Theoretical Calculations of the Raman Intensities by the Vibronic Method

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The values of the transition moment of Raman scattering have been calculated according to the formula derived from the vibronic expansion approach. The calculations have been performed for the symmetry coordinates of several small molecules and for the normal vibrations of methane. The electronic wave functions were calculated by the CNDO/2-CI method. The calculated results are large in comparison with the experimental ones. The calculated Raman intensities for the symmetric stretching vibrations were almost all contributed by the term *A* in the vibronic expansion theory. From the calculated results for the normal vibrations of methane, it was found that the vibronic method used in this work leads to more appropriate values than those obtained from the polarizability theory which was used in the previous paper.

The development of the research technique using the laser Raman instrument has aided the discussion of the problem of the Raman intensity. Therefore there is now enhanced interest in the theoretical calculation of the Raman intensity. The theory of the Raman intensity has been discussed on the basis of the Kramers-Heisenberg dispersion formula.[1] Placzek[2] approximated the term of the transition moment of Raman scattering in this formula by the term of the polarizability derivative of the ground state in the nuclear coordinate, provided that the incident light is far away from the resonance region and the ground state of the molecule is not degenerate. There have since been several reports[3] in which the Raman intensities of H_2 and H_2^+ have been calculated according to Placzek's polarizability theory. Recently the calculations of the polarizability derivatives for small polyatomic molecules have been performed by several investigators, the electronic wave functions being evaluated by the LCAO-ASMO-SCF method.[4] By the use of the wave functions obtained from the finite perturbation method within the CNDO version, Hush and Williams[5] calculated the polarizabilities for some diatomic molecules and estimated their polarizability derivatives. They concluded that these polarizability derivatives are suitable for interpreting the factors determining the Raman transition probabilities within a valence orbital scheme. Yamada[6] calculated the polarizability derivatives with the symmetric stretching vibrations of four hydrocarbons, CH_4, C_2H_2, C_2H_4, and C_2H_6, the polarizabilities being calculated according to the expression derived from the second-order perturbation theory. She concluded that the CNDO calculations might useful in understanding the Raman intensities, although the calculated results were small in comparison with the experimental ones. Moreover the present author and Miyazaki[7] calculated the polarizability derivatives for several small molecules by the use of the formula derived from the time-dependent perturbation theory. The calculations described above were performed on the basis of Placzek's polarizability theory. On the other hand, there have been several reports[8–12] in which the theory of the Raman intensity has been discussed. In this work, then, the values of the Raman intensity have been calculated according to the formula derived from the vibronic expansion approach.[8–10] The electronic wave functions were evaluated by the CNDO/2-CI method. For the symmetric stretching vibrations of small molecules, the transition moments of Raman scattering were calculated in the approximation of the symmetry coordinate. Moreover, the intensities and the depolarization ratios of the Raman scattering for the normal vibrations of methane were calculated. The calculated results were discussed in comparison with the experimental ones and with the results obtained from the polarizability method, based on Placzek's theory, which was used in the previous work.[7]

Methods of Calculations

Raman Intensity. The vibronic expansion approach for the Raman intensity used in these calculations has been discussed in detail in Ref. 13. The total intensity of a Raman line after averaging all the molecular orientations is given as follows:

$$I_{mn} = \frac{2^3\pi}{3^2c^4} I_0\omega^4 \sum_{\rho,\sigma} |(\alpha_{\rho\sigma})_{mn}|^2, \tag{1}$$

where c is the velocity of light; I_0 is the intensity of the incident light; ω is the frequency of the scattered light; m is the initial state; n is the final state and $(\alpha_{\rho\sigma})_{mn}$ is the $\rho\sigma$-th component of the polarizability tensor for the $m\to n$ transition; the sum goes over $\rho=x,y,z$, and $\sigma=x,y,z$, which independently refer to the molecule fixed coordinate system. As has been described in Ref. 13, the general vibronic representation of $(\alpha_{\rho\sigma})_{mn}$ has been given as following equation, involving the terms A, B, and C:

$$(\alpha_{\rho\sigma})_{mn} = A + B + C, \tag{2}$$

$$A = \sum_{r\neq g}\sum_{i}\left[\frac{1}{E_{ri}-E_{gm}-E_0}+\frac{1}{E_{ri}-E_{gn}+E_0}\right] \times\langle g^0|R_\rho|r^0\rangle\langle r^0|R_\sigma|g^0\rangle\langle\psi_m^g|\psi_i^r\rangle\langle\psi_i^r|\psi_n^g\rangle, \tag{3}$$

$$B = \sum_{a}\sum_{r\neq g}\sum_{i}\sum_{s\neq r}\left[\left\{\frac{\langle g^0|R_\rho|r^0\rangle\langle r^0|h_a|s^0\rangle\langle s^0|R_\sigma|g^0\rangle}{(E_{ri}-E_{gm}-E_0)(\varepsilon_r^0-\varepsilon_s^0)} + \frac{\langle g^0|R_\sigma|r^0\rangle\langle r^0|h_a|s^0\rangle\langle s^0|R_\rho|g^0\rangle}{(E_{ri}-E_{gn}+E_0)(\varepsilon_r^0-\varepsilon_s^0)}\right\} \times\langle\psi_m^g|\psi_i^r\rangle\langle\psi_i^r|Q_a|\psi_n^g\rangle + \left\{\frac{\langle g^0|R_\rho|s^0\rangle\langle s^0|h_a|r^0\rangle\langle r^0|R_\sigma|g^0\rangle}{(E_{ri}-E_{gm}-E_0)(\varepsilon_r^0-\varepsilon_s^0)}\right.$$

$$+\frac{\langle g^0|R_\rho|s^0\rangle\langle s^0|h_a|r^0\rangle\langle r^0|R_\tau|g^0\rangle}{(E_{ri}-E_{gn}+E_0)(\varepsilon_r^0-\varepsilon_s^0)}\Big\}$$
$$\times\langle\psi_m^g|Q_a|\psi_i^r\rangle\langle\psi_i^r|\psi_n^g\rangle\Big], \quad (4)$$

and

$$C=\sum_a\sum_{r\neq g}\sum_i\sum_{s\neq g}\Big[\Big\{\frac{\langle g^0|h_a|s^0\rangle\langle s^0|R_\tau|r^0\rangle\langle r^0|R_\rho|g^0\rangle}{(E_{ri}-E_{gm}-E_0)(\varepsilon_g^0-\varepsilon_s^0)}$$
$$+\frac{\langle g^0|h_a|s^0\rangle\langle s^0|R_\rho|r^0\rangle\langle r^0|R_\tau|g^0\rangle}{(E_{ri}-E_{gn}+E_0)(\varepsilon_g^0-\varepsilon_s^0)}\Big\}$$
$$\times\langle\psi_m^g|Q_a|\psi_i^r\rangle\langle\psi_i^r|\psi_n^g\rangle$$
$$+\Big\{\frac{\langle g^0|R_\tau|r^0\rangle\langle r^0|R_\rho|s^0\rangle\langle s^0|h_a|g^0\rangle}{(E_{ri}-E_{gm}-E_0)(\varepsilon_g^0-\varepsilon_s^0)}$$
$$+\frac{\langle g^0|R_\rho|r^0\rangle\langle r^0|R_\sigma|s^0\rangle\langle s^0|h_a|g^0\rangle}{(E_{ri}-E_{gn}+E_0)(\varepsilon_g^0-\varepsilon_s^0)}\Big\}$$
$$\times\langle\psi_m^g|\psi_i^r\rangle\langle\psi_i^r|Q_a|\psi_n^g\rangle\Big], \quad (5)$$

where E_{gm} and E_{gn} are the energies of the initial vibronic state, $|g\rangle|\psi_m^g\rangle$, and the final vibronic state, $|g\rangle|\psi_n^g\rangle$, respectively; here $|g\rangle$ is the wave function of the electronic ground state, and $|\psi_m^g\rangle$ and $|\psi_n^g\rangle$ are the wave functions of the m-th and n-th vibrational states respectively in the electronic ground state; E_{ri} is the energy of the intermediate vibronic state, $|r\rangle|\psi_i^r\rangle$; here $|r\rangle$ is the wave function of the electronic excited state and $|\psi_i^r\rangle$ is the wave function of the i-th vibrational state in the $|r\rangle$ electronic state; E_0 is the energy of the incident light; ε_g^0 is the energy of the $|g^0\rangle$ electronic ground state; ε_r^0 and ε_s^0 are the energies of the $|r^0\rangle$ and $|s^0\rangle$ electronic states respectively; here the superscript 0 denotes the equilibrium nuclear position in the ground state; R_ρ and R_σ are the operators of the ρ- and σ-components respectively of the electronic dipole moment; Q_a is the normal coordinate of the a vibrational mode, and $h_a=(\partial H/\partial Q_a)$, the first-order vibronic coupling operator introduced initially by Herzberg and Teller.[14] Equations (3)—(5) can not be used directly in the calculation of $(\alpha_{\rho\sigma})_{mn}$ because we have meager knowledge of the vibrational wave function of a molecule in the electronic excited state. Therefore, we have to rearrange the equations in order to express $(\alpha_{\rho\sigma})_{mn}$ in a form without the vibrational wave functions. The expression of the term A is rearranged by Verlan's technique,[10] an expansion of the energy denominators around a fixed energy in a power series. When only the first-order terms in the expansion are retained, and when E_{gn} and E_{gm} are put approximately equal to ε_g^0, the term A is given by:

$$A=-\sum_a\sum_{r\neq g}\Big[\frac{\langle g^0|R_\sigma|r^0\rangle\langle r^0|h_a|r^0\rangle\langle r^0|R_\rho|g_0\rangle}{(\varepsilon_r^0-\varepsilon_g^0-E_0)^2}$$
$$+\frac{\langle g^0|R_\sigma|r^0\rangle\langle r^0|h_a|r^0\rangle\langle r^0|R_\rho|g^0\rangle}{(\varepsilon_r^0-\varepsilon_g^0+E_0)^2}\Big]\langle\psi_m^g|Q_a|\psi_n^g\rangle. \quad (6)$$

The terms B and C are simplified as follows by the use of the approximation that the energy, E_{ri}, is regarded as constant over i and put equl to ε_r^0:

$$B=-\sum_a\sum_r\sum_{s\neq r}\Big[\frac{\langle g^0|R_\sigma|r^0\rangle\langle r^0|h_a|s^0\rangle\langle s^0|R_\tau|g^0\rangle}{(\varepsilon_r^0-\varepsilon_g^0-E_0)(\varepsilon_s^0-\varepsilon_g^0-E_0)}$$
$$+\frac{\langle g^0|R_\rho|s^0\rangle\langle s^0|h_a|r^0\rangle\langle r^0|R_\sigma|g^0\rangle}{(\varepsilon_r^0-\varepsilon_g^0+E_0)(\varepsilon_s^0-\varepsilon_g^0+E_0)}\Big]\langle\psi_m^g|Q_a|\psi_n^g\rangle \quad (7)$$

and

$$C=-\sum_a\sum_{r\neq g}\sum_{s\neq g}\Big[\frac{\langle g^0|h_a|s^0\rangle\langle s^0|R_\sigma|r^0\rangle\langle r^0|R_\rho|g^0\rangle}{(\varepsilon_r^0-\varepsilon_g^0-E_0)(\varepsilon_s^0-\varepsilon_g^0)}$$
$$+\frac{\langle g^0|h_a|s^0\rangle\langle s^0|R_\rho|r^0\rangle\langle r^0|R_\sigma|g^0\rangle}{(\varepsilon_r^0-\varepsilon_g^0+E_0)(\varepsilon_s^0-\varepsilon_g^0)}$$
$$+\frac{\langle g^0|R_\tau|r^0\rangle\langle r^0|R_\rho|s^0\rangle\langle s^0|h_a|g^0\rangle}{(\varepsilon_r^0-\varepsilon_g^0-E_0)(\varepsilon_s^0-\varepsilon_g^0)}$$
$$+\frac{\langle g^0|R_\rho|r^0\rangle\langle r^0|R_\sigma|s^0\rangle\langle s^0|h_a|g^0\rangle}{(\varepsilon_r^0-\varepsilon_g^0+E_0)(\varepsilon_s^0-\varepsilon_g^0)}\Big]\langle\psi_m^g|Q_a|\psi_n^g\rangle. \quad (8)$$

By using the expressions in Eqs. (6)—(8), the equation for $(\alpha_{\rho\sigma})_{mn}$ can be written as:

$$(\alpha_{\rho\sigma})_{mn}=\sum_a(\alpha_{\rho\sigma}^a)'\langle\psi_m^g|Q_a|\psi_n^g\rangle, \quad (9)$$

where:

$$(\alpha_{\rho\sigma}^a)'=\sum_{r\neq g}\sum_{s\neq g}\Big[\frac{\langle g^0|R_\sigma|r^0\rangle\langle r^0|h_a|s^0\rangle\langle s^0|R_\rho|g^0\rangle}{(\varepsilon_r^0-\varepsilon_g^0+E_0)(\varepsilon_s^0-\varepsilon_g^0-E_0)}$$
$$+\frac{\langle g^0|R_\sigma|r^0\rangle\langle r^0|h_a|s^0\rangle\langle s^0|R_\rho|g^0\rangle}{(\varepsilon_r^0-\varepsilon_g^0+E_0)(\varepsilon_s^0-\varepsilon_g^0+E_0)}$$
$$+\frac{\langle g^0|h_a|s^0\rangle\langle s^0|R_\tau|r^0\rangle\langle r^0|R_\rho|g^0\rangle}{(\varepsilon_r^0-\varepsilon_g^0-E_0)(\varepsilon_s^0-\varepsilon_g^0)}$$
$$+\frac{\langle g^0|h_a|s^0\rangle\langle s^0|R_\rho|r^0\rangle\langle r^0|R_\sigma|g^0\rangle}{(\varepsilon_r^0-\varepsilon_g^0+E_0)(\varepsilon_s^0-\varepsilon_g^0)}$$
$$+\frac{\langle g^0|R_\sigma|r^0\rangle\langle r^0|R_\rho|s^0\rangle\langle s^0|h_a|g^0\rangle}{(\varepsilon_r^0-\varepsilon_g^0-E_0)(\varepsilon_s^0-\varepsilon_g^0)}$$
$$+\frac{\langle g^0|R_\rho|r^0\rangle\langle r^0|R_\sigma|s^0\rangle\langle s^0|h_a|g^0\rangle}{(\varepsilon_r^0-\varepsilon_g^0+E_0)(\varepsilon_s^0-\varepsilon_g^0)}\Big]$$
$$-2\sum_{r\neq g}\frac{1}{(\varepsilon_r^0-\varepsilon_g^0-E_0)(\varepsilon_r^0-\varepsilon_g^0-E_0)}$$
$$\times[\langle g^0|R_\tau|r^0\rangle\langle r^0|h_a|g^0\rangle\langle g^0|R_\rho|g^0\rangle$$
$$+\langle g^0|R_\tau|g^0\rangle\langle g^0|h_a|r^0\rangle\langle r^0|R_\rho|g^0\rangle]. \quad (10)$$

In the above expression, all the terms have been multiplied by (-1). $(\alpha_{\rho\sigma}^a)'$ corresponds to the polarizability derivative $(\partial\alpha_{\rho\sigma}/\partial Q_a)_0$ in Placzek's theory and will hereafter be called the $\rho\sigma$-component of the Raman tensor for a normal vibration, a.

Electronic Wave Functions. One-electron wave functions, φ_n's, were obtained by the CNDO/2 method, an approximate self-consistent molecular orbital theory, proposed by Pople *et al.*[4] The wave function of the ground state, $|g^0\rangle$, was given by an antisymmetrized product with a closed-shell structure, Φ_0. The wave functions of the excited states, $|r^0\rangle$ and $|s^0\rangle$, in Eq. (10) were described by a linear combination of singly-excited configurations, $\Phi_{(i-k)}$'s.[15] By the use of the coefficients, $C_{(i-k)}^r$'s, of the configurations, the integrals in Eq. (10) could be rewritten as follows:

$$\langle g^0|H'|g^0\rangle=\langle\Phi_0|H'|\Phi_0\rangle, \quad (11)$$

$$\langle g^0|H'|r^0\rangle=\sum_i^{\text{occ}}\sum_k^{\text{unocc}}C_{(i-k)}^r\langle\Phi_0|H'|\Phi_{(i-k)}\rangle, \quad (12)$$

and

$$\langle r^0|H'|s^0\rangle = \sum_{i,j}^{occ}\sum_{k,l}^{unocc} C^r_{(i-k)}C^s_{(j-l)}\langle\Phi_{(i-k)}|H'|\Phi_{(j-l)}\rangle, \quad (13)$$

where H' denotes R_ρ, R_σ, or h_a. Since H' is defined as the sum of one-electron operators, $H'=\sum f$; the integrals on the right-hand sides of Eqs. (11)—(13) can thus be described by the integral terms with the one-electron wave functions:

$$\langle\Phi_0|H'|\Phi_0\rangle = 2\sum_n^{occ}\langle\varphi_n|f|\varphi_n\rangle, \quad (14)$$

$$\langle\Phi_0|H'|\Phi_{(i-k)}\rangle = \sqrt{2}\langle\varphi_i|f|\varphi_k\rangle, \quad (15)$$

and

$$\langle\Phi_{(i-k)}|H'|\Phi_{(j-l)}\rangle = \delta_{ij}\delta_{kl}\,2\sum_n^{occ}\langle\varphi_n|f|\varphi_n\rangle + \delta_{ij}\langle\varphi_k|f|\varphi_1\rangle - \delta_{kl}\langle\varphi_i|f|\varphi_j\rangle, \quad (16)$$

where the sums in the above equations go over the occupied orbitals in the ground state. When H' is R_ρ or R_σ, the integrals, $\langle\varphi_i|f|\varphi_k\rangle$'s, are calculated by the method described in a previous report.[16] When H' is h_a, the integrals are expressed as follows:[17]

$$\langle\varphi_i|f|\varphi_k\rangle = \sum_\beta\sum_\mu\sum_\nu e^2Z_\beta d_{i\mu}d_{k\nu}\left(\frac{\partial \boldsymbol{r}_\beta}{\partial Q_a}\right)\cdot\left\langle\chi_\mu\left|\frac{\boldsymbol{r}_{t\beta}}{r^3_{t\beta}}\right|\chi_\nu\right\rangle, \quad (17)$$

where e is the charge of the electron; Z_β is the core charge of the β atom; $\boldsymbol{r}_{t\beta}$ is the distance vector of the electron, t, from the β atom; $r_{t\beta}$ is the norm of the vector; $\boldsymbol{r}_\beta$ is the position vector of the β atom, and $d_{k\nu}$ is the coefficient of the atomic orbital, χ_ν, in the molecular orbital, φ_k. $(\partial\boldsymbol{r}_\beta/\partial Q_a)$ in Eq. (17) indicates the elements of the L_x matrix obtained by the usual **GF** method. In this work, the integrals on the right-hand side of Eq. (17) were calculated with the approximation that the integrals were neglected unless the atomic orbitals, χ_μ and χ_ν, belong to the same atom. This is consistent with the CNDO version used to obtain electronic wave functions. When χ_μ and χ_ν belong to an A atom which differs from the β atom, the integral is approximated by the following expression:

$$\left\langle\chi_\mu\left|\frac{\boldsymbol{r}_{t\beta}}{r^3_{t\beta}}\right|\chi_\nu\right\rangle = \delta_{\mu\nu}\frac{\boldsymbol{r}_{A\beta}}{r^3_{A\beta}}, \quad (18)$$

where $r_{A\beta}$ is the norm of the distance vector, $\boldsymbol{r}_{A\beta}$. When χ_μ and χ_ν belong to the β atom, the integration is performed rigorously.

Polarizability Method. According to Method I, described in a previous paper,[16] the polarizabilities were calculated for the molecule distorted in the manner dictated by the normal coordinate. The values of the Raman tensor were obtained by fitting the calculated polarizabilities to a cubic function with respect to the normal coordinate and by taking the first derivative at the equilibrium position.

Results and Discussions

In the calculations according to the vibronic method, the wavelength of the incident light was fixed at 5145 Å, which is the wavelength of an Ar^+ laser line, but in the calculation of the polarizabilities in the polarizability method, the energy of the incident light was taken to be zero.

Symmetric Stretching Vibrations: The symmetric stretching coordinates discussed in this work were the C–H and C–C vibrations of acetylene, ethylene, and ethane, the C–H vibration of methane, and the N–H vibration of ammonia. Since the Raman tensor with respect to symmetry coordinate, S_a's, were calculated with reference to the symmetric stretching modes, $(\partial\boldsymbol{r}_\beta/\partial Q_a)$ in Eq. (17) had to be replaced by $(\partial\boldsymbol{r}_\beta/\partial S_a)$, which was approximated as will be described below. For the C–H and N–H stretching modes, $(\partial\boldsymbol{r}_\beta/\partial S_a)$ was zero unless β denoted the hydrogen atom, while for C–C stretching modes $(\partial\boldsymbol{r}_\beta/\partial S_a)$ was zero unless β denoted the carbon atom. The vector $(\partial\boldsymbol{r}_\beta/\partial S_a)$ had a direction along the bond referring to the symmetry coordinate involving the displacement of the β atom.

The calculated results of $\bar{\alpha}_a'$ and $(\gamma_a')^2$ are listed in Table 1, where $\bar{\alpha}_a'=[(\partial\alpha_{xx}/\partial S_a)+(\partial\alpha_{yy}/\partial S_a)+(\partial\alpha_{zz}/\partial S_a)]/3$ and $(\gamma_a')^2=[\{(\partial\alpha_{xx}/\partial S_a)-(\partial\alpha_{yy}/\partial S_a)\}^2+\{(\partial\alpha_{yy}/\partial S_a)-(\partial\alpha_{zz}/\partial S_a)\}^2+\{(\partial\alpha_{zz}/\partial S_a)-(\partial\alpha_{xx}/\partial S_a)\}^2+6\{(\partial\alpha_{xy}/\partial S_a)^2+(\partial\alpha_{yz}/\partial S_a)^2+(\partial\alpha_{zx}/\partial S_a)^2\}]/2$. In the table, the calculated results in the polarizability method and the experimental results are also given. It is found that the values of $\bar{\alpha}'$ calculated by the vibronic method are 2—6 times larger than the experimental ones. The values in the parentheses in Table 1 are those obtained by the calculation using only the term A in Eq. (6). It is indicated that the Raman tensor for the symmetric stretching vibration is almost entirely explained by the term A. This fact supports the conclusion suggested by Verlan.[10] Practically,

Table 1. Trace terms, $\bar{\alpha}'$, and anisotropy terms, $(\gamma')^2$, of Raman tensor with respect to symmetry coordinates for symmetric stretching modes

Molecule		$\bar{\alpha}'$ [Å²] vib.[a]	$\bar{\alpha}'$ [Å²] pol.[a]	$\bar{\alpha}'$ [Å²] obsd.[b]	$(\gamma')^2$ [Å⁴] vib.[a]	$(\gamma')^2$ [Å⁴] pol.[a]
CH_4	S_{CH}	4.271(4.302)	0.876	2.08	0.0	0.0
C_2H_2	S_{CH}	4.707(4.716)	0.638	1.44	80.57	2.827
	S_{CC}	6.652(6.911)	1.655	2.94	159.8	14.23
C_2H_4	S_{CH}	13.36 (13.53)	1.243	2.08	431.1	3.242
	S_{CC}	10.47 (10.03)	1.130	1.89	314.7	18.76
C_2H_6	S_{CH}	13.87 (14.03)	1.373	2.65	0.006	0.656
	S_{CC}	7.628(7.965)	−0.362	0.92	0.883	0.809
NH_3	S_{NH}	5.198(5.375)	0.991		17.29	1.616

a) The abbreviations vib. and pol. mean vibronic and polarizability methods, respectively. b) From Ref. 18.

TABLE 2. L_x MATRIX ELEMENTS OF METHANE USED IN THE CALCULATION

		Equilibrium position of atom[a] [Å]	L_x matrix elements $\times N_0^{-1/2}$ [$g^{-1/2}$][b]			
			$Q_1(A_1)$	$Q_2(E)$	$Q_3(T_2)$	$Q_4(T_2)$
			(2919.4 cm^{-1})	(1548.1 cm^{-1})	(3015.9 cm^{-1})	(1319.2 cm^{-1})
C^1	x	0.0	0.0	0.0	0.03534	−0.01583
	y	0.0	0.0	0.0	0.02909	−0.07063
	z	0.0	0.0	0.0	−0.07493	0.08931
H^2	x	0.63104	0.28753	0.24678	0.22629	0.34453
	y	−0.63104	−0.28753	−0.15649	−0.21285	−0.07378
	z	0.63104	0.28753	−0.40327	0.20329	−0.16416
H^3	x	0.63104	0.28753	0.24678	−0.43682	−0.25022
	y	0.63104	0.28753	0.15649	−0.43812	0.01492
	z	−0.63104	−0.28753	0.40327	0.42857	−0.10529
H^4	x	−0.63104	−0.28753	−0.24678	−0.25135	0.01243
	y	0.63104	0.28753	0.15649	0.26479	0.40589
	z	0.63104	0.28753	−0.40327	0.24310	−0.36794
H^5	x	−0.63104	−0.28753	−0.24678	0.04082	0.08189
	y	−0.63104	−0.28753	−0.15649	0.03952	0.34703
	z	−0.63104	−0.28753	0.40327	0.01783	−0.42680

a) In molecule fixed coordinate. b) N_0 is the Avogadro number.

the calculated values of the terms B and C were very small.

The anisotropy term $(\gamma_a')^2$ is an effective factor for the theoretical calculation of a Raman intensity and is closely related to the depolarization ratio, ρ_n; $\rho_n = 6(\gamma_a')^2/[45(\bar{\alpha}_a')^2+7(\gamma_a')^2]$. In comparing the values of ρ_n calculated from the Raman tensor with respect to the symmetry coordinates, it is found that the values of ρ_n obtained from the vibronic method are smaller than those obtained from the polarizability method, with the exception of the C–H stretching in ethylene. In order to discuss the magnitude of $(\gamma_a')^2$ relative to the values of $\bar{\alpha}_a'$ in the calculated results, these values were compared with the experimental results. From the measurement by Schrötter and Bernstein,[18] the depolarization ratios of the Raman spectrum of acetylene are 0.27 and 0.06 for the C–H and C–C stretching vibrations respectively. The corresponding values are 0.310 and 0.308 in the vibronic method, and 0.445 and 0.383 in the polarizability method. It may be said that the theoretical calculations lead to an overestimation of the anisotropy terms in comparison with the magnitudes of $\bar{\alpha}'$.

Normal Vibrations of Methane: The normal modes were obtained by the usual **GF** method, using the **F** matrix reported by Shimanouchi *et al.*[19] The L_x matrix elements used in the calculations are given in Table 2. The calculated results of the Raman intensities, I/I_0, and the depolarization ratios, ρ_n, are listed in Table 3. In the table, the results calculated by the polarizability method and the experimental results are also listed. At a glance it may be seen that the results of the vibronic method show an entirely different tendency with respect to the relative intensities in comparison with the results calculated from the polarizability method. In the results of the vibronic method, the Raman intensity of the ν_1 vibration is strong, while those of the other vibrations are nearly equal to zero. In the results of the polarizability method, however, the Raman intensity of the ν_2 vibration is larger than that of the ν_1 vibration. In the experiments[20–22] a ν_1 vibration with a very strong intensity and ν_2 and ν_3 vibrations with weak intensities are observed. Moreover, for the depolarization ratio of the ν_2 vibration the two methods give different values. The values of the elements of the Raman tensors calculated in the vibronic method are listed in Table 4. The values for the ν_2 vibration are very small; they may be regarded as zero in comparison with those for the other vibrations. For the ν_3 and ν_4 vibrations, the values of the diagonal elements are zero. However the values from the terms A and B are not zero, and the absolute value of one element, for example $(\alpha_{xx})'$, from the term A is equal to that of the corresponding element from the term B, and their signs are opposite. The values of the $\bar{\alpha}'$ calculated by the use of only the term A or the term B are zero. Then, the depolarization ratio calculated by the use of one term, A, B, or C, is the same value, 0.857, as that calculated with the total values of the elements. This is not the case for the ν_2 vibration. The Raman tensors calculated in the polarizability method are shown in Table 5. The values of the three diagonal elements of the Raman tensor for the

TABLE 3. RAMAN INTENSITIES AND DEPOLARIZATION RATIOS OF STOKES LINES OF METHANE

	$I/I_0 \times 10^{30}$ [cm^2]			ρ_n	
	vib.[a]	pol.[a]	obsd.[b]	vib.[a]	pol.[a]
ν_1	101.4	4.260	vs	0	0
ν_2	0.000	12.68	w	0.015	0.857
ν_3	0.021	3.881	w	0.857	0.857
ν_4	0.124	0.116		0.857	0.857

a) See footnote a in Table 1. b) From Refs. 20—22.

TABLE 4. RAMAN TENSORS OF METHANE CALCULATED BY THE VIBRONIC METHOD $(\alpha^{\alpha}_{\rho\sigma})' \times 10^4$ [cm^2 g$^{-1/2}$]

		Term A[a]	Term B[a]	Term C[a]	Total[b]
$\nu_1(A_1)$	$(\alpha_{xx})'$	−3.326	−0.0051	0.0289	−3.302
	$(\alpha_{yy})'$	−3.326	−0.0051	0.0289	−3.302
	$(\alpha_{zz})'$	−3.326	−0.0051	0.0289	−3.302
	$(\alpha_{xy})'=(\alpha_{yx})'$	0.0	0.0	0.0	0.0
	$(\alpha_{xz})'=(\alpha_{zx})'$	0.0	0.0	0.0	0.0
	$(\alpha_{yz})'=(\alpha_{zy})'$	0.0	0.0	0.0	0.0
$\nu_2(E)$	$(\alpha_{xx})'$	0.1198×10^{-6}	0.0057×10^{-6}	-0.0011×10^{-6}	0.1244×10^{-6}
	$(\alpha_{yy})'$	0.1252×10^{-6}	0.0003×10^{-6}	-0.0011×10^{-6}	0.1244×10^{-6}
	$(\alpha_{zz})'$	0.1310×10^{-6}	-0.0055×10^{-6}	-0.0011×10^{-6}	0.1244×10^{-6}
	$(\alpha_{xy})'=(\alpha_{yx})'$	-0.0042×10^{-6}	0.0015×10^{-6}	-0.0161×10^{-6}	-0.0188×10^{-6}
	$(\alpha_{xz})'=(\alpha_{zx})'$	-0.0006×10^{-6}	-0.0006×10^{-6}	-0.0074×10^{-6}	-0.0086×10^{-6}
	$(\alpha_{yz})'=(\alpha_{zy})'$	0.0033×10^{-6}	-0.0016×10^{-6}	0.0105×10^{-6}	0.0122×10^{-6}
$\nu_3(T_2)$	$(\alpha_{xx})'$	−0.0311	0.0311	0.0	0.0000
	$(\alpha_{yy})'$	−0.0022	0.0022	0.0	0.0000
	$(\alpha_{zz})'$	0.0333	−0.0333	0.0	0.0000
	$(\alpha_{xy})'=(\alpha_{yx})'$	−0.0496	0.0333	0.0678	0.0515
	$(\alpha_{xz})'=(\alpha_{zx})'$	0.0123	−0.0059	−0.0263	−0.0199
	$(\alpha_{yz})'=(\alpha_{zy})'$	0.0069	0.0008	−0.0320	−0.0243
$\nu_4(T_2)$	$(\alpha_{xx})'$	0.0289	−0.0289	0.0	0.0000
	$(\alpha_{yy})'$	0.0007	−0.0007	0.0	0.0000
	$(\alpha_{zz})'$	−0.0296	0.0296	0.0	0.0000
	$(\alpha_{xy})'=(\alpha_{yx})'$	0.0669	−0.0474	−0.0808	−0.0613
	$(\alpha_{xz})'=(\alpha_{zx})'$	−0.0324	0.0170	0.0639	0.0485
	$(\alpha_{yz})'=(\alpha_{zy})'$	0.0156	−0.0191	0.0143	0.0108

a) See text. b) Sum of the terms A, B, and C.

TABLE 5. RAMAN TENSORS OF METHANE CALCULATED BY THE POLARIZABILITY METHOD $(\alpha^{\alpha}_{\rho\sigma})' \times 10^4$ [cm^2 g$^{-1/2}$]

	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(T_2)$	$\nu_4(T_2)$
$(\alpha_{xx})'$	0.6768	0.6233	0.0	0.0
$(\alpha_{yy})'$	0.6768	0.3927	0.0	0.0
$(\alpha_{zz})'$	0.6768	−1.0161	0.0	0.0
$(\alpha_{xy})'=(\alpha_{yx})'$	0.0	0.0	−0.6940	−0.0595
$(a_{xz})'=(\alpha_{zx})'$	0.0	0.0	0.2689	0.0470
$(\alpha_{yz})'=(\alpha_{zy})'$	0.0	0.0	0.3289	0.0106

ν_2 vibration are different from one another. This contradicts the conclusion obtained from the group-theoretical consideration, as indicated in the review by Loudon.[23]

In comparison with the experimental results, the results of methane calculated by the vibronic method will now be discussed in detail. Schrötter and Bernstein[18] determined the Raman intensity by the use of the rotational Raman line, $J=1\rightarrow3$, of hydrogen as the standard. From their experimental results, the Raman intensity of the ν_1 vibration is 23.6×10^{-30} cm^2, this value being, in magnitude, about one-fourth of the calculated result. Furthermore, the Raman line from the ν_2 and ν_3 vibrations are also observed to have weak intensities. However, Dickinson *et al.*[21] reported, from the experimental results, that the relative intensity of the ν_3 vibration is 5 in comparison with the value of 20 for the intensity of the ν_1 vibration. On the other hand, this calculation showed that the Raman intensity of ν_4 is stronger than those of the ν_2 and ν_3 vibrations, although their intensities are so small as to be unobserved. The experimental results for the ν_2 and ν_3 vibrations may be explained by a theoretical calculation involving factors which are not considered in this work.

Conclusions

For the symmetric stretching vibrations of several small molecules and the normal vibrations of methane, the theoretical calculations of Raman tensors were performed in the vibronic method. From the results, the following conclusions can be drawn:

(a) Verlan's conclusion that the intensity for symmetric stretching vibration is almost entirely contributed by the term A is confirmed.

(b) The calculated intensities for the symmetric stretching vibrations are large in comparison with the experimental values.

From a comparison of the results for the normal coordinates of methane in the vibronic method with those in the polarizability method:

(c) The vibronic method is more suitable for theoretical calculations of the Raman intensity than is the polarizability method.

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References

1) H. A. Kramers and W. Heisenberg, *Z. Phys.*, **31**, 681 (1925).

2) G. Placzek, "Handbuch der Radiologie," ed. by E. Marx, Akademische Verlagsgesellschaft, Leipzig, (1934), Vol. 6, Pt. 2.

3) J. O. Hirschfelder, *J. Chem. Phys.*, **3**, 555 (1935); W. Kolos and L. Eolniewicz, *ibid.*, **46**, 1426 (1967); R. P. Bell and D. A. Long, *Proc. Roy. Soc. Ser. A*, **203**, 364 (1950); E. Ishiguro, T. Arai, M. Mizushima, and M. Kotani, *Proc. Phys. Soc.* (London), **A65**, 178 (1952).

4) 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); J. A. Pople and G. A. Segal, *ibid.*, **44**, 3239 (1966).

5) N. S. Hush and M. L. Williams, *Theoret. Chim. Acta* (Berl.), **26**, 141 (1972).

6) H. Yamada, *Kwansei Gakuin Univ. Ann. Studies*, **21**, 95 (1972).

7) H. Shinoda and T. Miyazaki, *Chem. Lett.*, **1973**, 563.

8) A. C. Albrecht, *J. Chem. Phys.*, **34**, 1476 (1961).

9) F. A. Savin, *Opt. Spectry.*, **19**, 308,412 (1965); **20**, 549 (1966).

10) E. M. Verlan, *ibid.*, **20**, 341,447 (1966).

11) J. Tang and A. C. Albrecht, *J. Chem. Phys.*, **49**, 1144 (1968).

12) W. L. Peticolas, L. Nafie, P. Stein, and B. Fanconi, *ibid.*, **52**, 1576 (1970).

13) J. Tang and A. C. Albrecht, "Raman Spectroscopy," ed. by H. A. Szymanski, Vol. 2, Plenum Press, New York-London (1970), p. 33—68.

14) G. Herzberg and E. Teller, *Z. Phys. Chem.* (Leipzig), **B21**, 410 (1933); see also Ref. 17.

15) The notation $\Phi_{(i-k)}$ means the configuration χ_i^k as Murrell and McEwen's notation in *J. Chem. Phys.*, **25**, 1143 (1956).

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

17) J. N. Murrell and J. A. Pople, *Proc. Phys. Soc.*, **A69**, 245 (1956).

18) H. W. Schrötter and H. J. Bernstein, *J. Mol. Spectrosc.*, **12**, 1 (1964).

19) T. Shimanouchi, I. Nakagawa, J. Hiraishi, and M. Ishii, *ibid.*, **19**, 78 (1966).

20) G. E. MacWood and H. C. Urey, *J. Chem. Phys.*, **4**, 402 (1936).

21) R. G. Dickinson, R. T. Dillon, and F. Rosetti, *Phys. Rev.*, **34**, 582 (1928).

22) M. A. Thomas and H. L. Welsh, *Can. J. Phys.*, **38**, 1291 (1960).

23) R. Loudon, *Advan. Phys.*, **13**, 423 (1964).