Theoretical Calculations of the Infrared Absorption Intensities of Simultaneous Transitions

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The formula of the infrared absorption intensity of a simultaneous transition has been derived on the basis of the vibronic expansion technique, with two simple assumptions. By the use of the foumula, the theoretical calculations of the intensities for the CO_2–N_2 and CO_2–H_2 systems have been done, the electronic wave functions being calculated by the CNDO/2 method. In both cases, it was found that the main contribution to the absorption intensity arises from the coupling between the electronic state of CO_2 and the nuclear vibration of the homonuclear diatomic molecule. Furthermore, the intensities of the fundamental, first-overtone, and combination bands of CO_2 have been calculated according to the formula corresponding to an intramolecular process, and the intensities of the overtone and combination bands caused by the intermolecular process have been calculated. These calculated results have been discussed in comparison with one another.

In their investigations of the infrared absorption spectra of the compressed gaseous mixture of carbon dioxide and nitrogen, Fahrenfort and Ketelaar[1] found new bands which were not observed in compressed gas of pure carbon dioxide. They attributed the bands to simultaneous transitions in each of the two compounds. The same phenomenon was found in the mixture of CO_2 and H_2 and also in CO_2 and O_2. Fahrenfort and Ketelaar suggested that the phenomena depend on the polarization of the symmetrical diatomic molecule under the influence of the electric field of the rather large quadrupole moment arising from the partial dipoles presented in CO_2. Ketelaar and his co-workers went on to investigate the simultaneous transitions in several liquified mixtures[2] and proposed a theoretical development of the simultaneous transition.[3] Their development is based on the idea that the dipole moment of the system is expanded in a power series of the vibrational normal coordinates. This idea has been used to explain the infrared absorption intensities of the vibrational transitions in a separate molecule;[4] in the expansion, the first derivatives with respect to the normal coordinates are related to the intensities of the fundamental tones, the second derivatives are related to the first overtones, and so on. For the intensity of a Raman scattering, a similar approach has been adopted in the form of the expansion of a molecular polarizability.[5] On the other hand, the formula of the Raman intensity has been derived by the use of the vibronic expansion technique,[6] which is different from that described above.

In this work the formulas of the infrared absorption intensities have been derived by the use of the vibronic expansion technique; the formula of the intensity for the simultaneous transition has also been derived. Moreover, by the use of these formulas, the intensities of the simultaneous transition for the CO_2–N_2 and CO_2–H_2 systems and of the fundamental, overtone, and combination bands of CO_2 have been calculated. The electronic wave functions have been evaluated by the CNDO/2 method.

Theoretical

Intramolecular Transition. The expression of the infrared absorption intensity for the vibrational transition from the ground state, *o*, to the excited state, *m*, of a molecule is given as:[7]

$$A_{m\leftarrow o} = \frac{8\pi^3}{3ch}\nu_{mo}(N_o-N_m)\,|\mu_{m,o}|^2; \tag{1}$$

$$\mu_{m,o} = \langle m|\hat{\mu}|o\rangle, \tag{2}$$

where c is the velocity of light; h, Planck's constant; ν_{mo}, the frequency of the absorbed light; N_o and N_m, the number of molecules per unit volume in the o and m states respectively, and $\hat{\mu}$, the electric dipole moment operator. The wave functions, $|o\rangle$ and $|m\rangle$, are described by the product of an electronic wave function and a vibrational wave function:

$$|o\rangle = |\psi_g\rangle|\varphi_0^g\rangle \tag{3}$$

and:

$$|m\rangle = |\psi_g\rangle|\varphi_m^g\rangle, \tag{4}$$

where $|\psi_g\rangle$ is the wave function of the electronic ground state involving the nuclear coordinates as parameters and where $|\varphi_0^g\rangle$ and $|\varphi_m^g\rangle$ are the wave functions of the vibrational ground and the vibrational m-th states respectively, both of which belong to the electronic ground state. The Hamiltonian for the electronic system could be expanded in a Taylor series with respect to the normal coordinates, Q_a's, around the equilibrium nuclear position:

$$H = H_0 + \sum_a H_a'Q_a + \frac{1}{2}\sum_a\sum_b H_{ab}''Q_aQ_b + \textit{higher-order terms}, \tag{5}$$

where

$$H_a' = (\partial H/\partial Q_a)_0$$

and

$$H_{ab}'' = (\partial^2 H/\partial Q_a\partial Q_b)_0.$$

When H_0 is regarded as the unperturbed Hamiltonian which has the eigenvalues, ε_i^0's, and the corresponding eigenfunctions, $|\psi_i^0\rangle$'s, and when the other terms on the right-hand side in Eq. (5) are regarded as the perturbation on H_0, we can make use of the perturbation method for obtaining the $|\psi_g\rangle$. The expression of $|\psi_g\rangle$ with the zeroth-, the first-, and the second-order terms of normal coordinates can be written as:[8]

$$|\psi_g> = |\psi_g^0> + \sum_a \sum_{i\neq g} \frac{\langle\psi_i^0|H_a'|\psi_g^0\rangle Q_a}{\varepsilon_g^0-\varepsilon_i^0}|\psi_i^0>$$
$$+ \sum_{a,b}\sum_{i\neq g}\left\{\frac{1}{2}\frac{\langle\psi_i^0|H_{ab}''|\psi_g^0\rangle}{\varepsilon_g^0-\varepsilon_i^0}\right.$$
$$+ \sum_{j\neq g}\frac{\langle\psi_g^0|H_a'|\psi_j^0\rangle\langle\psi_j^0|H_b'|\psi_i^0\rangle}{(\varepsilon_g^0-\varepsilon_j^0)(\varepsilon_g^0-\varepsilon_i^0)}$$
$$\left.-\frac{\langle\psi_g^0|H_a'|\psi_g^0\rangle\langle\psi_g^0|H_b'|\psi_i^0\rangle}{(\varepsilon_g^0-\varepsilon_i^0)^2}\right\}Q_aQ_b|\psi_i^0\rangle. \quad (6)$$

It is convenient for the following development to show that $\hat{\boldsymbol{\mu}}$ can be expressed as follows:[9)]

$$\hat{\boldsymbol{\mu}} = \hat{\boldsymbol{\mu}}_{\mathrm{e}} + \hat{\boldsymbol{\mu}}_{\mathrm{n}} = \hat{\boldsymbol{\mu}}_{\mathrm{e}} + \hat{\boldsymbol{\mu}}_n^0 + \sum_a \mathbf{k}_aQ_a$$
$$= \hat{\boldsymbol{\mu}}_0 + \sum \mathbf{k}_aQ_a, \quad (7)$$

where $\hat{\boldsymbol{\mu}}_{\mathrm{e}}$ and $\hat{\boldsymbol{\mu}}_{\mathrm{n}}$ are the electronic and nuclear parts of $\hat{\boldsymbol{\mu}}$ respectively, where $\hat{\boldsymbol{\mu}}_{\mathrm{n}}^0$ is $\hat{\boldsymbol{\mu}}_{\mathrm{n}}$ with the equilibrium nuclear position, and where $\hat{\boldsymbol{\mu}}_0$ is the sum of $\hat{\boldsymbol{\mu}}_{\mathrm{e}}$ and $\hat{\boldsymbol{\mu}}_n^0$. By applying Eq. (6) to Eqs. (3) and (4), and considering the orthonormality between $|\psi_i^0>$'s, $\boldsymbol{\mu}_{m,o}$ is rewritten as:

$$\boldsymbol{\mu}_{m,o} = \langle\psi_g^0|\hat{\boldsymbol{\mu}}_0|\psi_g^0\rangle\langle\varphi_m^g|\varphi_o^g\rangle + \sum_a\left\{\mathbf{k}_a - 2\sum_{i\neq g}\frac{\langle\psi_g^0|H_a'|\psi_i^0\rangle\langle\psi_i^0|\hat{\boldsymbol{\mu}}_0|\psi_g^0\rangle}{\varepsilon_i^0-\varepsilon_g^0}\right\}\langle\varphi_m^g|Q_a|\varphi_o^g\rangle$$
$$+\sum_{a,b}\left[\sum_{i\neq g}\sum_{j\neq g}\left\{\frac{\langle\psi_g^0|H_a'|\psi_i^0\rangle\langle\psi_i^0|\hat{\boldsymbol{\mu}}_0|\psi_j^0\rangle\langle\psi_j^0|H_b'|\psi_g^0\rangle}{(\varepsilon_i^0-\varepsilon_g^0)(\varepsilon_j^0-\varepsilon_g^0)} + 2\frac{\langle\psi_g^0|H_a'|\psi_i^0\rangle\langle\psi_i^0|H_b'|\psi_j^0\rangle\langle\psi_j^0|\hat{\boldsymbol{\mu}}_0|\psi_g^0\rangle}{(\varepsilon_i^0-\varepsilon_g^0)(\varepsilon_j^0-\varepsilon_g^0)}\right\}\right.$$
$$\left.-\sum_{i\neq g}\left\{\frac{\langle\psi_g^0|H_{ab}''|\psi_i^0\rangle\langle\psi_i^0|\hat{\boldsymbol{\mu}}_0|\psi_g^0\rangle}{\varepsilon_i^0-\varepsilon_g^0} + 2\frac{\langle\psi_g^0|H_a'|\psi_g^0\rangle\langle\psi_g^0|H_b'|\psi_i^0\rangle\langle\psi_i^0|\hat{\boldsymbol{\mu}}_0|\psi_g^0\rangle}{(\varepsilon_i^0-\varepsilon_g^0)^2}\right\}\right]\langle\varphi_m^g|Q_aQ_b|\varphi_o^g\rangle. \quad (8)$$

with the harmonic oscillator approximation, the transition moments for the fundamental tone and the first overtone of the *a* normal vibration and for the combination tone of the *a* and *b* normal vibrations are given as:

Fundamental tone:

$$\boldsymbol{\mu}_{1,0}^a = \left\{\mathbf{k}_a - 2\sum_{i\neq g}\frac{\langle\psi_g^0|H_a'|\psi_i^0\rangle\langle\psi_i^0|\hat{\boldsymbol{\mu}}_0|\psi_g^0\rangle}{\varepsilon_i^0-\varepsilon_g^0}\right\}\langle\varphi_1^g|Q_a|\varphi_0^g\rangle: \quad (9)$$

First overtone:

$$\boldsymbol{\mu}_{2,0}^a = \left[\sum_{i\neq g}\sum_{j\neq g}\left\{\frac{\langle\psi_g^0|H_a'|\psi_i^0\rangle\langle\psi_i^0|\hat{\boldsymbol{\mu}}_0|\psi_j^0\rangle\langle\psi_j^0|H_a'|\psi_g^0\rangle}{(\varepsilon_i^0-\varepsilon_g^0)(\varepsilon_j^0-\varepsilon_g^0)} + 2\frac{\langle\psi_g^0|H_a'|\psi_i^0\rangle\langle\psi_i^0|H_a'|\psi_j^0\rangle\langle\psi_j^0|\hat{\boldsymbol{\mu}}_0|\psi_g^0\rangle}{(\varepsilon_i^0-\varepsilon_g^0)(\varepsilon_j^0-\varepsilon_g^0)}\right\}\right.$$
$$\left.-\sum_{i\neq g}\left\{\frac{\langle\psi_g^0|H_{aa}''|\psi_i^0\rangle\langle\psi_i^0|\hat{\boldsymbol{\mu}}_0|\psi_g^0\rangle}{\varepsilon_i^0-\varepsilon_g^0} + 2\frac{\langle\psi_g^0|H_a'|\psi_g^0\rangle\langle\psi_g^0|H_a'|\psi_i^0\rangle\langle\psi_i^0|\hat{\boldsymbol{\mu}}_0|\psi_g^0\rangle}{(\varepsilon_i^0-\varepsilon_g^0)^2}\right\}\right]\langle\varphi_2^g|Q_a^2|\varphi_0^g\rangle: \quad (10)$$

Combination tone:

$$\boldsymbol{\mu}_{(1,1),0}^{a,b} = \left[2\sum_{i\neq g}\sum_{j\neq g}\left\{\frac{\langle\psi_g^0|H_a'|\psi_i^0\rangle\langle\psi_i^0|\hat{\boldsymbol{\mu}}_0|\psi_j^0|H_b'\rangle\langle\psi_i^0|\psi_g^0\rangle}{(\varepsilon_i^0-\varepsilon_g^0)(\varepsilon_j^0-\varepsilon_g^0)} + \frac{\langle\psi_g^0|H_a'|\psi_i^0\rangle\langle\psi_i^0|H_b'|\psi_j^0\rangle\langle\psi_j^0|\hat{\boldsymbol{\mu}}_0|\psi_g^0\rangle}{(\varepsilon_i^0-\varepsilon_g^0)(\varepsilon_j^0-\varepsilon_g^0)}\right.\right.$$
$$\left.+\frac{\langle\psi_g^0|H_b'|\psi_i^0\rangle\langle\psi_i^0|H_a'|\psi_j^0\rangle\langle\psi_j^0|\hat{\boldsymbol{\mu}}_0|\psi_g^0\rangle}{(\varepsilon_i^0-\varepsilon_g^0)(\varepsilon_j^0-\varepsilon_g^0)}\right\} - 2\sum_{i\neq g}\left\{\frac{\langle\psi_g^0|H_{ab}''|\psi_i^0\rangle\langle\psi_i^0|\hat{\boldsymbol{\mu}}_0|\psi_g^0\rangle}{\varepsilon_i^0-\varepsilon_g^0}\right.$$
$$\left.\left.+\frac{\langle\psi_g^0|H_a'|\psi_g^0\rangle\langle\psi_g^0|H_b'|\psi_i^0\rangle\langle\psi_i^0|\hat{\boldsymbol{\mu}}_0|\psi_g^0\rangle}{(\varepsilon_i^0-\varepsilon_g^0)^2} + \frac{\langle\psi_g^0|H_b'|\psi_g^0\rangle\langle\psi_g^0|H_a'|\psi_i^0\rangle\langle\psi_i^0|\hat{\boldsymbol{\mu}}_0|\psi_g^0\rangle}{(\varepsilon_i^0-\varepsilon_g^0)^2}\right\}\right]\langle\varphi_{(1,1)}^g|Q_aQ_b|\varphi_0^g\rangle. \quad (11)$$

Simultaneous Transition. In order to derive the expression of the transition moment for a simultaneous transition, we introduce two assumptions:

(i) The normal modes in a separate molecule remain in a two-molecule system.

(ii) The electron-transfer and -exchange between molecules do not appear.

The first assumption is supported by the experimental fact that the wave number of a simultaneous transition is equal to the sum of the wave numbers of the constituent fundamental tones. There is no experimental evidence to support the second assumption. On the basis of their theoretical investigation of intermolecular forces, however, Murrell *et al.*[10)] suggested that the effect of the electron-exchange appears in the region of intermolecular distances shorter than 3 Å, as is shown in the figures in their report, and that the electron-transfer is not important when the charge-transfer states are not detected spectroscopically. Therefore, the use of the second assumption will not bring a fatal error into the results of the calculations for a gas phase; also, it has the merit that the expression of the transition moment becomes very simple, as will be shown later.

With the first assumption, the electronic Hamiltonian of two-molecule system is given as:

$$H = H^{\mathrm{A}} + H^{\mathrm{B}} + U^0 + \sum_a U_a'Q_a + \sum_b U_b'Q_b, \quad (12)$$

$$H^{\mathrm{A}} = H_0^{\mathrm{A}} + \sum_a H_a'Q_a \quad [\text{where } H_a' = (\partial H^{\mathrm{A}}/\partial Q_a)_0], \quad (13)$$

$$H^{\mathrm{B}} = H_0^{\mathrm{B}} + \sum_b H_b'Q_b \quad [\text{where } H_b' = (\partial H^{\mathrm{B}}/\partial Q_b)_0], \quad (14)$$

$$U_a' = (\partial U/\partial Q_a)_0, \quad (15)$$

and

$$U_b' = (\partial U/\partial Q_b)_0, \quad (16)$$

where H^{A} and H^{B} are the electronic Hamiltonians of the separate molecules, A and B respectively; U, the intermolecular interaction operator including the nuclear coordinates as parameter, and U^0, U with a specified molecular configuration, each molecule keeping the equilibrium geometry. Since the wave number of the simultaneous transition considered in this work is the sum of those of the constituent fundamental tones, it is sufficient to consider the first-order term in each normal coordinate. Hereafter, Q_a in the A molecule and Q_b in the B molecule will be considered typical. The electronic wave function of the two-molecule system with an infinite separation is consistently given by the product of the wave functions of the separate molecules:

$$|\Psi^0_{ik}> = |\phi^{\mathrm{A}}_i>|\phi^{\mathrm{B}}_k>, \tag{17}$$

$$|\phi^{\mathrm{A}}_i> = |\phi^{\mathrm{A}0}_i> + \sum_{j\neq i} \frac{\langle\phi^{\mathrm{A}0}_j|H_a'|\phi^{\mathrm{A}0}_i\rangle Q_a}{\varepsilon^{\mathrm{A}0}_i - \varepsilon^{\mathrm{A}0}_j}|\phi^{\mathrm{A}0}_j\rangle, \tag{18}$$

and

$$|\phi^{\mathrm{B}}_k> = |\phi^{\mathrm{B}0}_k> + \sum_{l\neq k} \frac{\langle\phi^{\mathrm{B}0}_l|H_b'|\phi^{\mathrm{B}0}_k\rangle Q_b}{\varepsilon^{\mathrm{B}0}_k - \varepsilon^{\mathrm{B}0}_l}|\phi^{\mathrm{B}0}_l\rangle, \tag{19}$$

where the A and B superscripts indicate the separate molecules, A and B respectively, and where the 0 superscript in $|\Psi^0_{ik}>$ indicates the infinite separation. For the simultaneous transition, the initial state, o, and the final state, m, in Eq. (1) are given by the following expressions respectively:

$$|o> = |\Psi_g>|\Phi^g_{00}\rangle \tag{20}$$

and

$$|m> = |\Psi_g>|\Phi^g_{11}\rangle, \tag{21}$$

where $|\Psi_g>$ is the wave function of the electronic ground state of two-molecule system and where $|\Phi^g_{00}>$ and $|\Phi^g_{11}>$ are the wave functions of the vibrational initial and final states respectively. Regarding the last three terms in Eq. (12) as a perturbation caused by an interaction between neighbouring molecules, we can expand the wave function $|\Psi_g>$ by the use of the first-order perturbation method:

$$|\Psi_g> = |\Psi^0_{gg}> + \sum_{(ik)}{}' \frac{\langle\Psi^0_{ik}|U^0 + U_a'Q_a + U_b'Q_b|\Psi^0_{gg}\rangle}{E^0_{gg} - E^0_{ik}}|\Psi^0_{ik}\rangle, \tag{22}$$

where E^0_{ik} is the energy of the $|\Psi^0_{ik}>$ state and where the prime in Σ' indicates that the sum over (ik) does not include (gg). From the second assumption, the wave functions corresponding to the electron-transfers between molecules are also omitted. By substituting Eq. (22) into Eqs. (20) and (21), the following expression of $\boldsymbol{\mu}_{m,o}$ in Eq. (2) can be obtained:

$$\boldsymbol{\mu}_{m,o} = \langle\Phi^g_{11}|\boldsymbol{\mu}_{m,o}(0) + \boldsymbol{\mu}_{m,o}(1) + \boldsymbol{\mu}_{m,o}(2)|\Phi^g_{00}\rangle, \tag{23}$$

where:

$$\boldsymbol{\mu}_{m,o}(0) = \langle\Psi^0_{gg}|\hat{\boldsymbol{\mu}}|\Psi^0_{gg}\rangle + 2\sum_{(ik)}{}' \frac{\langle\Psi^0_{gg}|\hat{\boldsymbol{\mu}}|\Psi^0_{ik}\rangle\langle\Psi^0_{ik}|U_a'Q_a + U_b'Q_b|\Psi^0_{gg}\rangle}{E^0_{gg} - E^0_{ik}}$$
$$+ \sum_{(ik)}{}' \sum_{(jl)}{}' \frac{\langle\Psi^0_{gg}|U_a'Q_a + U_b'Q_b|\Psi^0_{ik}\rangle\langle\Psi^0_{ik}|\hat{\boldsymbol{\mu}}|\Psi^0_{jl}\rangle\langle\Psi^0_{jl}|U_a'Q_a + U_b'Q_b|\Psi^0_{gg}\rangle}{(E^0_{gg} - E^0_{ik})(E^0_{gg} - E^0_{jl})}, \tag{24}$$

$$\boldsymbol{\mu}_{m,o}(1) = 2\sum_{(ik)}{}' \frac{\langle\Psi^0_{gg}|\hat{\boldsymbol{\mu}}|\Psi^0_{ik}\rangle\langle\Psi^0_{ik}|U^0|\Psi^0_{gg}\rangle}{E^0_{gg} - E^0_{ik}} + 2\sum_{(ik)}{}' \sum_{(jl)}{}' \frac{\langle\Psi^0_{gg}|U^0|\Psi^0_{ik}\rangle\langle\Psi^0_{ik}|\hat{\boldsymbol{\mu}}|\Psi^0_{jl}\rangle\langle\Psi^0_{jl}|U_a'Q_a + U_b'Q_b|\Psi^0_{gg}\rangle}{(E^0_{gg} - E^0_{ik})(E^0_{gg} - E^0_{jl})} \tag{25}$$

and

$$\boldsymbol{\mu}_{m,o}(2) = \sum_{(ik)}{}' \sum_{(jl)}{}' \frac{\langle\Psi^0_{gg}|U^0|\Psi^0_{ik}\rangle\langle\Psi^0_{ik}|\hat{\boldsymbol{\mu}}|\Psi^0_{jl}\rangle\langle\Psi^0_{jl}|U^0|\Psi^0_{gg}\rangle}{(E^0_{gg} - E^0_{ik})(E^0_{gg} - E^0_{jl})} \tag{26}$$

In the above expressions, $\boldsymbol{\mu}_{m,o}(0)$, $\boldsymbol{\mu}_{m,o}(1)$, and $\boldsymbol{\mu}_{m,o}(2)$ are the zeroth-, the first-, and the second-order terms of U^0 respectively. If the higher-order perturbations were considered in the expansion of $|\Psi_g>$, some other terms would be added to Eqs. (24)—(26). The terms contributing to the simultaneous transitions must include three kinds of matrix elements, two of them being those of the vibronic coupling operators referring to Q_a and Q_b respectively, and one of them being that of $\hat{\boldsymbol{\mu}}$. Therefore, the lowest-order term contributing to the simultaneous transitions is the third-order one. The terms in $\boldsymbol{\mu}_{m,o}(1)$ and $\boldsymbol{\mu}_{m,o}(2)$ always include the matrix elements of U^0; therefore, their contributions to the simultaneous transitions arise from higher-order terms than the third-order one. In this work, the intensities of the simultaneous transitions have been calculated by considering only $\boldsymbol{\mu}_{m,o}(0)$, which gives the lowest-order contribution. The influences of $\boldsymbol{\mu}_{m,o}(1)$ and $\boldsymbol{\mu}_{m,o}(2)$ will be investigated in the future. When $|\Psi^0_{ik}>$'s in Eq. (24) were rewritten by the use of the expressions in Eqs. (17)—(19), and only the terms including Q_aQ_b were retained, $\boldsymbol{\mu}_{m,o}(0)$ was given as:

$$\boldsymbol{\mu}_{m,o}(0) = 2\sum_{i\neq g}\sum_{k\neq g} C^{\mathrm{A}}_{ig}C^{\mathrm{B}}_{kg}\{\langle gg|\hat{\boldsymbol{\mu}}_0|ik\rangle + \langle ig|\hat{\boldsymbol{\mu}}_0|gk\rangle\}Q_aQ_b + 2\sum_{(ik)}{}' \frac{1}{E^0_{gg} - E^0_{ik}}\Big[\sum_{n\neq i} C^{\mathrm{A}}_{ni}\{\langle gg|U_b'|nk\rangle\langle ik|\hat{\boldsymbol{\mu}}_0|gg\rangle$$
$$+ \langle gg|U_b'|ik\rangle\langle nk|\hat{\boldsymbol{\mu}}_0|gg\rangle\} + \sum_{m\neq g} C^{\mathrm{A}}_{mg}\{\langle mg|U_b'|ik\rangle\langle ik|\hat{\boldsymbol{\mu}}_0|gg\rangle$$
$$+ \langle gg|U_b'|ik\rangle\langle ik|\hat{\boldsymbol{\mu}}_0|mg\rangle\} + \sum_{s\neq k} C^{\mathrm{B}}_{sk}\{\langle gg|U_a'|is\rangle\langle ik|\hat{\boldsymbol{\mu}}_0|gg\rangle$$
$$+ \langle gg|U_a'|ik\rangle\langle is|\hat{\boldsymbol{\mu}}_0|gg\rangle\} + \sum_{r\neq g} C^{\mathrm{B}}_{rg}\{\langle gr|U_a'|ik\rangle\langle ik|\hat{\boldsymbol{\mu}}_0|gg\rangle + \langle gg|U_a'|ik\rangle\langle ik|\hat{\boldsymbol{\mu}}_0|gr\rangle\}\Big]Q_aQ_b$$
$$+ \sum_{(ik)}{}' \sum_{(jl)}{}' \frac{1}{(E^0_{gg} - E^0_{ik})(E^0_{gg} - E^0_{jl})}\{\langle gg|U_a'|ik\rangle\langle ik|\hat{\boldsymbol{\mu}}_0|jl\rangle\langle jl|U_b'|gg\rangle + \langle gg|U_b'|ik\rangle\langle ik|\hat{\boldsymbol{\mu}}_0|jl\rangle\langle jl|U_a'|gg\rangle\}Q_aQ_b, \tag{27}$$

where $C^{\mathrm{A}}_{ij} = \langle\phi^{\mathrm{A}0}_i|H_a'|\phi^{\mathrm{A}0}_j\rangle/(\varepsilon^{\mathrm{A}0}_j - \varepsilon^{\mathrm{A}0}_i)$; $C^{\mathrm{B}}_{kl} = \langle\phi^{\mathrm{B}0}_k|H_b'|\phi^{\mathrm{B}0}_l\rangle/(\varepsilon^{\mathrm{B}0}_l - \varepsilon^{\mathrm{B}0}_k)$; and $|ij\rangle = |\phi^{\mathrm{A}0}_i\rangle|\phi^{\mathrm{B}0}_j\rangle$. From the second assumption and the facts that the operators, U_a', U_b' and $\hat{\boldsymbol{\mu}}_0$, are sums of the one-electron operators and that the electronic wave functions in the separated molecules are orthonormalized, the integrals on the right-hand side of Eq. (27) are reduced to one-molecule integrals as follows:

$$\left.\begin{aligned}
\langle ij|U_a'|kl\rangle &= \langle\phi^{\mathrm{B}0}_j|U_a'|\phi^{\mathrm{B}0}_l\rangle\delta_{ik}, \\
\langle ij|U_b'|kl\rangle &= \langle\phi^{\mathrm{A}0}_i|U_b'|\phi^{\mathrm{A}0}_k\rangle\delta_{jl}, \\
\langle ij|\hat{\boldsymbol{\mu}}_0|kl\rangle &= \langle\phi^{\mathrm{A}0}_i|\hat{\boldsymbol{\mu}}_0|\phi^{\mathrm{A}0}_k\rangle\delta_{jl} + \langle\phi^{\mathrm{B}0}_j|\hat{\boldsymbol{\mu}}_0|\phi^{\mathrm{B}0}_l\rangle\delta_{ik}.
\end{aligned}\right\} \tag{28}$$

Considering Eq. (28) and adopting the approximation that $E^0_{ik}=\varepsilon_i^{A0}+\varepsilon_k^{B0}$, we can divide $\boldsymbol{\mu}_{m,o}(0)$ into two parts:

$$\boldsymbol{\mu}_{m,o}(0) = \{\boldsymbol{\mu}^{A}_{m,o}(0)+\boldsymbol{\mu}^{B}_{m,o}(0)\}Q_aQ_b, \tag{29}$$

where

$$\begin{aligned}\boldsymbol{\mu}^{A}_{m,o}(0) = 2\Bigg[&\sum_{i\neq g}\sum_{j\neq g}\left\{\frac{\langle\phi_g^{A0}|\hat{\boldsymbol{\mu}}_0|\phi_i^{A0}\rangle\langle\phi_i^{A0}|U_b'|\phi_j^{A0}\rangle\langle\phi_j^{A0}|H_a'|\phi_g^{A0}\rangle}{(\varepsilon_g^{A0}-\varepsilon_i^{A0})(\varepsilon_g^{A0}-\varepsilon_j^{A0})}+\frac{\langle\phi_g^{A0}|U_b'|\phi_i^{A0}\rangle\langle\phi_i^{A0}|\hat{\boldsymbol{\mu}}_0|\phi_j^{A0}\rangle\langle\phi_j^{A0}|H_a'|\phi_g^{A0}\rangle}{(\varepsilon_g^{A0}-\varepsilon_i^{A0})(\varepsilon_g^{A0}-\varepsilon_j^{A0})}\right\}\\
&+\sum_{\substack{i\neq g\\(i\neq j)}}\sum_{j\neq g}\frac{\langle\phi_g^{A0}|U_b'|\phi_i^{A0}\rangle\langle\phi_i^{A0}|H_a'|\phi_j^{A0}\rangle\langle\phi_j^{A0}|\hat{\boldsymbol{\mu}}_0|\phi_g^{A0}\rangle}{(\varepsilon_g^{A0}-\varepsilon_i^{A0})(\varepsilon_g^{A0}-\varepsilon_j^{A0})}-\sum_{i\neq g}\left\{\frac{\langle\phi_g^{A0}|U_b'|\phi_g^{A0}\rangle\langle\phi_g^{A0}|H_a'|\phi_i^{A0}\rangle\langle\phi_i^{A0}|\hat{\boldsymbol{\mu}}_0|\phi_g^{A0}\rangle}{(\varepsilon_g^{A0}-\varepsilon_i^{A0})^2}\right.\\
&\left.+\frac{\langle\phi_g^{A0}|U_b'|\phi_i^{A0}\rangle\langle\phi_i^{A0}|H_a'|\phi_g^{A0}\rangle\langle\phi_g^{A0}|\hat{\boldsymbol{\mu}}_0|\phi_g^{A0}\rangle}{(\varepsilon_g^{A0}-\varepsilon_i^{A0})^2}\right\}\Bigg]\end{aligned} \tag{30}$$

$$\begin{aligned}\boldsymbol{\mu}^{B}_{m,o}(0) = 2\Bigg[&\sum_{k\neq g}\sum_{l\neq g}\left\{\frac{\langle\phi_g^{B0}|\hat{\boldsymbol{\mu}}_0|\phi_k^{B0}\rangle\langle\phi_k^{B0}|U_a'|\phi_l^{B0}\rangle\langle\phi_l^{B0}|H_b'|\phi_g^{B0}\rangle}{(\varepsilon_g^{B0}-\varepsilon_k^{B0})(\varepsilon_g^{B0}-\varepsilon_l^{B0})}+\frac{\langle\phi_g^{B0}|U_a'|\phi_k^{B0}\rangle\langle\phi_k^{B0}|\hat{\boldsymbol{\mu}}_0|\phi_l^{B0}\rangle\langle\phi_l^{B0}|H_b'|\phi_g^{B0}\rangle}{(\varepsilon_g^{B0}-\varepsilon_k^{B0})(\varepsilon_g^{B0}-\varepsilon_l^{B0})}\right\}\\
&+\sum_{\substack{k\neq g\\(k\neq l)}}\sum_{l\neq g}\frac{\langle\phi_g^{B0}|U_a'|\phi_k^{B0}\rangle\langle\phi_k^{B0}|H_b'|\phi_l^{B0}\rangle\langle\phi_l^{B0}|\hat{\boldsymbol{\mu}}_0|\phi_g^{B0}\rangle}{(\varepsilon_g^{B0}-\varepsilon_k^{B0})(\varepsilon_g^{B0}-\varepsilon_l^{B0})}-\sum_{k\neq g}\left\{\frac{\langle\phi_g^{B0}|U_a'|\phi_g^{B0}\rangle\langle\phi_g^{B0}|H_b'|\phi_k^{B0}\rangle\langle\phi_k^{B0}|\hat{\boldsymbol{\mu}}_0|\phi_g^{B0}\rangle}{(\varepsilon_g^{B0}-\varepsilon_k^{B0})^2}\right.\\
&\left.+\frac{\langle\phi_g^{B0}|U_a'|\phi_k^{B0}\rangle\langle\phi_k^{B0}|H_b'|\phi_g^{B0}\rangle\langle\phi_g^{B0}|\hat{\boldsymbol{\mu}}_0|\phi_g^{B0}\rangle}{(\varepsilon_g^{B0}-\varepsilon_k^{B0})^2}\right\}\Bigg].\end{aligned} \tag{31}$$

$\boldsymbol{\mu}^{A}_{m,o}(0)$ indicates the contribution of the coupling between the electronic state of the A molecule and the nuclear vibration of the B molecule to the intensity of the simultaneous transition, and $\boldsymbol{\mu}^{B}_{m,o}(0)$, the coupling between the electronic state of the B molecule and the nuclear vibration of the A molecule.

Methods of Calculations

In order to calculate the transition moment according to the expressions derived in the previous section, the electronic wave function, $|\phi_g^0>$, and the energy, ε_g^0, of the separate molecule in the ground state were obtained by the CNDO/2 method, an approximate elf-consistent molecular orbital theory, proposed by Pople *et al.*[11] The excited states, $|\phi_i^0>$'s, were approximated by the singly-excited configurations, $\chi_l^{m'}$'s,[12] and their energies, $\varepsilon_l^{m'}$'s, were evaluated from the well-known expression:[13]

$$\varepsilon_l^m = \varepsilon_g^0 - e_l + e_m - J_{lm} + 2K_{lm}, \tag{32}$$

where e_l and e_m are the orbital energies of the l-th and the m-th molecular orbitals respectively, and where J_{lm} and K_{lm} are the Coulomb- and exchange-integrals respectively. In this work, the terms including the operator, H_{ab}'', were neglected. The integrals in Eqs. (9)—(11), (30), and (31), *i.e.*, $\langle\phi_i^0|\hat{\boldsymbol{\mu}}_0|\phi_j^0\rangle$, *etc.*, were expanded to the integral terms with the one-electron molecular orbitals and were calculated by the methods in Refs. 14 and 15. The calculations of the absorption intensities with reference to the intermolecular interaction were performed for 20 different arrangements, including variations in the intermolecular distance and in the orientation of the two molecules; the distances were fixed at 4.0, 6.0, 8.0, 15.0, and 30.0 Å, and the four kinds of the orientation shown in Fig. 1 were employed.

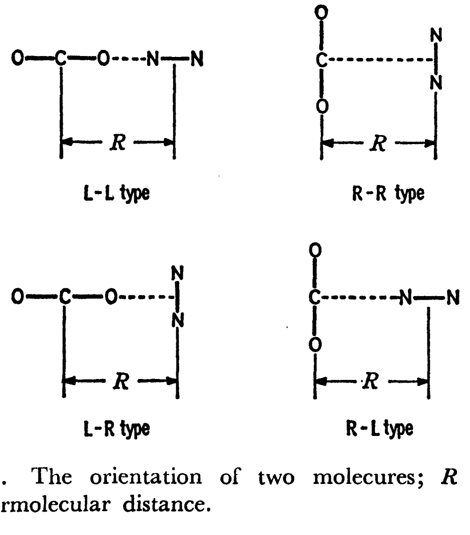

Fig. 1. The orientation of two molecures; R is the intermolecular distance.

Results and Discussion

The results will be discussed for the cases of the simultaneous transitions in the CO_2–N_2 and CO_2–H_2 systems and for the case of the vibrational transition of the CO_2 system, with reference to the intramolecular and intermolecular processes. In the following discussions, the same notations, ν_1, ν_2, and ν_3, for the fundamental bands of CO_2 as those in Ref. 16 are employed, while ν_{N_2} and ν_{H_2} denote the fundamental bands of N_2 and H_2 respectively. The L_x matrices, which are required in calculating the matrix elements of the vibronic coupling operator, were evaluated by the usual **GF** method, the **F** matrix elements in Ref. 16 being employed.

Simultaneous Transition. In the first place, in order to make a brief discussion of the results, the averaged values of the intensities of the simultaneous transition, as calculated for four kinds of orientations at a specified intermolecular distance, were compared with the experimental results. If a certain orientation between molecules should be considered in the compressed system, there will be a problem in the adoption of the averaged values as described above. However, in the level of the approximation used in this work, there was little reason to choose between the four orientations. The variations in the averaged value of the intensities with the intermolecular distance are shown in Figs. 2 and 3 for the CO_2–N_2 and CO_2–H_2 systems respectively. In the experiment with the CO_2–N_2 system,[1] the simultaneous transitions, $\nu_2+\nu_{N_2}$ and $\nu_3+\nu_{N_2}$, are observed, but $\nu_1+\nu_{N_2}$ is not ob-

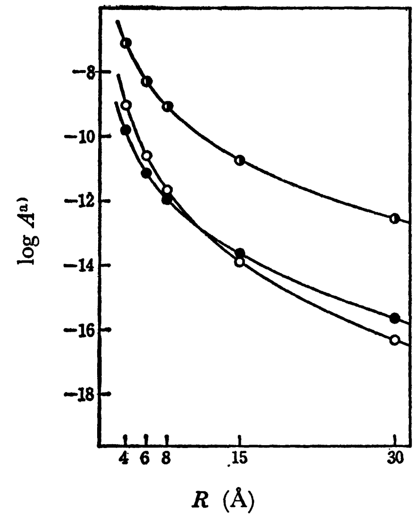

Fig. 2. The infrared absorption intensity of the simultaneous transition in the CO_2-N_2 system; a) A is the absolute intensity, unit of which is in cm^2 s^{-1} molecule-pair^{-1}.
○: $\nu_1+\nu_{N_2}$, ●: $\nu_2+\nu_{N_2}$, ◑: $\nu_3+\nu_{N_2}$.

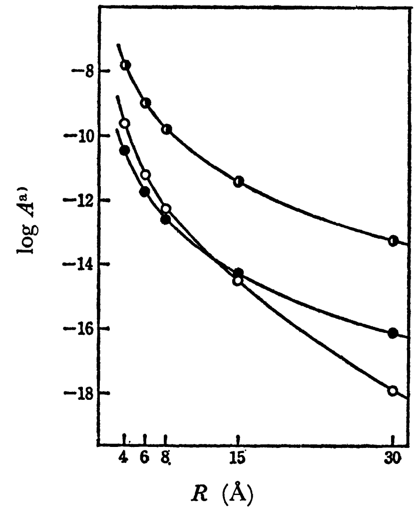

Fig. 3. The infrared absorption intensity of the simultaneous transition in the CO_2-H_2 system; a) A is the absolute intensity, unit of which is in cm^2 s^{-1} molecule-pair^{-1}.
○: $\nu_1+\nu_{H_2}$, ●: $\nu_2+\nu_{H_2}$, ◑: $\nu_3+\nu_{H_2}$.

served. There is difference between the observed and theoretical results with reference to the $\nu_1+\nu_{N_2}$ transition; the calculated intensity of $\nu_1+\nu_{N_2}$ was comparable to that of $\nu_2+\nu_{N_2}$. The difference may be derived from the overestimation in the approximate calculation of the integral which is required in the estimation of the matrix elements of the vibronic coupling operators, and which is connected with the intensities of the $\nu_1+\nu_{N_2}$ and $\nu_3+\nu_{N_2}$ transitions. There is a reason for this. That is, from the comparison between the values of the approximate and rigorous calculations of the integral which contributes to the absorption intensity related to the C–O stretching mode in CO_2, it is found that the difference between those values is remarkably large (see Fig. 4). The defect in the approximate calculation, however, has no influence on the value of the absorption intensity with reference to the bending mode of a linear molecule, because the scalar product in Eq. (17) in Ref. 15 is always equal to zero.

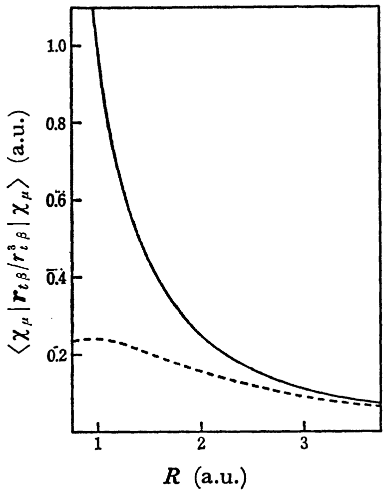

Fig. 4. Comparison between the approximate and rigorous values of the $\langle \chi_\mu | \boldsymbol{r}_{t\beta}/r_{t\beta}^3 | \chi_\mu \rangle$ integral in Eq. (18) of Ref. 15. χ_μ is the $2p_\pi$ atomic orbital of carbon and R is the distance between the β atom and the carbon which are located on the z-axis.
——: Approximate, ----: Rigorous.

The theoretical intensities of the simultaneous transitions were calculated from the transition moments, which were divided into two parts, $\mu^A_{m,o}(0)$ and $\mu^B_{m,o}(0)$, as indicated in Eq. (29). In the CO_2–N_2 system, the A part is the transition moment derived from the coupling between the electronic state of CO_2 and the nuclear vibration of N_2, while the B part is that derived from the coupling between the electronic state of N_2 and the nuclear vibration of CO_2. The calculated intensities are listed in Tables 1—3, in which the first line indicates the value from the A part of the transition moment, and the second line, the value from the B part. In the cases of the L-R, R-R, and R-L types of orientation between the molecules, the intensities from the B part were affected by the degenerate bending vibrations, one of which is set on the plane involving the two molecules and the other one of which is set out of the plane; the intensities in the case of the out-of-plane bending vibration were zero. On the other hand, in cases of the other orientations, the intensities from the A and B parts were not affected by the different bending modes. Therefore, the values in Table 2 indicate only the case of the in-plane bending vibration. From the tables, it is found that the contributions of the A and B parts of the transition moment to the absorption intensity caused by the simultaneous transition differ from each other. The A part is effective on the intensities of $\nu_2+\nu_{N_2}$ and $\nu_3+\nu_{N_2}$ at all the orientations. The B part is, however, effective on the intensity of $\nu_2+\nu_{N_2}$ at the L-R and R-L types of orientation and on that of $\nu_3+\nu_{N_2}$ at the L-L and R-R types. The intensity of $\nu_1+\nu_{N_2}$ arises from the restricted parts, the A part at the L-L and L-R types of the orientation, and the

TABLE 1. THE ABSORPTION INTENSITY OF THE SIMULTANEOUS TRANSITION, $\nu_1+\nu_{N_2}$ [cm^2 s^{-1} pair^{-1}][a,b]

Orientation[c]	R[d] [Å]				
	4.0	6.0	8.0	15.0	30.0
L-L	0.389×10^{-8} 0.515×10^{-10}	0.980×10^{-10} 0.130×10^{-11}	0.851×10^{-11} 0.113×10^{-12}	0.491×10^{-13} 0.650×10^{-15}	0.185×10^{-15} 0.245×10^{-17}
L-R	0.722×10^{-9} 0.0	0.219×10^{-10} 0.0	0.201×10^{-11} 0.0	0.121×10^{-13} 0.0	0.460×10^{-16} 0.0
R-R	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0
R-L	0.0 0.447×10^{-11}	0.0 0.207×10^{-12}	0.0 0.219×10^{-13}	0.0 0.151×10^{-15}	0.0 0.600×10^{-18}

a) The unit of the intensity is the cross section per unit time per molecule-pair. b) The upper values are calculated with the term of the coupling between the electronic state of CO_2 and the nuclear vibration of N_2 and the lower ones with the term of the coupling between the electronic state of N_2 and the nuclear vibration of CO_2. c) The orientation of the molecules is shown in Fig. 1. d) R is the intermolecular distance as shown in Fig. 1.

TABLE 2. THE ABSORPTION INTENSITY OF THE SIMULANEOUS TRANSITION, $\nu_2+\nu_{N_2}$ [cm^2 s^{-1} pair^{-1}][a,b]

Orientation[c]	R[d] [Å]				
	4.0	6.0	8.0	15.0	30.0
L-L	0.469×10^{-9} 0.0	0.181×10^{-10} 0.0	0.239×10^{-11} 0.0	0.413×10^{-13} 0.0	0.591×10^{-15} 0.0
L-R	0.900×10^{-10} 0.332×10^{-11}	0.415×10^{-11} 0.384×10^{-13}	0.572×10^{-12} 0.328×10^{-14}	0.102×10^{-13} 0.282×10^{-16}	0.147×10^{-15} 0.294×10^{-18}
R-R	0.649×10^{-11} 0.0	0.127×10^{-11} 0.0	0.291×10^{-12} 0.0	0.841×10^{-14} 0.0	0.140×10^{-15} 0.0
R-L	0.459×10^{-10} 0.206×10^{-12}	0.643×10^{-11} 0.305×10^{-17}	0.133×10^{-11} 0.582×10^{-15}	0.349×10^{-13} 0.460×10^{-16}	0.567×10^{-15} 0.932×10^{-18}

a, b, c, d) See the footnotes in Table 1.

TABLE 3. THE ABSORPTION INTENSITY OF THE SIMULTANEOUS TRANSITION, $\nu_3+\nu_{N_2}$ [cm^2 s^{-1} pair^{-1}][a,b]

Orientation[c]	R[d] [Å]				
	4.0	6.0	8.0	15.0	30.0
L-L	0.196×10^{-6} 0.428×10^{-11}	0.105×10^{-7} 0.768×10^{-13}	0.159×10^{-8} 0.614×10^{-14}	0.318×10^{-10} 0.504×10^{-16}	0.476×10^{-12} 0.520×10^{-18}
L-R	0.396×10^{-7} 0.0	0.244×10^{-8} 0.0	0.384×10^{-9} 0.0	0.786×10^{-11} 0.0	0.119×10^{-12} 0.0
R-R	0.121×10^{-7} 0.574×10^{-13}	0.143×10^{-8} 0.226×10^{-15}	0.283×10^{-9} 0.122×10^{-16}	0.720×10^{-11} 0.413×10^{-17}	0.116×10^{-11} 0.982×10^{-19}
R-L	0.637×10^{-7} 0.0	0.649×10^{-8} 0.0	0.122×10^{-8} 0.0	0.294×10^{-10} 0.0	0.467×10^{-12} 0.0

a, b, c, d) See the footnotes in Table 1.

B part at the L-L and R-L types. For the intensities of all the simultaneous transitions, the A part at the L-L type of orientation makes the dominant contribution.

The following general considerations can be derived from these results. On the simultaneous transition of the A–B system, when the vibrational mode of the A molecule is infrared-active, the intermolecular vibronic coupling between the electronic state of the A molecule and the nuclear vibration of the B molecule is always effective. When both the vibrational modes of the molecules, A and B, are infrared-inactive, it does not necessarily follow that a simultaneous transition is not found. Rather, the finding of the phenomenon depends on the orientation of the molecules. Special attention should be paid to the latter conclusion.

These conclusions disagree with those suggested by Hooge and Ketelaar,[3)] who discussed the problem on the basis of the expansion of the dipole moment with the normal coordinates. They suggested that the necessary condition for the appearance of a simul-

TABLE 4. THE INFRARED ABSORPTION INTENSITY OF CO_2

	Obsd	Intra.[a]	Inter.[a] [$cm^2\ s^{-1}\ pair^{-1}$][b] R[c] [Å]				
	[$cm^2\ s^{-1}\ molecule^{-1}$]		4.0	6.0	8.0	15.0	30.0
ν_1		0.0					
ν_2	0.18×10^{-6} [d] 0.27×10^{-6} [e,f]	0.196×10^{-7}					
ν_3	0.30×10^{-5} [d] 0.33×10^{-5} [f]	0.196×10^{-4}					
$2\nu_1$		0.0	0.173×10^{-8}	0.671×10^{-10}	0.662×10^{-11}	0.424×10^{-13}	0.165×10^{-15}
$2\nu_2$		0.0	0.582×10^{-11}	0.150×10^{-12}	0.154×10^{-12}	0.205×10^{-12}	0.140×10^{-14}
$2\nu_3$		0.0	0.192×10^{-7}	0.170×10^{-8}	0.346×10^{-9}	0.161×10^{-10}	0.817×10^{-12}
$\nu_1+\nu_2$	0.16×10^{-9} [d]	0.114×10^{-6}	0.169×10^{-8}	0.497×10^{-10}	0.743×10^{-11}	0.115×10^{-12}	0.169×10^{-14}
$\nu_1+\nu_3$	0.31×10^{-7} [d,g] 0.44×10^{-7} [d,g]	0.192×10^{-5}	0.793×10^{-6}	0.436×10^{-7}	0.699×10^{-8}	0.149×10^{-9}	0.228×10^{-11}
$\nu_2+\nu_3$		0.0	0.114×10^{-8}	0.273×10^{-9}	0.173×10^{-9}	0.228×10^{-11}	0.161×10^{-11}

a) The abbreviations, Intra. and Inter., mean the intramolecular and intermolecular processes, respectively. b) See the footnote a in Table 1. c) See the footnote d in Table 1. d) From Ref. 17. e) From Ref. 18. f) From Ref. 19. g) The assignment of these values was not exactly given because of the Fermi resonance between $\nu_1+\nu_3$ and $2\nu_2+\nu_3$.

taneous band is that one of the vibrational modes is infrared-active, while the other mode is Raman-active. The results of the CO_2–H_2 system are analogous to those of the CO_2–N_2 system. Therefore, their discussions are omitted.

Carbon Dioxide: The infrared absorption intensities of CO_2 have been measured by several investigators for the gas[17–19] and solid phases.[20] The calculated values of the intensities, with reference to the intramolecular and intermolecular processes, are shown in Table 4; the experimental results in the gas phase are also included. For the intensities from the intermolecular process, the averaged values are adopted for the same reason as has been presented before. The table shows that the intermolecular interaction contributes slightly to the absorption intensities at the atmospheric pressure and at the intermolecular distance of about 30 Å. Therefore, it is considered that the experimental results at the ordinary pressure correspond to the results caused by the intramolecular process. In the experiment, two fundamental bands, ν_2 and ν_3, with very strong intensities and two combination bands, $\nu_1+\nu_2$ and $\nu_1+\nu_3$, with medium and strong intensities respectively are observed. In the calculated results, the intensity of ν_3 is the strongest, while that of ν_2 is weaker than those of $\nu_1+\nu_2$ and $\nu_1+\nu_3$. From the comparison between the experimental and the calculated results, it is found that the calculated intensity of ν_2 is underestimated and that the theoretical values for the other absorption bands are overestimated. It is considered that these overestimations arise from the defect in the approximate calculation described before. It is noteworthy that the intensity from the intermolecular process increases with a decrease in the intermolecular distance (see Table 4). In any case, it is found that the intermolecular interaction contributes, more or less, to the intensities of the overtone and combination bands, some of which have no intensity from the intramolecular process. These results establish that the intermolecular vibronic coupling is an important factor for the infrared absorption intensity of the compressed gas of a one-component system. Also, the following statement might be made; in discussing the intensity of the vibrational spectra of the liquid phase, it is necessary to include an argument based on the intermolecular vibronic coupling.

Summary

The formulas of the infrared-absorption intensity for the intramolecular and intermolecular processes have been derived by the use of the vibronic expansion technique. The intensities for the simultaneous transitions of the CO_2–N_2 and CO_2–H_2 systems and for CO_2 have been calculated. Since the matrix elements of the vibronic coupling operator were only approximately calculated, quantitative conclusions could not be obtained. The qualitative conclusion is that, for any pair of vibrational modes between molecules, the intensities of the simultaneous transitions are not zero, although their magnitudes depend on the orientation of the molecules and are not always large enough to be observed. One remarkable suggestion is that the intermolecular interaction, like the intramolecular anharmonicities, is an important factor in discussing infrared absorption intensities in liquids and solutions. In that case, the method used in averaging the orientation of molecules will become an essential problem in the treatment of intermolecular interactions.

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References

1) J. Fahrenfort and J. A. A. Ketelaar, *J. Chem. Phys.*, **22**, 1631 (1954).

2) J. A. A. Ketelaar and F. N. Hooge, *ibid.*, **23**, 749, 1549 (1955); *Rec. Trav. Chim. Pays-Bas.*, **76**, 529 (1957).

3) F. N. Hooge and J. A. A. Ketelaar, *Physica*, **23**, 423 (1957).

4) A. M. Thorndike, A. J. Wells, and E. B. Wilson, Jr., *J. Chem. Phys.*, **15**, 157 (1947); T. Miyazaki and H. Yamamoto, This Bulletin, **45**, 1669 (1972); T. Miyazaki, T. Shigetani, and H. Yamamoto, *ibid.*, **45**, 678 (1972); T. Miyazaki, M. Ikeda, and M. Shibata, *ibid.*, **48**, 1138 (1975); See Ref. 7, p. 39.

5) G. Placzek, "Handbuch der Radiologie," Vol. 6, ed. by E. Marx, Akademische Verlagsgesellschaft, Leipzig (1934), Pt. 2; H. Shinoda and T. Miyazaki, *Chem. Lett.*, **1973**, 563.

6) J. Tang and A. C. Albrecht, "Raman Spectroscopy," Vol. 2, ed. by. S. Szymanski, Plenum Press, New York-London (1970), p. 33; see also Ref. 15.

7) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Company, New York-Toronto-London (1955), p. 163.

8) L. I. Schiff, "Quantum Mechanics," 3rd Ed., McGraw-Hill Book Company, New York-Toronto-London (1968), p. 247.

9) When the translation and the rotation are neglected, $\hat{\mu}_{\mathrm{n}}$ can be expressed as $\hat{\mu}_{\mathrm{n}}=\sum_i Z_i(\mathbf{r}_i^0+\Delta\mathbf{r}_i)$, where Z_i is the nuclear charge of the i atom, $\mathbf{r}_i^0$ the vector of the equilibrium position of the i atom from the origin of the molecular fixed coordinate system, and $\Delta\mathbf{r}_i$ is the vector of the displacement of the i atom from the equilibrium position. $\hat{\mu}_n^0$ in Eq. (7) means $\sum_i Z_i\mathbf{r}_i^0$ and $\sum_a \mathbf{k}_a Q_a$ in Eq. (7) is casily derived from $\sum_i Z_i\Delta\mathbf{r}_i$ by transforming $\Delta\mathbf{r}_i$ to Q_a by the use of the L_{x} matrix elements.

10) J. N. Murrell, M. Randic, and D. R. Williams, *Proc. Roy. Soc.* (London), *A*, **284**, 566 (1965).

11) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965); **44**, 3289 (1966).

12) The notation of the singly-excited configuration, χ_l^m, follows the Murrell and McEwen's in *J. Chem. Phys.*, **25**, 1143 (1956).

13) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

14) T. Miyazaki and H. Shinoda, This Bulletin, **46**, 1216 (1973).

15) H. Shinoda, *ibid.*, **48**, 1777 (1975).

16) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. 1, 2nd Ed. (1950) and Vol. 2 (1945), Van Nostrand, New York.

17) D. F. Eggers, Jr., and B. L. Crawford, Jr., *J. Chem. Phys.*, **19**, 1554 (1951).

18) J. Overend, M. J. Youngquist, E. C. Curtis, and B. L. Crawford, Jr., *ibid.*, **30**, 532 (1959).

19) B. Schurin, *ibid.*, **33**, 1878 (1960).

20) H. Yamada and W. B. Person, *ibid.*, **41**, 2478 (1964)