}v|\mathrm{g}n\rangle/(c+v) =\sqrt{n!/2^n}(-\delta_{\mathrm{e}})^n/\{c^*(c^*+1)\cdots\cdots(c^*+n)\} \tag{12}$$

where, according to Eq. (10):

$$c^* = c + \delta_{\mathrm{e}}^2/2. \tag{12a}$$

Thus, we have:

$$A_{0n} = (1/h)\mathrm{Q}_n \sum_{\mathrm{e}} (M_\rho)^0_{\mathrm{ge}}(M_\sigma)^0_{\mathrm{ge}}(-\delta_{\mathrm{e}}\nu_{\mathrm{e}})^n \times\{\prod_{p=0}^{n}(\nu_{\mathrm{eg}}-\nu_0+i\gamma_{\mathrm{e}}+p\nu_{\mathrm{e}})^{-1} + \prod_{p=0}^{n}(\nu_{\mathrm{eg}}+\nu_0+i\gamma+p\nu_{\mathrm{e}})^{-1}\} \tag{13}$$

where:

$$\mathrm{Q}_n = \langle \mathrm{g}0|\mathrm{Q}^n|\mathrm{g}n\rangle = \sqrt{n!/2^n} \tag{13a}$$

$$\mathrm{Q} = \alpha_{\mathrm{g}}(r-r_{\mathrm{g}}^0) \tag{14}$$

ν_{eg} is the effective transition frequency from $|\mathrm{g}\rangle$ to $|\mathrm{e}\rangle$ and may be represented approximately, according to Eq. (12a), by:

$$\nu_{\mathrm{eg}} \doteqdot \nu_{\mathrm{e}0,\mathrm{g}0} + \nu_{\mathrm{e}}\delta_{\mathrm{e}}^2/2 \tag{15}$$

which equals the vertical transition frequency from the $|\mathrm{g}\rangle$ to the $|\mathrm{e}\rangle$ state. Equation (15) indicates that the maximum Raman scattering would occur at the position of the absorption maximum. However, this statement should be modified slightly when applied to the real system, because we neglected the effect of the anharmonicity of the potential curves and the effect of the other virtual states. Therefore, there may occur the case in which the position of the maximum Raman scattering differs to some extent from that of the absorption maximum.

Next, let us deal with another specialized case where $\mathrm{r_g}^0=\mathrm{r_e}^0$ but where $\nu_{\mathrm{e}}\neq\nu_{\mathrm{g}}$. The Franck-Condon overlap integrals in Eq. (4a) are calculated by a method similar to that used before. Then, the scattering tensor may be represented as:

$$A_{0,2n} = (1/h)\,\mathrm{Q}_{2n} \sum_{\mathrm{e}} (M_\rho)^0_{\mathrm{ge}}(M_\sigma)^0_{\mathrm{ge}}(-\nu_{\mathrm{e}}\Delta_{\mathrm{e}})^n \times\{\prod_{p=0}^{n}(\nu_{\mathrm{eg}}-\nu_0+i\gamma_{\mathrm{e}}+p\nu_{\mathrm{e}})^{-1} + \prod_{p=0}^{n}(\nu_{\mathrm{eg}} + \nu_0 + i\gamma_{\mathrm{e}} + p\nu_{\mathrm{e}})^{-1}\} \tag{16}$$

where

$$\Delta_{\mathrm{e}} = (\nu_{\mathrm{e}}-\nu_{\mathrm{g}})/(\nu_{\mathrm{e}}+\nu_{\mathrm{g}}) \tag{17}$$

retaining only the term which has the lowest order of Δ_{e}.[12]

The general case of $r_{\mathrm{e}}{}^0\neq r_{\mathrm{g}}{}^0$ and $\nu_{\mathrm{e}}=\nu_{\mathrm{g}}$ may be

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[10] W. Siebrand, *ibid.*, **46**, 440 (1967).
[11] E. Hutchinson, *Phys. Rev.*, **36**, 410 (1930).
[12] C. Ting, *Spectrochim. Acta*, **24A**, 1177 (1968).

treated by introducing explicitly ν_e and ν_g into Eq. (12), in which $\nu_e=\nu_g$ has been assumed, and by then combining this with Eq. (16). This leads to the following expression of $A_{0,n}$:

$$A_{0n} = \langle g0|A_- + A_+|gn\rangle \tag{18}$$

where:

$$\begin{aligned} A_{\mp} = (1/h) \sum_e \{ (M_\rho)_{ge}^0 (M_\sigma)_{ge}^0 / (\nu_{eg} \mp \nu_0 + i\gamma_e) \\ \times (1 + \nu_e \delta_e Q / \langle \nu_{eg} \mp \nu_0 + i\gamma_e \rangle)^{-1} \\ \times (1 + \nu_e \Delta_e Q^2 / \langle \nu_{eg} \mp \nu_0 + i\gamma_e \rangle)^{-1} \end{aligned} \tag{18a}$$

The bracket notation is used for the sake of simplicity. It indicates that, in expanding the above equation, $\langle \nu_{eg} \mp \nu_0 + i\gamma_e \rangle^q$ must be replaced by $\prod_{p=1}^{q} (\nu_{eg} \mp \nu_0 + i\gamma_e + p\nu_e)$. The contribution of Eq. (16) to the scattering tensor must be considerably smaller than that of Eq. (12), because usually $\Delta_e \ll 1$.

Supposing the A term is dominant in Eq. (4), and neglecting the contribution of Eq. (16), the intensity of the n-th overtone, I_{0n}, is expressed as:

$$\begin{aligned} I_{0n} = K(\nu_0 - n\nu_g)^4 n! (\nu_0^2 \delta_e^2 / 2)^n \\ \times \prod_{p=0}^{n} \{ (\nu_0 - \nu_{eg} + p\nu_e)^2 + \gamma_e^2 \}^{-1} \end{aligned} \tag{19}$$

when ν_0 approaches ν_{eg}.

Equation (19) has a form similar to Eq. (2) of Peticolas *et al*,[2] apart from the hot-band summation, which is neglected in our treatment. The main differences between our Eq. (19) and Eq. (2) of Peticolas *et al.* are, in the energy denominator, the presence of the effective transition frequency, ν_{eg}, and the vibrational frequency, ν_e, of the electronic excited state, instead of the 0–0 transition frequency and the vibrational frequency, ν_g, of the electronic ground state. In order to take into account of the effect of $\nu_e \neq \nu_g$ on the Raman intensity by means of the formulation of Peticolas *et al.* it is necessary to carry out a higher-order perturbation expansion. The physical meaning of the appearance of ν_e instead of ν_g is apparent, because the resonance should occur at the incident light frequency, $\nu_0 = \nu_{eg} + p\nu_e$. When the vibrational frequencies, ν_g and ν_e, are quite different as in the case of iodine and bromine, the presence of ν_e instead of ν_g has a significant effect upon the resonance Raman intensity. The necessity of introducing the effective transition frequency, ν_{eg}, has clearly been shown experimentally by Yu and Shen using a tunable dye laser.[13] They have shown that the resonance Raman scattering cross-section of InSb as a function of the incident-light frequency has a maximum at an appreciably higher position than that of the reflectivity spectra.

The B_{mn} and B_{mn}' Vibronic Terms. In order to estimate the contribution of the B_{0n} and B_{0n} vibronic terms of Eqs. (4b) and (4c), it is necessary to carry out the following types of summation:

$$\sum_v \langle g0|ev\rangle\langle ev|Q|gn\rangle/(c+v) \quad \text{and}$$

$$\sum_v \langle g0|Q|ev\rangle\langle ev|gn\rangle/(c+v) \tag{20}$$

Using the relations applicable to a harmonic oscillator;

$$2Q|gn\rangle = \sqrt{n}\,|g, n-1\rangle + \sqrt{(n+1)}\,|g, n+1\rangle$$
$$Q|g0\rangle = |g, 1\rangle$$

we can transform the above summation into the following form:

$$\sum_v \langle g0|ev\rangle\langle ev|g,\ n\pm 1\rangle/(c+v) \tag{21a}$$

$$\sum_v \langle g1|ev\rangle\langle ev|gm\rangle/(c+v) \tag{21b}$$

Eq. (21a) is the same type of summation as appears in the calculation of the A-term (Eq. (8)); Eq. (21b) is generally difficult to estimate. When there is an ordinary Raman effect, $|c| \gg 0$, however, this summation may be written as:

$$\sum_v \langle g1|ev\rangle\langle ev|gm\rangle/(c+v) =$$

$$\sqrt{n!/2^{n-1}}\,(-\delta_e)^{n-1} \prod_{p=1}^{n} (c+p)^{-1} \tag{22}$$

We assume that this equation holds approximately in the case of the resonance and preresonance Raman effect if we replace the c of Eq. (22) with the c^* of Eq. (11a), *i.e.*, if we introduce the effective transition frequency, ν_{eg}, and the damping constant, γ_e. Thus, the vibronic terms may be represented as:

$$\begin{aligned} B_{0n} = (1/h) Q_n \sum_e (-\nu_e \delta_e)^{n-1} \\ \times \{ (M_\rho)_{ge}^0 (M_\sigma)'_{ge} + (M_\rho)'_{ge} (M_\sigma)_{ge}^0 \} \\ \times \prod_{p=1}^{n-1} \{ (\nu_0 - \nu_{eg} + i\gamma_e) + p\nu_e \}^{-1} \end{aligned} \tag{23}$$

$$\begin{aligned} B'_{0n} = (1/h) Q_n \sum_e (-\nu_e \delta_e)^{n-1} \\ \times \{ (M_\rho)_{ge}^0 (M_\sigma)'_{ge} + (M_\rho)'_{ge} (M_\sigma)_{ge}^0 \} \\ \times \prod_{p=1}^{n-1} \{ (\nu_0 + \nu_{eg} + i\gamma_e) + p\nu_e \}^{-1}. \end{aligned} \tag{24}$$

Equations (23) and (24) indicate that, for the appearance of overtones by the vibronic mechanism, it is necessary, along with $M_{ge}' \neq 0$, that a molecule has a different geometry in the excited state from that of ground state, as in the A-term (Eq. 13).

As a summary of the above discussions of the A-term and the vibronic terms, the scattering tensor may be represented, using the same bracket notation as in Eq. (18b), by:

$$\begin{aligned} (\alpha_{\rho\sigma})_{0n} = \langle g0|S_- + S_+|gn\rangle \\ S_{\mp} = (1/h) \sum_e \{ (M_\rho(Q))_{ge} (M_\sigma(Q))_{ge} / (\nu_{eg} \mp \nu + i\gamma_e) \} \\ \times (1 + \nu_e \delta_e Q / \langle \nu_{eg} \mp \nu_0 + i\gamma_e \rangle)^{-1} \\ \times (1 + \nu_e \Delta_e Q^2 / \langle \nu_{eg} \mp \nu_0 + i\gamma_e \rangle)^{-1} \end{aligned} \tag{25}$$

where $(M_\rho(Q))_{ge} = (M_\rho)_{ge}{}^0 + (M_\rho)_{ge}{}'Q + \cdots$.
It may easily be seen that, under the appropriate conditions of the pre-resonant case, Eq. (25) gives the Shorygins semiclassical equation for the fundamental $n=1$,[6] using the relation:

$$\nu'_{eg} = (\partial \nu_{eg} / \partial Q)_0 = \nu_e \delta_e \tag{26}$$

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13) P. Y. Yu and Y. R. Shen, *Phys. Rev. Lett.*, **29**, 468 (1972).

Comparison with Experiments

Holzer *et al.* observed the resonance Raman effect of iodine in a gas state up to the 15-th overtone using 4880 Å line of the argon ion laser as the exciting light.[1,3] Peticolas *et al.* have carried out a quantitative calculation of the relative intensities of these overtones with respect to the fundamental. The agreement with the observed data has been poor for the higher overtones.

Although several authors have emphasized the role of the continuous upper electronic state in the resonance Raman effect, we assume tentatively that the equations derived above are applicable to the case of the resonance Raman effect of iodine.[14–16]

Supposing that the contributions of the vibronic terms and Eq. (17) are negligible in the resonance Raman region, we re-calculated the relative intensities of the overtones of iodine with respect to the fundamental intensity: $R_n = I_{0n}/I_{01}$. R_n is represented, following Eq. (19), by:

$$R_n = (\nu_0 - n\nu_g)^4/(\nu_0-\nu_g)^4(\nu_e^2\delta_e^2/2)^{n-1}n!$$

$$\times \prod_{p=2}^{n}\{(\nu_{eg}-\nu_0+p\nu_e)^2+\gamma_e^2\}^{-1} \tag{28}$$

The δ_e, ν_{eg}, and γ_e values were determined so as to fit with the observed R_n, *i.e.*, so as to minimize $\sum_n |R_n^{\text{calc}} - R_n^{\text{obs}}|$, $(n=2,3,\cdots\cdots,15)$. The ν_g and ν_e values were taken to be 215 cm^{-1} and 128 cm^{-1} respectively.[17] The results are shown in Table 1, along with the experimental data (Calc. 1 and Calc. 2). Although the results differ to some extent depending on the initial choice of the values of δ_e, ν_{eg} and γ_e, in any event the agreement between the calculated and the observed relative intensities are fairly good through the 15 overtones. The value, $|r_g{}^0 - r_e{}^0| = 0.368 \sim 0.408$ Å, calculated from δ_e using Eq. (9) coincides reasonably well with the observed value, 0.346 Å (Table 2). As to the effective transition frequency, a value of $\nu_{eg} = 20890 \sim 21200$ cm^{-1} is obtained. This value is near to the frequency of the absorption maximum of iodine in gas ($\sim$20000 cm^{-1}). The ν_{eg} value calculated from Eq. (5), 17800$\sim$18200 cm^{-1}, is a little smaller than these. This difference probably arises from the neglect of the effect of anharmonicity and from the effect of the other virtual states in Eq. (5). It should be noted that the calculated value of the damping constant, $\gamma = 200 \sim 600$ cm^{-1}, corresponds to the rate of the vibrational relaxation and the internal conversion, and is considerably larger than those of the fluorescence and the phosphorescence.[16] The calculations show that the introduction of the effective transition frequency, ν_{eg}, and the vibrational frequency, ν_e, of the electronic excited state in the energy denominator is important in obtaining agreement with the observed R_n.

Table 1. Intensities of overtones of iodine in gas relative to the fundamental

	Observed[1,2]	Calcd 1	Calcd 2	Calcd 3
R_2	0.71	0.672	0.675	0.708
R_3	0.55	0.531	0.550	0.538
R_4	0.45	0.450	0.486	0.450
R_5	0.36(±0.02)	0.391	0.442	0.388
R_6	0.25(±0.02)	0.340	0.402	0.339
R_7	0.22(±0.02)	0.293	0.359	0.296
R_8	0.22(±0.02)	0.248	0.312	0.257
R_9	0.194(±0.02)	0.204	0.263	0.219
R_{10}	0.194(±0.02)	0.163	0.213	0.183
R_{11}	0.167(±0.02)	0.127	0.167	0.151
R_{12}	0.139(±0.02)	0.096	0.126	0.121
R_{13}	0.111(±0.02)	0.070	0.091	0.096
R_{14}	0.084(±0.02)	0.050	0.063	0.074
R_{15}	0.084(±0.02)	0.034	0.042	0.056
δ_e		−6.34	−5.71	−6.37
$\nu_{eg}-\nu_0$ (cm^{-1})		691	397	737
γ_e (cm^{-1})		206	578	212
$\lvert r_g^0-r_e^0\rvert$ (Å)		−0.408	−0.368	−0.410
Δ_e		0	0	−0.36

To see the effect of Δ_e, we have calculated R_n on the basis of Eq. (18), considering Δ_e to be an adjustable parameter along with δ_e, ν_{eg} and γ_e. The results are shown in Table 1 (Calc. 3). As may be seen from Table 1, the introduction of Δ_e improves the agreement between the calculated and the observed relative intensities to some extent, but not very much. The calculated value of $\Delta_e = -0.36$ is reasonable compared with the observed value, −0.254 (Table 2).

Strictly speaking, the equations derived above are applicable only to an isolated molecule. It is interesting, however, to apply these equations to a molecule in solution and to compare the results with that of gas obtained above. The intensity variation in the fundamental and the first overtone of iodine as a function of the exciting light frequency have been obtained by Mortensen in a chloroform solution.[18]

The relative intensities of the fundamental and the first overtone at the exciting light frequency, ν, relative to that of ν_0, $R_1(\nu,\nu_0)$ and $R_2(\nu,\nu_0)$, are given, following Eq. (19), by:

$$R_1(\nu,\nu_0) = \{(\nu-\nu_g)^4/(\nu_0-\nu_g)^4\}$$

$$\times \prod_{p=0}^{1}\{(\nu_{eg}-\nu_0+p\nu_e)^2+\gamma_e^2\}$$

$$\Big/ \prod_{p=0}^{1}\{(\nu_{eg}-\nu+p\nu_e)^2+\gamma_e^2\} \tag{29}$$

$$R_2(\nu,\nu_0) = \{(\nu-2\nu_g)^4/(\nu_0-2\nu_g)^4\}$$

$$\times \prod_{p=0}^{2}\{(\nu_{eg}-\nu_0+p\nu_e)^2+\gamma_e^2\}$$

$$\Big/ \prod_{p=0}^{2}\{(\nu_{eg}-\nu_0+p\nu_e)^2+\gamma_e^2\} \tag{30}$$

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14) J. Behringer, *Z. Physik.*, **229**, 209 (1969).

15) M. Jacon, M. Berjot, and L. Bernard, *C. R. Acad. Sci., Paris, Ser. B*, **273**, 595 (1971).

16) M. Berjot, M. Jacon, and L. Bernard, *Opt. Commun.*, **4**, 246 (1971).

17) G. Herzberg, "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules," 2nd Ed. Van Nostrand, Princeton, N. J. (1950).

18) O. S. Mortensen, *J. Mol. Spectry.*, **39**, 48 (1971).

Table 2. Molecular constants of iodine[17)]

	D_e (eV)	r^0 (Å)	ν (cm^{-1})	$\nu_e x_e$ (cm^{-1})	$r_g^0-r_e^0$	δ_e[a)]	Δ_e[b)]
$\vert g\rangle$	1.54	2.67	215	0.6127	−0.346	−5.432	−0.254
$^3\Pi^+_{0u}$	0.54	3.016	128	0.834			

a) Calculated by Eq. (9). b) Calculated by Eq. (17).

Table 3. The exciting light frequency dependence of Raman intensity of iodine in $CHCl_3$ soln[a)]

	R_1 (ν, ν_0)		R_2 (ν, ν_0)		R_2 (ν)	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
5145 Å	1.00	1.00	1.00	1.00	0.70	0.74
5017 Å	0.91	0.94	0.97	0.91	0.75	0.68
4965 Å			0.74	0.81		
4880 Å	0.77	0.72	0.60	0.60	0.56	0.59
4765 Å	0.52	0.55	0.37	0.36	0.50	0.51
ν_{eg}	19220 cm^{-1}		19240		18600	
γ_e	2160 cm^{-1}		2140		2990	
$\vert r_g^0-r_e^0\vert$					0.329 Å	

a) The observed data are taken from Ref. 18.

Applying these equations to the observed data, we can estimate γ_e and ν_{eg} so as to fit the observed data. The results are shown in Table 3. The agreement between the calculated and the observed values is fairly good. Furthermore, the values of $\gamma_e=2160$ cm^{-1} and $\nu_{eg}=19220$ cm^{-1} obtained from $R_1(\nu,\nu_0)$ coincide well with those of $\gamma_e=2140$ cm^{-1} and $\nu_{eg}=19240$ cm^{-1} obtained from $R_2(\nu,\nu_0)$. We have also determined ν_{eg}, γ_e, and δ_e from the exciting-light-frequency dependence of the first overtone with respect to the fundamental intensity, using the $R_2(\nu)$ of Eq. (28).

In the above calculations, we have neglected the effect of the hot-band summation. This effect is important in the higher overtones. The values of γ_e and δ_e derived from the R_n value of iodine gas would be increased and decreased respectively to some extent by taking into account the effect of the hot-band summation. This point will be investigated in a subsequent paper.

Finally, then, we can estimate $\gamma_e=2000$—3000 cm^{-1} for iodine in a chloroform solution. This value is quite large compared with that of $\gamma_e=200$—600 cm^{-1} of iodine in gas. This indicates that the damping constant is sensitively influenced by molecular interactions. The trend $\gamma_e(\text{soln})\gg\gamma_e(\text{gas})$ seems reasonable because, in a solution, the molecular interactions are larger in gas, therefore, the excited state of a molecule usually has a smaller life-time.[19)]

As a summary of the above discussions, we can say that the trend of the observed Raman intensities of iodine is explained well quantitatively by Eq. (19) in the resonance region. This would indicate that *A*-term of Eq. (4a) *i.e.*, the effect of the deformation of the molecular geometry and the vibrational frequency change in the excited state compared with that of the ground state, is a dominant factor in determining the resonance Raman intensities of iodine. Therefore, an analysis of the resonance Raman effect offers a means of estimating the molecular geometry and vibrational frequencies in the electronic excited state. The idea of the effective transition frequency and the introduction of the vibrational frequency, ν_e, of the electronic excited state in the energy denominator is necessary to obtain the simpler expressions and also to obtain an agreement with the observed data.

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[19)] R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence," John Wiley & Sons, Inc., New York (1969).