IR absorption and Raman scattering QM theory for some lab. members: Raman

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1 Born-Oppenheimer approximation

The Hamiltonian of the system which composed by the atomic position $\{\mathbf{R}_I\}$ and electron $\{\mathbf{r}_i\}$.

$$\hat{H} = \sum_I \frac{-\hbar^2}{2M_I}\frac{\partial^2}{\partial \mathbf{R}_I^2} + \sum_i \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial \mathbf{r}_i^2} + V[\{\mathbf{R}_I\},\{\mathbf{r}_i\}]] \tag{1}$$

The total energy of the system is
$$E = \langle \Psi | \hat{H} | \Psi \rangle \tag{2}$$

Here

$$\begin{aligned}
\Psi &= \Psi(\{\mathbf{R}_I\},\{\mathbf{r}_i\}) \tag{3}\\
&= \sum_n \chi_n(\{\mathbf{R}_I\})\phi_n(\{\mathbf{r}_i\},\{\mathbf{R}_I\}) \tag{4}
\end{aligned}$$

In the wavefunction of electron $\phi_n(\{\mathbf{r}_i\},\{\mathbf{R}_I\})$ satisfies the Schrödinger equation

$$\left\{ \sum_i \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial \mathbf{r}_i^2} + V[\{\mathbf{R}_I\},\{\mathbf{r}_i\}] \right\}\phi_n(\{\mathbf{r}_i\},\{\mathbf{R}_I\}) = \epsilon_n(\{\mathbf{R}_I\})\phi_n(\{\mathbf{r}_i\},\{\mathbf{R}_I\}) \tag{5}$$

If we calculate

$$\begin{aligned}
\langle \phi_m | \hat{H} | \psi \rangle &= E\chi_m \tag{6}\\
&= \langle \phi_m | \sum_I \frac{-\hbar^2}{2M_I}\nabla_I^2 + \sum_i \frac{-\hbar^2}{2m}\nabla_i^2 + V | \sum_n \chi_n(\{\mathbf{R}_I\})\phi_n(\{\mathbf{r}_i\},\{\mathbf{R}_I\}) \rangle \tag{7}\\
&= \sum_n \chi_n \langle \phi_m | \sum_i \frac{-\hbar^2}{2m}\nabla_i^2 + V | \phi_n \rangle \tag{8}\\
&\quad + \sum_n \langle \phi_m | \sum_I \frac{-\hbar^2}{2M_I}\nabla_I^2 | \chi_n(\{\mathbf{R}_I\})\phi_n(\{\mathbf{r}_i\},\{\mathbf{R}_I\}) \rangle \tag{9}\\
&= \sum_n \epsilon_n \langle \phi_m | \phi_n \rangle \chi_n \\
&\quad + \sum_n \sum_I \frac{-\hbar^2}{2M_I}\left[\nabla_I^2 \chi_n \langle \phi_m | \phi_n \rangle + \langle \phi_m | \nabla_I^2 | \phi_n \rangle \nabla_I \chi_n \cdot \langle \phi_m | \nabla_I | \phi_n \rangle \right] \tag{10}
\end{aligned}$$

We get

$$\begin{aligned}
\left[\sum_I \frac{-\hbar^2}{2M_I}\nabla_I^2 + \epsilon_m(\{\mathbf{R}_I\}) - E \right]\chi_m &= \sum_I \frac{\hbar^2}{2M_I}\sum_n \left[\chi_n \langle \phi_m | \nabla_I^2 | \phi_n \rangle + \nabla_I \chi_n \cdot \langle \phi_m | \nabla_I | \phi_n \rangle \right] \\
&= \sum_n \hat{\Lambda}_{mn}\chi_n \tag{11}\\
\hat{\Lambda}_{mn} &= \sum_I \frac{\hbar^2}{2M_I}\left[\langle \phi_m | \nabla_I^2 | \phi_n \rangle + \langle \phi_m | \nabla_I | \phi_n \rangle \cdot \nabla_I \right] \tag{12}
\end{aligned}$$

In the 0-th order approximation (**adiabatic approximation**) the lhs of the above equation can be neglected, i.e. we can get

$$\left[\sum_I \frac{-\hbar^2}{2M_I}\nabla_I^2 + \epsilon_n(\{\mathbf{R}_I\})\right]\chi_{n\nu}^0(\{\mathbf{R}_I\}) = E_{n\nu}^0\chi_{n\nu}^0(\{\mathbf{R}_I\}) \tag{13}$$

The wavefunction of nuclear is now written as the Schrödinger equation with the adiabatic potential $\epsilon_n(\{\mathbf{R}_I\})$. If we can write the $\epsilon_n(\{\mathbf{R}_I\})$ with the displacement $q_{I\alpha}$ from the equilibrium position $\{\mathbf{R}_I^0\}$ in the α direction.

$$\epsilon_n(\{\mathbf{R}_I\}) = \epsilon_0 + \sum_{I,J,\alpha,\beta}\left(\frac{\partial\epsilon_n}{\partial q_{I\alpha}\partial q_{J,\beta}}\right)_0 q_{I\alpha}q_{J,\beta} \tag{14}$$

Then the wavefunction $\chi_{n\nu}^0(\{\mathbf{R}_I\})$ becomes the wavefunction of the vibrational motion of displacements q in the the harmonic oscillator .

The Eq.4 becomes

$$\Psi_{n\nu} = \chi_{n\nu}^0(\{\mathbf{R}_I\})\phi_n(\{\mathbf{r}_i\},\{\mathbf{R}_I\}) \tag{15}$$

The condition of the adiabatic approximation can be held is

$$|\langle\chi_{m\nu}^0|\hat{\Lambda}_{mn}|\chi_{n\nu'}^0\rangle| \ll |E_{m\nu}^0 - E_{n\nu'}^0| \tag{16}$$

Born and Oppenheimer showed that the the energy of a molecule which have a vibrational and rotational motion and is in the electronic state n can be described

$$
\begin{aligned}
E =\ & E_n(\{\mathbf{R}_I^0\}) + [(m/M)^{1/4}]^2(\text{harmonic vib. E}) + [(m/M)^{1/4}]^4[(\text{rot. E})\\
& +(\text{unharmonic vib. E contribution}) + (non-\text{adiabatic contribution from vibrationalmotion})]
\end{aligned}
$$

Here $\{\mathbf{R}_I^0\}$ is the equilibrium position of nucleus. Then we can approximate

$$\Psi_{n\nu} = \chi_{n\nu}^0(\{\mathbf{R}_I\})\phi_n(\{\mathbf{r}_i\},\{\mathbf{R}_I^0\}) \tag{17}$$

2   time-dependent perturbation theory

From the time-dependent perturbation theory(   ) we can get "Fermi's Golden rule" for the transition from i to f state. The rate of transition

$$w(I \to F) = \frac{2\pi}{\hbar}|\langle F|H'|I\rangle|^2\delta(E_F - E_I) \tag{18}$$

Here H' is the perturbation Hamiltonian.

3   :IR absorption

The second quantized form of the interaction Hamiltonian H' between the electron and the photon

$$H' = \frac{e}{m}\left[\frac{\hbar}{2\epsilon_0 V}\right]^{1/2}\sum_j\sum_{\mathbf{k},\gamma}\frac{1}{\sqrt{\omega_\mathbf{k}}}\left[e^{i\mathbf{k}\cdot\mathbf{r}_j}(\mathbf{e}_{\mathbf{k}\gamma}\cdot\mathbf{p}_j)a_{\mathbf{k}\gamma} + e^{-i\mathbf{k}\cdot\mathbf{r}_j}(\mathbf{e}_{\mathbf{k}\gamma}\cdot\mathbf{p}_j)a_{\mathbf{k}\gamma}^\dagger\right] \tag{19}$$

Here $\mathbf{r}_j$ and $\mathbf{p}_j$ is the position and momentum of the electron j, $\mathbf{k}$ is the wave vector of the photon that have the angular frequency $\omega_\mathbf{k}$ and the polarization unit vector $\mathbf{e}_{\mathbf{k}\gamma}$. $a_{\mathbf{k}\gamma}\dagger$ and $a_{\mathbf{k}\gamma}$ is the creation and annihilation operators of photon. The light is the transverse wave and has two component *gamma*. In the surface reflection mode we define that p-wave is in the scattering plane and s-wave is out of the scattering plane. For the $a_{\mathbf{k}\gamma}$ related term we can determine the absorption rate of light in the steric angle $d\Omega$ direction in the $\mathbf{k}$-space

$$w_{\text{abs}}d\Omega = \frac{\omega_{fi}}{8\pi^2\epsilon_0\hbar c^3}\bar{n}_{\mathbf{k}\gamma}\left|\langle f|\frac{e}{m}\sum_j e^{i\mathbf{k}\cdot\mathbf{r}_j}(\mathbf{e}_{\mathbf{k}\gamma}\cdot\mathbf{p}_j)|i\rangle\right|^2 d\Omega \tag{20}$$

Here $\omega_{fi} = (\epsilon_f - \epsilon_i)/\hbar$ and ϵ_i and ϵ_f is the energy level of the electronic system.

$$\omega_\mathbf{k} = \omega_{fi} \tag{21}$$

The wavelength of the light is usually much longer than the atomic scale (k is small), then the exponential can be expanded as

$$e^{i\mathbf{k}\cdot\mathbf{r}_j} \sim 1 + i\mathbf{k}\cdot\mathbf{r}_j - (\mathbf{k}\cdot\mathbf{r}_j)^2/2 + ... \tag{22}$$

If we pick up the first term, the matrix element becomes $\langle f|\frac{e}{m}\sum_j \mathbf{e}_{\mathbf{k}\gamma}\cdot\mathbf{p}_j|i\rangle$. From the communtation relation

$$\mathbf{p}_j = \frac{im}{\hbar}[H_0, \mathbf{r}_j] \tag{23}$$

Here H_0 is the unperturbed Hamiltonian and

$$\langle f|\frac{e}{m}\sum_j \mathbf{e}_{\mathbf{k}\gamma}\cdot\mathbf{p}_j|i\rangle = \frac{i}{\hbar}(\epsilon_f - \epsilon_i)\langle f|e\sum_j \mathbf{e}_{\mathbf{k}\gamma}\cdot\mathbf{r}_j|i\rangle \tag{24}$$

$$= -\frac{i}{\hbar}(\epsilon_f - \epsilon_i)\langle f|\mathbf{e}_{\mathbf{k}\gamma}\cdot\vec{\mu}|i\rangle = -\frac{i}{\hbar}(\epsilon_f - \epsilon_i)\mathbf{e}_{\mathbf{k}\gamma}\cdot\langle f|\vec{\mu}|i\rangle \tag{25}$$

Then the absorption rate of light in the electric dipole transition

$$w_{\text{abs}}d\Omega = \frac{\omega_{fi}^3}{8\pi^2\epsilon_0\hbar^3 c^3}\bar{n}_{\mathbf{k}\gamma}\left|\langle f|\mathbf{e}_{\mathbf{k}\gamma}\cdot\vec{\mu}|i\rangle\right|^2 d\Omega \tag{26}$$

If the polarization unit vector $\mathbf{e}_{\mathbf{k}\gamma}$ is in the z-direction, the absorption rate can be written by the polar angle θ

$$w_{\text{abs}} \propto \cos^2\theta \tag{27}$$

The electric dipole transition comes from the potential energy change by the vibrating electric field at the electron position.

The oscillator strength is defined by

$$f_{ni} \equiv \frac{2m\omega_{ni}}{e^2\hbar}\left|\langle n|\mathbf{e}_{\mathbf{k}\gamma}\cdot\vec{\mu}|i\rangle\right|^2 \tag{28}$$

It is straightforward to establish the Thomas-Reiche-Kuhn sum rule

$$\sum_n f_{ni} = 1 \tag{29}$$

The dipole matrix element can be written as

$$\vec{\mu}_{fi} = \langle f|\vec{\mu}|i\rangle, \qquad \vec{\mu} = -e\sum_i \mathbf{r}_i \tag{30}$$

Here the initial and the final states can be described as in the same electronic state e and different vibrational state ν, ν'. (The rotation of molecule is neglected here.)

$$|f\rangle = |e\nu'\rangle \tag{31}$$
$$|i\rangle = |e\nu\rangle \tag{32}$$

If we assume the ν and ν' vibrational states that can be described the harmonic oscillator, i.e.

$$|\nu(q)\rangle = (2^\nu\nu!)^{-1/2}\left(\frac{\mu\omega}{\pi\hbar}\right)^{1/4}e^{-\xi^2/2}H_\nu(\xi) \tag{33}$$

Here $\xi = (\mu\omega/\hbar)^{1/2}q$. If the vector $\vec{\mu}$ can be obtained

$$\langle f|\vec{\mu}|i\rangle = (2^{\nu'}\nu'!)^{-1/2}(2^\nu\nu!)^{-1/2}\left(\frac{\mu\omega}{\pi\hbar}\right)^{1/2}\int dq H_{\nu'}(\xi)e^{-\xi^2/2}\vec{\mu}_e(q)H_\nu(\xi)e^{-\xi^2/2} \tag{34}$$

$$\vec{\mu}_e(q) = \langle e|\vec{\mu}|e\rangle \tag{35}$$

$$\vec{\mu}_e(q) = \vec{\mu}_e(0) + \left(\frac{d\mu_e}{dq}\right)_0 q\hat{\mathbf{q}} + ... \tag{36}$$

$$d\xi = \left(\frac{\mu\omega}{\hbar}\right)^{1/2}dq \tag{37}$$

$$\langle f|\vec{\mu}|i\rangle = \frac{(2^{\nu'}\nu'!)^{-1/2}(2^\nu\nu!)^{-1/2}}{\pi^{1/2}}\int d\xi H_{\nu'}(\xi)\left[\vec{\mu}_0 + \left(\frac{d\mu}{dq}\right)_0 q\hat{\mathbf{q}}\right]H_\nu(\xi)e^{-\xi^2} \tag{38}$$

$$= \frac{(2^{\nu'}\nu'!)^{-1/2}(2^\nu\nu!)^{-1/2}}{\pi^{1/2}}\left[\vec{\mu}_e(0)\pi^{1/2}2^{\nu'}\nu'!\delta_{\nu'\nu}\right.$$

3

$$+\hat{\mathbf{q}}\left(\frac{d\mu_e}{dq}\right)_0 (\mu\omega/\hbar)^{-1/2}\int d\xi H_{\nu'}(\xi)\xi H_\nu(\xi)e^{-\xi^2}\Bigg]$$

$$\int d\xi H_{\nu'}(\xi)H_\nu(\xi)e^{-\xi^2} = \pi^{1/2}2^{\nu'}\nu!\delta_{\nu'\nu}$$

$$\xi H_i(\xi) = iH_{i-1}(\xi) + \frac{1}{2}H_{i+1}(\xi)$$

$$\langle f|\vec{\mu}|i\rangle = \frac{(2^{\nu'}\nu!)^{-1/2}(2^\nu\nu!)^{-1/2}}{\pi^{1/2}}\Bigg[\mu_e(0)\pi^{1/2}2^{\nu'}\nu!\delta_{\nu'\nu}+$$

$$\hat{\mathbf{q}}\left(\frac{d\mu_e}{dq}\right)_0 (\mu\omega/\hbar)^{-1/2}\int d\xi H_{\nu'}(\xi)\left(\nu H_{\nu-1}(\xi) + \frac{1}{2}H_{\nu+1}(\xi)\right)e^{-\xi^2}\Bigg]$$

$$= \mu_e(0)\delta_{\nu'\nu} + (2^{\nu'}\nu'!)^{1/2}(2^\nu\nu!)^{-1/2}\hat{\mathbf{q}}\left(\frac{d\mu_e}{dq}\right)_0 (\mu\omega/\hbar)^{-1/2}(\nu\delta_{\nu',\nu-1} + \frac{1}{2}\delta_{\nu',\nu+1})$$

(39)

The first term indicate no absorption and the second term shows the selection rule that are $\nu' - \nu = \pm 1$ and $\left(\frac{d\mu_e}{dq}\right)_0 \neq 0$.

We should consider the unharmonicity when q becomes large.

$$\mu_e(q) = \mu_e(0) + \left(\frac{d\mu_e}{dq}\right)_0 q + \frac{1}{2}\left(\frac{d^2\mu_e}{dq^2}\right)_0 q^2 + ... \quad (40)$$

$$\xi^2 H_i(\xi) = \xi\left[iH_{i-1}(\xi) + \frac{1}{2}H_{i+1}(\xi)\right] \quad (41)$$

$$= i(i-1)H_{i-2}(\xi) + \frac{2i+1}{2}H_i + \frac{1}{4}H_{i+2} \quad (42)$$

Then we have some probability for the higher harmonic transition from $i \to (i \pm 2)$, because the integral $\int d\xi H_f(\xi)\xi^2 H_i(\xi)e^{-\xi^2}$ can be included.

3.1 Herzberg-Teller expansion

Now we consider $\langle f|\vec{\mu}|i\rangle$ again. If we use the Eq.17

$$\langle f|\vec{\mu}|i\rangle = \langle \chi^0_{n\nu'}(\{\mathbf{R}_I\})\phi_n(\{\mathbf{r}_i\},\{\mathbf{R}^0_I\})|\vec{\mu}|\chi^0_{n\nu}(\{\mathbf{R}_I\})\phi_n(\{\mathbf{r}_i\},\{\mathbf{R}^0_I\})\rangle$$
$$= \langle \chi^0_{n\nu'}(\mathbf{Q})|\vec{\mu}_e|\chi^0_{n\nu}(\mathbf{Q})\rangle \quad (43)$$
$$\vec{\mu}_e = \langle \phi_n(\{\mathbf{r}_i\},\{\mathbf{R}^0_I\})|\vec{\mu}|\phi_n(\{\mathbf{r}_i\},\{\mathbf{R}^0_I\})\rangle \quad (44)$$

From the last equation $\vec{\mu}_e$ has no dependence on $\mathbf{Q}$ then

$$\langle \chi^0_{n\nu'}(\mathbf{Q})|\vec{\mu}_e|\chi^0_{n\nu}(\mathbf{Q})\rangle = \vec{\mu}_e\langle \chi^0_{n\nu'}(\mathbf{Q})|\chi^0_{n\nu}(\mathbf{Q})\rangle = \vec{\mu}_e\delta_{\nu',\nu} \quad (45)$$

Then the transition matrix element become zero. In the Born-Oppenheimer approximation the change of the electron wavefunctions by the change of the positions of nucleus is not included. The Hamiltonian of the system can be described by the series expansion of $\mathbf{Q}$

$$H(\mathbf{r},\mathbf{Q}) = H(\mathbf{r},0) + \sum_i \left(\frac{\partial H}{\partial Q_i}\right)_0 Q_i + ... \quad (46)$$

The second term is the perturbation of the system and the wavefunction becomes

$$\phi_n(\mathbf{r},\mathbf{Q}) = \phi_n(\mathbf{r},\mathbf{Q}=0) + \sum_i \sum_{m\neq n} \frac{\langle \phi_m(\mathbf{r},0)|(\partial H/\partial Q_i)_0|\phi_n(\mathbf{r},0)\rangle}{E_n - E_m}\phi_m(\mathbf{r},0)Q_i \quad (47)$$

The series expansion described above is called Herzberg-Teller expansion. The matrix element μ_e is now written as

$$\vec{\mu}_e = \langle \phi_n(\mathbf{r},0)|\vec{\mu}|\phi_m(\mathbf{r},0)\rangle + 2\sum_{m\neq n}\sum_i \frac{\langle \phi_m(\mathbf{r},0)|(\partial H/\partial Q_i)_0|\phi_n(\mathbf{r},0)\rangle}{E_n - E_m}\langle \phi_n(\mathbf{r},0)|\vec{\mu}|\phi_m(\mathbf{r},0)\rangle Q_i + ..$$

(48)

Then

$$\langle f|\vec{\mu}|i\rangle = \langle \phi_n(\mathbf{r},0)|\vec{\mu}|\phi_m(\mathbf{r},0)\rangle\delta_{\nu'\nu} +$$
$$2\sum_{m\neq n}\sum_i \frac{\langle \phi_m(\mathbf{r},0)|(\partial H/\partial Q_i)_0|\phi_n(\mathbf{r},0)\rangle}{E_n - E_m}\langle \phi_n(\mathbf{r},0)|\vec{\mu}|\phi_m(\mathbf{r},0)\rangle\langle \chi^0_{n\nu'}(\mathbf{Q})|Q_i|\chi^0_{n\nu}(\mathbf{Q})\rangle$$

(49)

The last equation gives the "accurate" selection rule $\nu' = \nu \pm 1$. I *n the ab-initio calculation, however, the dependence of the wavefunction by the nucleus configuration in a vibration mode is not considered as shown below.*

3.2 Ab-initio calculation (B. A. Hess et al. Chem. Rev. 1996, 86, 709-730.) Using G98 you can calculate IR vib. freq. and intensity, if you do not know this, anyway.

Integrated infrared band intensity for the k-th fundamental is defined as

$$A_k = \frac{1}{CL} \int \log\left(\frac{I_0}{I}\right) d\nu \tag{50}$$

Here C is the concentration (mol/L) and L is the optical path (cm). The unit of A_k is [cm / mol] and

$$A_k = \frac{\pi N_A g_k}{3000c^2 2.302581} \left|\frac{\partial \mu}{\partial Q_k}\right|^2 \tag{51}$$

Here N_A is the Avogadro's number (mol^{-1}), c is the speed of light (cm/s), g_k is the degeneracy, and $\partial \mu / \partial Q_k$ is the dipole derivative with respect to the $k_t h$ normal coordinate. In the Gaussian package the integrated infrared band intensity A_k is calculated in the name of "IR intensity (km/mol)".

If we consider the j component of the dipole moment vector of the system is given by

$$\mu_j = \frac{\partial E}{\partial F_j} \tag{52}$$

where E is the total energy of the system under a uniform electric field F. (The field is weak enough and the changes of the atomic charges are negligible.) The derivative of the dipole with the normal coordinate is

$$\frac{\partial \mu_j}{\partial Q_k} = \frac{\partial}{\partial Q_k} \frac{\partial E}{\partial F_j} = \frac{\partial}{\partial F_j} \frac{\partial E}{\partial Q_k} \tag{53}$$

The quantities $\partial E/\partial Q_k$ is transformed to

$$\frac{\partial E}{\partial Q_k} = \sum_i \frac{\partial R_i}{\partial Q_k} \frac{\partial E}{\partial R_i} \equiv \sum_i L_{ik} \frac{\partial E}{\partial R_i} \tag{54}$$

$\partial E/\partial R_i$ is the negative of the force components which are already available in the calculation of geometry optimization.

3.2.1 Normal coordinate (T. Inui et al. Group Theory)

We define the displacements of the atom $k(= 1, 2...., N)$ in the $\alpha(= x, y, z)$ direction by

$$u_{k\alpha} = (\mathbf{R})_{k\alpha} - (\mathbf{R}^0)_{k\alpha} \tag{55}$$

The Hamiltonian of the system is

$$H = \frac{1}{2}\sum_{k,\alpha} m_k \dot{u}_{k\alpha}^2 + \frac{1}{2}\sum_{kl\alpha\beta} \Phi_{k\alpha,l\beta} u_{k\alpha} u_{l\beta} \tag{56}$$

where $\Phi_{k\alpha,l\beta} = (\partial^2 V/\partial u_{k\alpha}\partial u_{l\beta})_0$ and V is the potential energy of the system. The equation of motion becomes

$$m_k \ddot{u}_{k\alpha} = -\sum_{l\beta} \Phi_{k\alpha,l\beta} u_{l\beta} \tag{57}$$

The equation of motion can be solved in the standard way

$$u_{k\alpha} = U_{k\alpha} e^{-i(\omega t + \delta)} \tag{58}$$

$$m_k \omega^2 U_{k\alpha} = \sum_{l\beta} \Phi_{k\alpha,l\beta} U_{l\beta} \tag{59}$$

$$\omega^2 \sqrt{m_k} U_{k\alpha} = \sum_{l\beta} D_{k\alpha,l\beta} \sqrt{m_l} U_{l\beta} \tag{60}$$

$$D_{k\alpha,l\beta} = \frac{\Phi_{k\alpha,l\beta}}{\sqrt{m_k m_l}} \tag{61}$$

$$\sum_{l\beta} (D_{k\alpha,l\beta} - \omega^2 \delta_{k\alpha,l\beta}) \sqrt{m_l} U_{l\beta} = 0 \tag{62}$$

This coupled equation can be solved by the secular equation, and we can get eigenvalue ω_s^2 and eigenvector $e_{k\alpha}^s$. If we normalize the eigenvector, the eigenvectors are orthogonal each other

$$\mathbf{e}^s \cdot \mathbf{e}^{s'} = \langle \mathbf{e}^s | \mathbf{e}^{s'} \rangle \mathbf{e}^{s\dagger} \mathbf{e}^{s'} = \sum_{k\alpha} e_{k\alpha}^s e_{k\alpha}^{s'} = \delta_{s,s'} \tag{63}$$

The dynamical matrix D is real and symmetric, then the eigenvalue and eigenvector are also real. The eigenvector is complete in $3N$-dimensional space

$$\mathbf{I} = \begin{pmatrix} 1 & 0 & 0 & ..... & 0 \\ 0 & 1 & 0 & ..... & 0 \\ 0 & 0 & 1 & ..... & 0 \\ ... & ... & ... & ... & ... \\ 0 & 0 & 0 & ..... & 1 \end{pmatrix} = \sum_s |\mathbf{e}^s\rangle\langle\mathbf{e}^s| = \sum_s \mathbf{e}^s \mathbf{e}^{s\dagger} \tag{64}$$

$$\sum_s \mathbf{e}^s \mathbf{e}^{s\dagger} = \sum_s e_{k\alpha}^s e_{l\beta}^s = \delta_{kl}\delta_{\alpha\beta} \tag{65}$$

The normal coordinate Q_s is defined as

$$u_{k\alpha} = \frac{1}{\sqrt{m_k}} \sum_s Q_s e_{k\alpha}^s \tag{66}$$

Then Q_s is the scalar quantity and the amplitude of the mode s. From the orthogonality

$$Q_s = \sum_{k\alpha} \sqrt{m_k} e_{k\alpha}^s u_{k\alpha}, \qquad (s = 1, 2, ..., 3N) \tag{67}$$

Q_s is the linear combination of $u_{k\alpha}$ and its equation motion is given by

$$\ddot{Q}_s + \omega_s^2 = 0, \qquad (s = 1, 2, ..., 3N) \tag{68}$$

Using normal coordinate the system is described as the sum of the independent harmonic vibration. The Hamiltonian of the system is

$$H = \frac{1}{2} \sum_s (\dot{Q}_s^2 + \omega_s^2 Q_s^2) \tag{69}$$

The summation s is from 1 to $3N$. For the freedom of translation 3 and rotation 3, this is no intratomic force, then $\omega_s = 0$.

4 Light reflection from metal (Au) surface

Previously[M. Yamamoto, Rev. Pol. 48, 2002 ,209-237] I have done the formulation of the reflectance for the air|metal system.

For IR light at 3100 nm the reflectance at the air|gold surface ($n = 1.728, \kappa = 19.2$) is shown below.
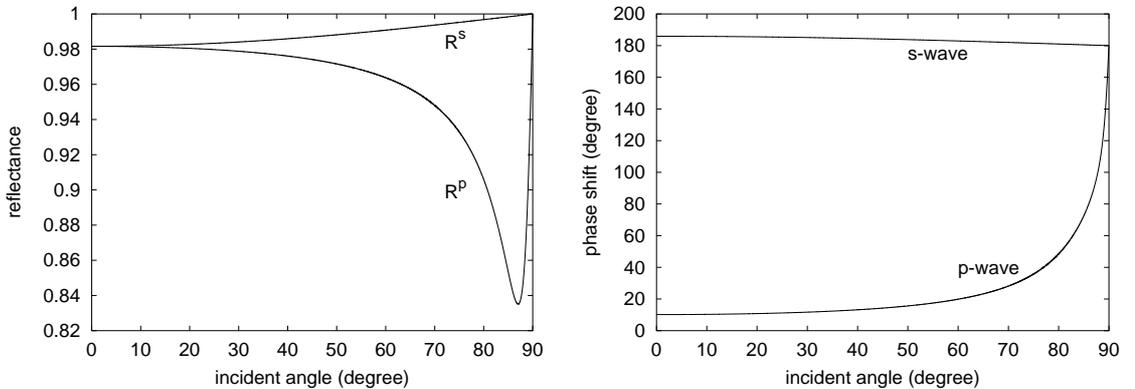
Figure 1: IR light (3100 nm) reflection from air|Au surface

The intensities of light in the z- and y-component per unit area on the Au surface becomes

$$
\begin{aligned}
(E_p^\perp/E_p)^2/\cos\theta &\equiv |\mathbf{E}_{0z} + \mathbf{R}_{0z}|^2/E_p^2/\cos\theta = |-E_p\sin\theta - R_p\sin\theta|^2/E_p^2/\cos\theta \\
&= |-E_p\sin\theta - r_p E_p\sin\theta|^2/E_p^2/\cos\theta \\
&= |-E_p\sin\theta - (\rho_p\cos\phi_p + i\rho_p\sin\phi_p)E_p\sin\theta_p|^2/E_p^2/\cos\theta \\
&= \sin\theta^2(1 + 2\rho_p\cos\phi_p + \rho_p^2)/\cos\theta \qquad\qquad (70) \\
(E_s^\parallel/E_s)^2/\cos\theta &\equiv |\mathbf{E}_{0y} + \mathbf{R}_{0y}|^2/E_s^2/\cos\theta \\
&= |E_s + R_s|^2/E_s^2/\cos\theta = |E_s + r_s E_s|^2/E_s^2\cos\theta \\
&= (1 + 2\rho_s\cos\phi_s + \rho_s^2)/\cos\theta \qquad\qquad (71)
\end{aligned}
$$

These equations give the basics of the surface sensitivity of the RAIRS(Reflection Absorption Infrared Spectroscopy) and Polarization-Modulation FTIR spectroscopy, and the angle dependence are shown in Fig.9. The 180 degree phase change of s-wave leads to destructive interference and no interaction with surface dynamic dipoles from molecular vibrations. [1] For the surface normal component of the p-wave the interference is constructive and it can excite the dynamic dipole perpendicular to the surface. The excitation is efficient for a higher angle of incidence.
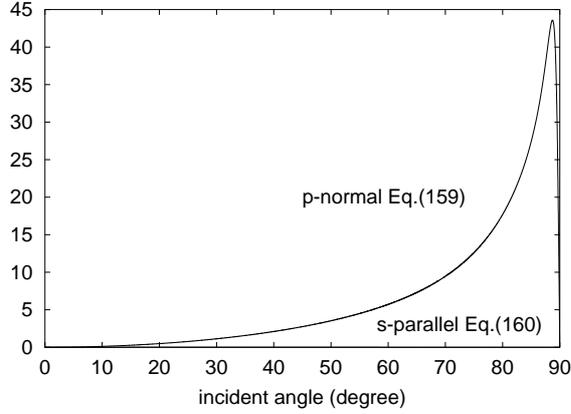
Figure 2: plots of $(E_p^\perp/E_p)^2/\cos\theta$ and $(E_s^\parallel/E_s)^2/\cos\theta$. The IR light is 3100 nm and the IR light is reflected from the air|Au surface. $(E_s^\parallel/E_s)^2/\cos\theta$ is negligible because the phase shift is almost 180 degree between the incident wave and the reflected wave.

From Eq.(8) the IR light absorption is proportional to $\mathbf{e}_{\mathbf{k}\gamma}\cdot\vec{\mu}_{fi}$. The vibrational mode of which the induced dipole moment have the surface normal is strongly interacts with the IR light but the interaction with the surface parallel mode is very small because the $\mathbf{e}_{\mathbf{k},s}$ of the incident light and the $\mathbf{e}_{\mathbf{k},s}$ is destructively interfered by the phase shift of π.

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[1] The surface parallel x-component (not shown here) of p-wave is also negligible.

5 Raman Scattering

5.1 Quantum theory (For example, G. C. Schatz and M. A. Ratner, Quantum Mechanics in Chemistry, Chap. 5.5)

The differential cross section for Raman scattering is given by

$$\frac{d\sigma}{d\Omega} = (N+1)\frac{\omega^3\omega'}{c^4}|\mathbf{e}'\alpha^{km}\mathbf{e}|^2 \tag{72}$$

where Ω is the solid angle, N is the number of emitted photon of frequency ω, the frequency of the absorbing photon is ω'. m is the initial ground state and k is the final vibrational-excited state. $\mathbf{e}'$ and $\mathbf{e}$ is the polarization vector of the absorbing and emitted light. If $\mathbf{e}' = \mathbf{e}$, we call the scattering polarized, and if $\mathbf{e}' \perp \mathbf{e}$, it is depolarized.

We can write

$$\mu_{i,induced}^{km} = \alpha_{i,j}^{km} E_j \tag{73}$$

$$\alpha_{i,j}^{km} = \frac{1}{\hbar}\sum_n \left\{ \frac{\langle k|\mu_i|n\rangle\langle m|\mu_j|n\rangle}{\omega + \omega_{nm}} - \frac{\langle n|\mu_i|m\rangle\langle k|\mu_j|n\rangle}{\omega - \omega_{nk}} \right\} \tag{74}$$

If we define the wave function $|k\rangle$ is the Hermite function, the matrix element $\langle k|\alpha_{ij}|m\rangle$ becomes

$$\langle k|\alpha_{ij}|m\rangle = \langle k|\alpha_{ij}^0 + \frac{\partial\alpha_{ij}}{\partial q} + ...|m\rangle \tag{75}$$

In the last equation the same formulation as the IR absorption QM theory can be applied. And we can find

$$\text{Raman } \mathbf{scattering} \text{ intensity} \quad \propto \quad (\frac{\partial\alpha}{\partial\mathbf{q}})^2 \tag{76}$$

$$\text{IR } \mathbf{absorption} \text{ intensity} \quad \propto \quad (\frac{\partial\vec{\mu}}{\partial\mathbf{q}})^2 \tag{77}$$

5.2 Ab-initio calculation (A. Stirling, J. Chem. Phys. 104, 1996, 1254-1262) Using G98 you can calculate Raman freq., intensity, and depolarization ratio, if you do not know this, anyway.

The total energy of the molecule of the system under the uniform field (weak enough) is described as

$$E(\mathbf{F}) = E^0 - \sum_i \mu_i^0 - \frac{1}{2}\sum_{i,j}\alpha_{ij}F_jF_k + ... \tag{78}$$

where E^0 is the total energy under the zero-field , μ_i^0 is the permanent dipole moment vector in the i component, α_{jk} is the polarizability tensor, F_i is the electric field in i direction. If we remind that t he interaction energy of the dipole with field is $-\vec{\mu}\cdot\vec{E}$, then the first derivative of this equation

$$\mu_i = -\frac{\partial E}{\partial F_i} = \mu_i^0 + \sum_j \alpha_{ij}F_j \tag{79}$$

The second derivative can be assumed

$$\alpha_{ij} = -\left(\frac{\partial^2 E}{\partial F_i\partial F_j}\right)_0 \tag{80}$$

The Raman intensities can be obtained as

$$J_s = g_s(45\alpha_s'^2 + 7\gamma_s'^2) \tag{81}$$

$$\alpha_s' = (1/3)\left[\left(\frac{\partial\alpha_{xx}}{\partial Q_s}\right) + \left(\frac{\partial\alpha_{yy}}{\partial Q_s}\right) + \left(\frac{\partial\alpha_{zz}}{\partial Q_s}\right)\right] \tag{82}$$

$$\gamma_s' = (1/2)\left\{ \left(\frac{\partial\alpha_{xx}}{\partial Q_s} - \frac{\partial\alpha_{yy}}{\partial Q_s}\right)^2 + \left(\frac{\partial\alpha_{yy}}{\partial Q_s} - \frac{\partial\alpha_{zz}}{\partial Q_s}\right)^2 + \left(\frac{\partial\alpha_{zz}}{\partial Q_s} - \frac{\partial\alpha_{xx}}{\partial Q_s}\right)^2 \right.$$

$$\left. +6\left[\left(\frac{\partial\alpha_{xy}}{\partial Q_s}\right)^2 + \left(\frac{\partial\alpha_{yz}}{\partial Q_s}\right)^2 + \left(\frac{\partial\alpha_{zx}}{\partial Q_s}\right)^2\right]\right\} \tag{83}$$

The depolarization ratio can be described

$$\rho_s = \frac{3\gamma_s'^2}{45\alpha_s'^2 + 4\gamma_s'^2} \tag{84}$$

6   Classical View :

Raman   Spectroscopy
                      ,   Anthony T. Tu   1988
        Placzek's   Theory   [Peter Brüesch, *Phonons: Theory and Experimens II*, Springer 1986, Chapter 3.]
        E.B. Wilson, Jr., J.C. Decius and P.C. Cross, *Molecular Vibrations*, Dover, 1980.

C. V. Raman

カルカッタ大学教授時代
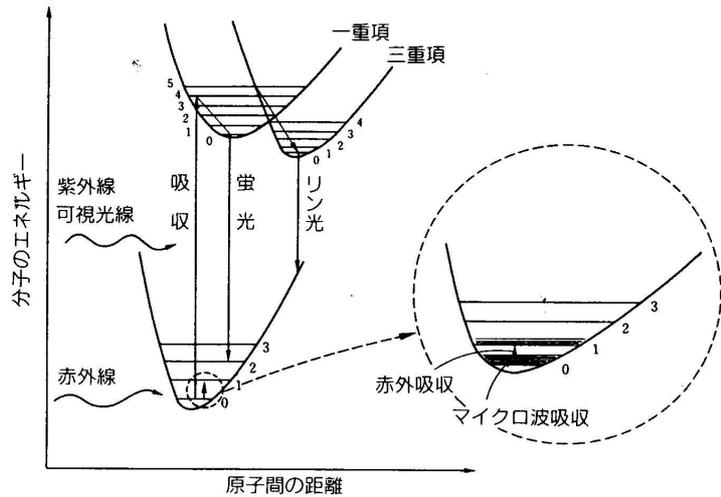
一重項
三重項

紫外線
可視光線   吸収   蛍光   リン光

分子のエネルギー

赤外線

原子間の距離

赤外吸収
マイクロ波吸収

分子のエネルギーレベルと光の吸収

                          3   2

        3n-6   3n-5

        Raman

$v = 1$
$v = 0$

ラマン散乱   赤外吸収

ラマン効果と赤外吸収の関係

(a)   (b)   (c)
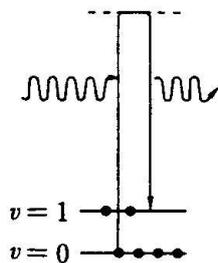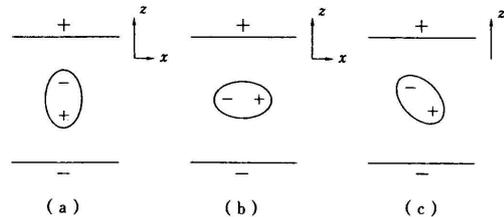
分子に誘起される双極子モーメント（μ）と電場（E）の方向
(a) E と μ が平行   (b) E と μ が直角   (c) E と μ は全然異なる方向

$$\text{Raman scattering intensity} \quad \propto \quad \left(\frac{\partial\alpha}{\partial\mathbf{q}}\right)^2 \tag{85}$$

$$\text{IR absorption intensity} \quad \propto \quad \left(\frac{\partial\vec{\mu}}{\partial\mathbf{q}}\right)^2 \tag{86}$$

where α is the polarization tensor   ), **q** is the displacement along a normal coordinate (   ), $\vec{\mu}$ is the dipole moment (

$$\vec{\mu} = \alpha\mathbf{E} \tag{87}$$

$$\begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \tag{88}$$

where **E** is the electric field and the polarization tensor is symmetric $\alpha_{ij} = \alpha_{ji}$.

Emission of radiation by oscillating dipole

ストークス光　　アンチストークス光

入射光と分子とのエネルギー交換によりラマン散乱が発生する.

レイリー散乱

ストークス線　　アンチストークス線

ラマンシフト (cm⁻¹)

ストークス線とアンチストークス線

$$\omega_0(= 2\pi\nu_0)$$
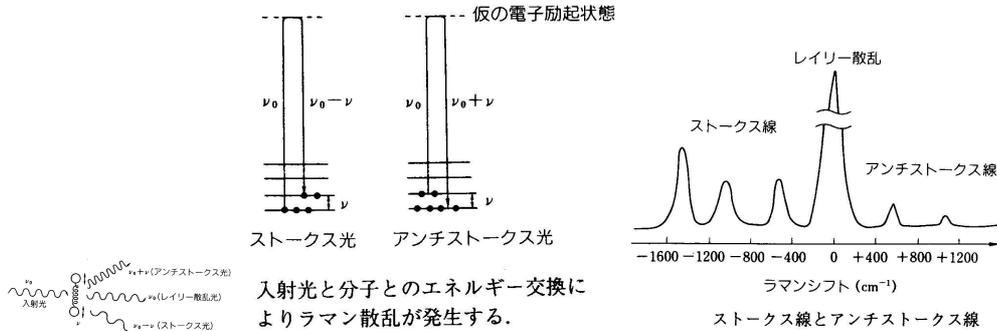
Rayleigh scattering(ω_0),

Stokes scattering($\omega_0 - \omega$),

anti-Stokes scattering($\omega_0 + \omega$)

$$\omega_0(= 2\pi\nu_0)$$
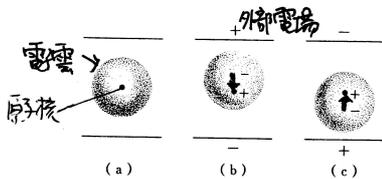
球状の原子からの光の散乱

(a) 光が相互作用する前
(b) 上が+，下が−の電場
(c) 上が−，下が+の電場
光の中では，(b)と(c)を繰り返す.
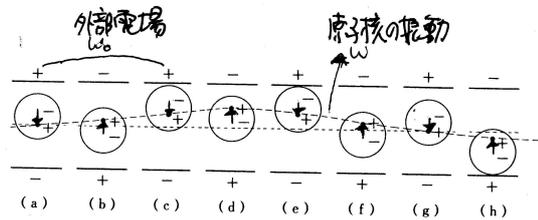
原子核が振動しているところへ電場が作用するときにラマン散乱が起こる.

(a)と(g)は原子核の位置が同じ. +は原子核，−は電子雲の中心を意味する.

$\vec{\mu}$　$\mathbf{E}$

$$E = E_0\cos(\omega_0 t) \tag{89}$$

$$\mu = \alpha E = \alpha E_0\cos(\omega_0 t) \tag{90}$$

α_0　　　　　　　　q　　　　　q

$$\alpha = \alpha_0 + \left(\frac{\partial\alpha}{\partial q}\right)_0 q + ... \tag{91}$$

q

$$q = q_0\cos(\omega t) \tag{92}$$

$$\mu = \left[\alpha_0 + \left(\frac{\partial\alpha}{\partial q}\right)_0 q_0\cos(\omega t)\right] E_0\cos(\omega_0 t) \tag{93}$$

10

$$= \alpha_0 E_0 \underbrace{\cos(\omega_0 t)}_{\text{Rayleigh}} + \frac{1}{2}\left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 E_0 \left\{ \underbrace{\cos[(\omega_0 + \omega)t]}_{\text{anti-Stokes}} + \underbrace{\cos[(\omega_0 - \omega)t]}_{\text{Stokes}} \right\} \tag{94}$$

$$\cos A \cos B = (1/4)(e^{iA} + e^{-iA})(e^{iB} + e^{-iB}) = (1/2)[\cos(A+B) + \cos(A-B)] \tag{95}$$

Raman
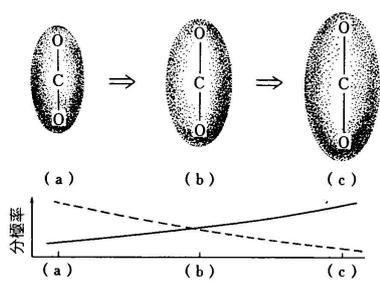
CO₂ の 2 本の C-O 結合がともに伸びたとき(c)と縮んだ
とき(a)の電子雲(上図)と，その場合の分極率(下図)
分極率は実線か破線のいずれかになり，いずれにしても(b)のところ
での傾き(∂α/∂Q)₀はゼロではない．
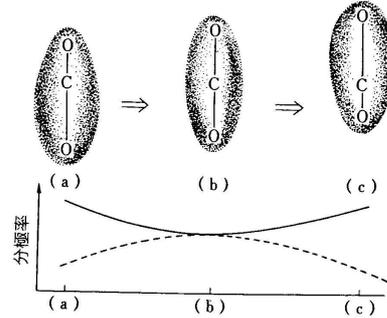
CO₂ の 2 本の C-O 結合が逆位相で伸縮するときの電子雲の
様子(上図)とその場合の分極率(下図)
分極率は実線か破線のいずれかになる．故に(b)のところでの傾き(∂α/∂Q)₀
はゼロとなる．

Intensity ratio between Stokes/anti-Stokes lines

$$I_{anti-Stokes}/I_{Stokes} = \exp\left(-\frac{\hbar\omega}{k_B T}\right) \tag{96}$$

Nd/YAG 1064nm, visible light 380-780nm)

Raman   :

Depolarization Ratio: z

$$\frac{I_\parallel}{I_\perp} = \left(\frac{\alpha_{yz}}{\alpha_{zz}}\right)^2 \tag{97}$$

Resonance Raman   :   I
SERS(Surface Enhanced Raman Spectroscopy):
Resoance Raman
CARS(Coherent Anti-Stokes Raman Scattering)
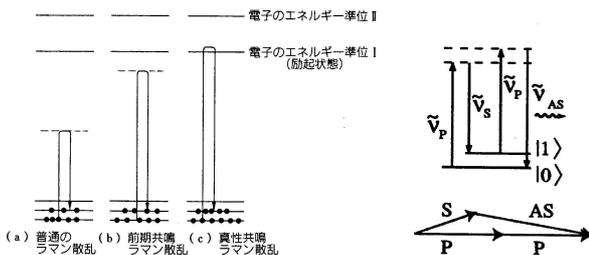
図 2-1　普通のラマン散乱と共鳴ラマン散乱との比較

	対称伸縮振動 (symmetric stretching mode)	逆対称伸縮振動 (antisymmetric stretching mode)	変 角 振 動 (bending mode)
	O=C=O O=C=O O═C═O	O═C=O O=C=O O=C═O	O〵C〵O O=C=O O〵C〟O
振動変位による分極率楕円体の変化			
分極率テンソル成分の微分	$\left(\dfrac{\partial\alpha}{\partial Q}\right)_0 \neq 0$	$\left(\dfrac{\partial\alpha}{\partial Q}\right)_0 = 0$	$\left(\dfrac{\partial\alpha}{\partial Q}\right)_0 = 0$
ラマン	活性（$\nu_1 = 1340\,cm^{-1}$）	不活性	不活性
振動変位による分子双極子モーメントの変化	O=C=O O=C=O O═C═O － ＋ － － ＋ － ＋ －	O═C=O O=C=O O=C═O ⟸ ＋ － － ＋ － ＋ ⟹	O〵C〟O O=C=O O〵C〟O －／＋ ＋＼－
双極子モーメントの微分	$\left(\dfrac{\partial\mu}{\partial Q}\right)_0 = 0$	$\left(\dfrac{\partial\mu}{\partial Q}\right)_0 \neq 0$	$\left(\dfrac{\partial\mu}{\partial Q}\right)_0 \neq 0$
赤外	不活性	活性 $\nu_3 = 2349\,cm^{-1}$	活性 $\nu_2 = 667\,cm^{-1}$

図 3-8 直線形分子の振動の例—— CO_2 分子が振動変位を起こしたときの分極率と双極子モーメント

	対称伸縮振動	逆対称伸縮振動	変 角 振 動
	O〵S〟O O〵S〟O O〵S〟O	O〵S〟O O〵S〟O O〵S〟O	O〵S〟O O〵S〟O O〵S〟O
振動変位による分極率楕円体の変化			
分極率成分の微分（一つの成分について）	$\left(\dfrac{\partial\alpha}{\partial Q}\right)_0 \neq 0$	$\left(\dfrac{\partial\alpha}{\partial Q}\right)_0 \neq 0$	$\left(\dfrac{\partial\alpha}{\partial Q}\right)_0 \neq 0$
ラマン	活性	活性	活性
振動変位による分子双極子モーメントの変化			
双極子モーメントの微分	$\left(\dfrac{\partial\mu}{\partial Q}\right)_0 \neq 0$	$\left(\dfrac{\partial\mu}{\partial Q}\right)_0 \neq 0$	$\left(\dfrac{\partial\mu}{\partial Q}\right)_0 \neq 0$
赤外	活性（$\nu_1 = 1151\,cm^{-1}$）	活性（$\nu_3 = 1361\,cm^{-1}$）	活性（$\nu_2 = 519\,cm^{-1}$）

図 3-9 非直線形分子の振動の例—— SO_2 分子が振動変位を起こしたときの分極率と双極子モーメント