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Theoretical Calculations of the Raman Intensities by the Vibronic Method. II. The In-plane Vibrations of Ethylene

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The values of the transition moment of Raman scattering have been calculated according to the formula derived from the vibronic method. The calculations have been performed for the in-plane vibrational modes of ethylene determined by three different sets of force constants. The electronic wave functions were calculated by the CNDO/2-CI method. From the relative Raman intensities of three A_{1g}-vibrations of ethylene in the respective cases, it was found that the Raman intensities are sensitive to the vibrational modes. Also, the Raman intensities of ethylene were calculated by the polarizability method in order to compare the results with those obtained from the vibronic method. From the results of these calculations, the conclusions of the previous work have been confirmed.

In a previous paper,[1)] which will hereafter be called Part I, the Raman intensities of the symmetric stretching vibrations of several small molecules and of the normal vibrations of methane were calculated by means of the semi-empirical molecular orbital method.[2)] In Part I, the Raman intensities were calculated by two methods: the polarizability method and the vibronic method. In the polarizability method, 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 molecular position. In the vibronic method, the expression of the Raman tensor was derived from the Kramers-Heisenberg dispersion formula by applying the Herzberg-Teller expansion. The results calculated by the two methods were compared with each other, and it was concluded that the vibronic method is more suitable for the theoretical calculation of the Raman intensity than is the other one.

The polarizability derivatives for small polyatomic molecules have been calculated by several investigators[3)] by means of the semi-empirical molecular orbital technique. In all of those calculations, the vibrations of diatomic molecules or the symmetric stretching vibrations of some polyatomic molecules have been treated by means of the polarizability method. Moreover, Bleckmann[4)] recently calculated the Raman intensities of the normal vibrations of cyclopropenon by the polarizability method. In his work, the polarizabilities were evaluated by means of the finite perturbation technique using the CNDO/2 method.[2)] However, his results contradicted the observed ones because the calculated Raman intensities of some non-totally symmetric vibrations were stronger than those of the totally symmetric ones. He attributed the contradiction to the insufficiency of the method of calculation: when the z-axis has its direction perpendicular to the molecular plane, the zz-component of the Raman tensor for the in-plane vibrations of the planar molecules was always zero. Also, the result from the polarizability method in Part I was contradictory to the observed one; the calculated Raman intensity of the ν_2 vibration of methane was stronger than that of the ν_1 vibration, which is observed as the strongest Raman line. From these results (Ref. 4 and Part I), it may be considered that the polarizability method within the framework of the CNDO method leads to unsatisfactory results for the theoretical evaluation of Raman intensities.

In the present work, the Raman intensities of the in-plane vibrations of ethylene have been calculated by the vibronic method. It acquires additional interest from the fact that different kinds of sets of force constants of ethylene have been presented by various investigators.[5—7)] Therefore, three sets of force constants have been used in this calculation, and the influence of the different sets on the calculated values of the Raman intensity has been discussed. In order to confirm the conclusion in Part I, furthermore, the calculation has been repeated by the polarizability method.

Methods of Calculation

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, the intensity of the incident light; ω, the frequency of the scattered light; m, the initial state; n, the final state, and $(\alpha_{\rho\sigma})_{mn}$, the $\rho\sigma$-th component of the polarizability tensor for the $m\rightarrow n$ transition. The sum goes over $\rho=x,y,z$ and $\sigma=x,y,z$, which refer to the molecular fixed coordinate system. The final expression of $(\alpha_{\rho\sigma})_{mn}$ has been given as follows:[1,8)]

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

$$A=-\sum_a\sum_{r\neq g}\left[\frac{\langle g^\circ|R_\sigma|r^\circ\rangle\langle r^\circ|h_a|r^\circ\rangle\langle r^\circ|R_\rho|g^\circ\rangle}{(\varepsilon_r{}^\circ-\varepsilon_g{}^\circ-E_0)^2}+\frac{\langle g^\circ|R_\sigma|r^\circ\rangle\langle r^\circ|h_a|r^\circ\rangle\langle r^\circ|R_\rho|g^\circ\rangle}{(\varepsilon_r{}^\circ-\varepsilon_g{}^\circ+E_0)^2}\right]\langle\psi_m{}^g|Q_a|\psi_n{}^g\rangle, \tag{3}$$

$$B=-\sum_a\sum_r\sum_{s\neq r}\left[\frac{\langle g^\circ|R_\sigma|r^\circ\rangle\langle r^\circ|h_a|s^\circ\rangle\langle s^\circ|R_\rho|g^\circ\rangle}{(\varepsilon_r{}^\circ-\varepsilon_g{}^\circ-E_0)(\varepsilon_s{}^\circ-\varepsilon_g{}^\circ-E_0)}+\frac{\langle g^\circ|R_\rho|s^\circ\rangle\langle s^\circ|h_a|r^\circ\rangle\langle r^\circ|R_\sigma|g^\circ\rangle}{(\varepsilon_r{}^\circ-\varepsilon_g{}^\circ+E_0)(\varepsilon_s{}^\circ-\varepsilon_g{}^\circ+E_0)}\right]\langle\psi_m{}^g|Q_a|\psi_n{}^g\rangle, \tag{4}$$

and

$$C=-\sum_a\sum_{r\neq g}\sum_{s\neq g}\left[\frac{\langle g^\circ|h_a|s^\circ\rangle\langle s^\circ|R_\sigma|r^\circ\rangle\langle r^\circ|R_\rho|g^\circ\rangle}{(\varepsilon_r{}^\circ-\varepsilon_g{}^\circ-E_0)(\varepsilon_s{}^\circ-\varepsilon_g{}^\circ)}+\frac{\langle g^\circ|h_a|s^\circ\rangle\langle s^\circ|R_\rho|r^\circ\rangle\langle r^\circ|R_\sigma|g^\circ\rangle}{(\varepsilon_r{}^\circ-\varepsilon_g{}^\circ+E_0)(\varepsilon_s{}^\circ-\varepsilon_g{}^\circ)}\right.$$

$$+\frac{\langle g^\circ|R_\sigma|r^\circ\rangle\langle r^\circ|R_\rho|s^\circ\rangle\langle s^\circ|h_a|g^\circ\rangle}{(\varepsilon_r{}^\circ-\varepsilon_g{}^\circ-E_0)(\varepsilon_s{}^\circ-\varepsilon_g{}^\circ)}$$

$$+\left.\frac{\langle g^\circ|R_\rho|r^\circ\rangle\langle r^\circ|R_\sigma|s^\circ\rangle\langle s^\circ|h_a|g^\circ\rangle}{(\varepsilon_r{}^\circ-\varepsilon_g{}^\circ+E_0)(\varepsilon_s{}^\circ-\varepsilon_g{}^\circ)}\right]\langle\psi_m{}^g|Q_a|\psi_n{}^g\rangle, \qquad (5)$$

where the superscript o denotes the equilibrium nuclear position in the electronic ground state; $|g^\circ\rangle$ is the electronic ground state, and $|r^\circ\rangle$ and $|s^\circ\rangle$ are the electronic excited states; $\varepsilon_g{}^\circ$, $\varepsilon_r{}^\circ$, and $\varepsilon_s{}^\circ$ are the energies of $|g^\circ\rangle$, $|r^\circ\rangle$, and $|s^\circ\rangle$ respectively; E_0 is the energy of the incident light; $|\psi_m{}^g\rangle$ and $|\psi_n{}^g\rangle$ are the wave functions of the m-th and n-th vibrational states respectively in the electronic ground state; Q_a is the normal coordinate of the a vibrational mode; R_ρ and R_σ are the operators of the ρ- and σ-components respectively of the electronic dipole operator, and $h_a=(\partial H/\partial Q_a)$, the first-order vibronic coupling operator introduced initially by Herzberg and Teller.[9] The Raman tensor for the a normal vibration, $(\alpha^a_{\rho\sigma})'$, can be defined by the following equation:

$$(\alpha_{\rho\sigma})_{mn} = \sum_a (\alpha^a_{\rho\sigma})' \langle\psi_m{}^g|Q_a|\psi_n{}^g\rangle \qquad (6)$$

The wave functions of the electronic states and the molecular integrals appearing in the above expressions were calculated by the methods described in Part I.

The different sets of the force constants of ethylene used in the calculation will now be described. The first set, which will be called Set 0 for convenience, consists of the modified Urey-Bradley force constants offered by Scherer and Overend.[6] This set is a modification of the simplified Urey-Bradley force field obtained by adding the *trans*-interaction, so called by them; it may be the most reliable set because the transferability of their set of force constants was successful in discussing the experimental results of several bromoethylenes. The second and third sets of the force constants used in this work were Proposed by Crawford *et al.*;[7] these sets will be called Set I and II below. There are differences in their force constants with respect to the symmetry coordinates of the A_{1g} symmetry species. In the calculation with Set 0, the equilibrium configuration of ethylene followed the data in Ref. 6, while in the calculations with Sets I and II it followed the data in Ref. 7.

Results and Discussion

In the calculations, the wavelength of the incident light was fixed at 5145 Å, the wavelength of an Ar^+ laser line. Five Raman-active in-plane vibrations, which include three vibrations of A_{1g} symmetry species and two of B_{1g}, will be discussed. The other vibrations will be omitted from the discussion because the values of their calculated Raman intensities were practically equal to zero. The vibrational modes obtained by the usual **GF** method with Sets 0, I, and II of the force constants are shown in Figs. 1—3 respectively.

In this work, the differential cross section, $(d\sigma/d\Omega)_{//}$, instead of the total cross section has been calculated because there are the experimental results of $(d\sigma/d\Omega)_{//}$ which can be used in the discussion. $(d\sigma/d\Omega)_{//}$ is expressed as follows:

$$(d\sigma/d\Omega)_{//} = \frac{\omega^4}{c^4}\langle\psi_m{}^g|Q_a|\psi_n{}^g\rangle^2\left\{(\bar{\alpha}_a{}')^2+\frac{4}{45}(\gamma_a{}')^2\right\}, \qquad (7)$$

where $\bar{\alpha}_a{}'$ and $\gamma_a{}'$ are the mean part and the anisotropy part of the Raman tensor of the a normal vibration. The values of the $(d\sigma/d\Omega)_{//}$ caluculated by the vibronic method with Sets 0, I, and II are shown in Table 1; the experimental results are also included. The calculated values of the $(d\sigma/d\Omega)_{//}$ for the A_{1g}-vibrations are larger than the experimental ones. The cause of the overestimations in the calculated results will be discussed later on the basis of the results shown in Table 3. The rela-

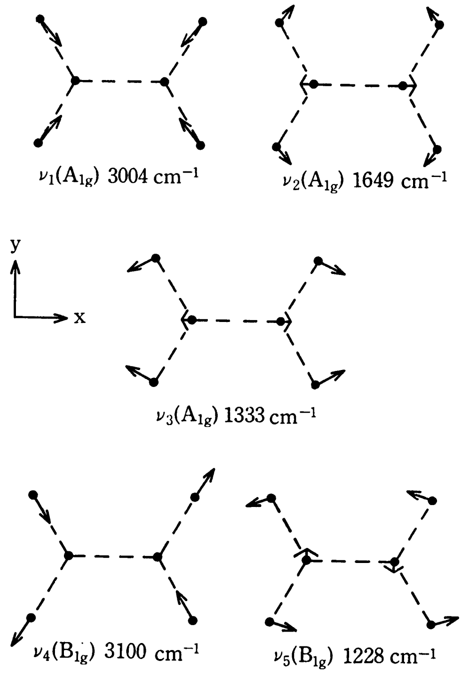


Fig. 1. Vibrational modes of ethylene obtained from the **GF** calculation with the force constants of Set 0.

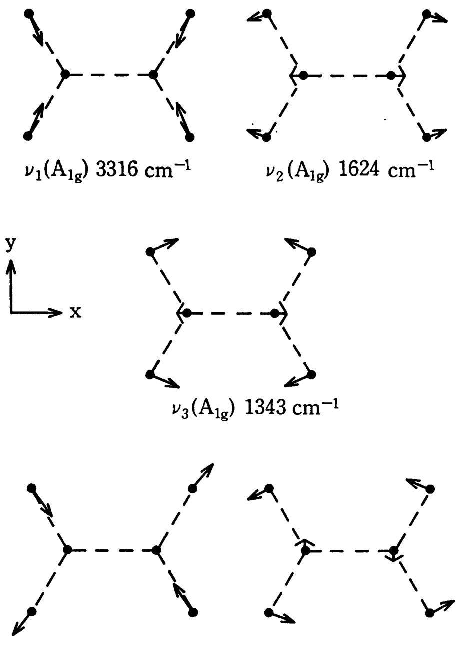
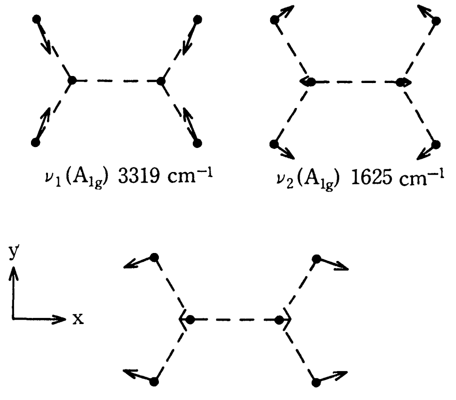


Fig. 2. Vibrational modes of ethylene obtained from the **GF** calculation with the force constants of Set I.



$\nu_1(A_{1g})$ 3319 cm^{-1} $\nu_2(A_{1g})$ 1625 cm^{-1}

$\nu_3(A_{1g})$ 1341 cm^{-1}

Fig. 3. Vibrational modes of ethylene obtained from the **GF** calculation with the force constants of Set II; ν_4 and ν_5 are the same as those in Fig. 2.

TABLE 1. THE RAMAN INTENSITY OF ETHYLENE CALCULATED BY THE VIBRONIC METHOD

	$(d\sigma/d\Omega)_{//}\times 10^{30}$[cm^2]					
	Calcd			Obsd		
	Set 0	Set I	Set II	Ref. 10	Ref. 11	Ref. 12
$\nu_1(A_{1g})$	110.1	91.4	91.7	15[a)]		vs
$\nu_2(A_{1g})$	58.9	126.9	39.1	5.6[a)]	10.6[a,b)] 0.74[b,c)]	vs
$\nu_3(A_{1g})$	69.4	20.2	114.6	9.0[a)]		vs
$\nu_4(B_{1g})$	0.0009	0.0003[d)]				s
$\nu_5(B_{1g})$	0.0607	0.0698[d)]				w

a) The wavelength of the incident light is 3371 Å.
b) The values correspond to $(d\sigma/d\Omega)$ which expresses as $(\omega^4/c^4)\langle\psi_m{}^g|Q_a|\psi_n{}^g\rangle^2\{(\bar{\alpha}_a{}')^2+(7/45)(\gamma_a{}')^2\}$.
c) The wavelength of the incident light is 5145 Å.
d) The values are common for Set I and Set II.

tive Raman intensities among the A_{1g}-vibrations calculated with one set of force constants are different from those with another set. The results calculated with Set 0 appear to be in good agreement with the ones observed by Shimizu *et al.*[10)] The results from Sets I and II differ from the experimental ones in the order of the intensities. If the suitabilities of Set I and Set II are compared with each other after the manner of the discussion by Crawford *et al.*, it appears, from the calculated Raman intensities, that Set II is appropriate to the force constants of ethylene, although Crawford *et al.* pointed out that Set I is more correct than Set II in view of the constancy of the C=C frequency of olefins. The reason for the situation in the present work is found partly in the similarity of the vibrational modes decided from Sets 0 and II (see Figs. 1 and 3).

In an effort to discuss the importance of the *trans*-interaction introduced to Set 0 of the force constants, $(d\sigma/d\Omega)_{//}$ value swere calculated while neglecting the *trans*-interaction term. The calculated values of the ν_1, ν_2, and ν_3 vibrations are 0.111×10^{-27}, 0.661×10^{-28}, and 0.593×10^{-28} cm^2 respectively. The relative intensities among them are less in agreement with the observed ones than with the results obtained with the original set including the *trans*-interaction term. The results show that the introduction of the *trans*-interaction to the set of force constants is very meaningful.

In the measurement of the Raman intensities, by Blumenfeld *et al.*,[12)] for the ν_4 and ν_5 vibrations with B_{1g} symmetry species, the former was observed with a strong intensity and the latter, with a very weak one, although the assignment of the latter was somewhat uncertain. However, both the calculated intensities for these Raman lines are very weak and the intensity of the ν_4 vibration is weaker than that of the ν_5 vibration. A similar situation for the non-totally symmetric vibrations was obtained in the treatment for methane in Part I. The calculated Raman intensity of the ν_2 vibration is very weak, less than those of the ν_3 and ν_4 vibrations; this contradicts the observed result. It will be shown in a future paper that the 2p-orbitals of the hydrogen atom play an important role in the theoretical calculation of the Raman intensities for these non-totally symmetric vibrations.

The calculated values of the depolarization ratios,

TABLE 2. THE DEPOLARIZATION RATIO, ρ_n, OF ETHYLENE CALCULATED BY THE VIBRONIC METHOD

	Set 0	Set I	Set II
$\nu_1(A_{1g})$	0.236	0.239	0.239
$\nu_2(A_{1g})$	0.223	0.230	0.224
$\nu_3(A_{1g})$	0.225	0.197	0.228
$\nu_4(B_{1g})$	0.857	0.857[a)]	
$\nu_5(B_{1g})$	0.857	0.857[a)]	

a) The values are common for Set I and Set II.

TABLE 3. RAMAN TENSORS OF ETHYLENE CALCULATED BY THE VIBRONIC METHOD WITH SET 0, $(\alpha^{a}_{\rho\sigma})'\times10^4$[cm^{2}g$^{-1/2}$]

	Term A[a)]	Term B[a)]	Term C[a)]	Total[b)]
$\nu_1(A_{1g})$				
$(\alpha_{xx})'$	−18.77	0.0105	0.0644	−18.70
$(\alpha_{yy})'$	−6.568	0.2335	0.1698	−6.165
$(\alpha_{zz})'$	−2.893	0.0	0.0	−2.893
$(\alpha_{xy})'=(\alpha_{yx})'$	0.0	0.0	0.0	0.0
$\nu_2(A_{1g})$				
$(\alpha_{xx})'$	−8.465	−0.1099	0.0610	−8.514
$(\alpha_{yy})'$	−2.814	−0.2899	0.0707	−3.033
$(\alpha_{zz})'$	−1.373	0.0	0.0	−1.373
$(\alpha_{xy})'=(\alpha_{yx})'$	0.0	0.0	0.0	0.0
$\nu_3(A_{1g})$				
$(\alpha_{xx})'$	−8.004	−0.0888	0.0552	−8.038
$(\alpha_{yy})'$	−2.684	−0.2169	0.0717	−2.829
$(\alpha_{zz})'$	−1.287	0.0	0.0	−1.287
$(\alpha_{xy})'=(\alpha_{yx})'$	0.0	0.0	0.0	0.0
$\nu_4(B_{1g})$				
$(\alpha_{xx})'$	0.0	0.0	0.0	0.0
$(\alpha_{yy})'$	0.0	0.0	0.0	0.0
$(\alpha_{zz})'$	0.0	0.0	0.0	0.0
$(\alpha_{xy})'=(\alpha_{yx})'$	0.0	0.0413	−0.0993	−0.0580
$\nu_5(B_{1g})$				
$(\alpha_{xx})'$	0.0	0.0	0.0	0.0
$(\alpha_{yy})'$	0.0	0.0	0.0	0.0
$(\alpha_{zz})'$	0.0	0.0	0.0	0.0
$(\alpha_{xy})'=(\alpha_{yx})'$	0.0	0.0536	−0.2952	−0.2416

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

ρ_n, are shown in Table 2. The values calculated with the different sets of force constants are similar to each other. The calculated values for the A_{1g}-vibrations are all about 0.23, with the one exception of 0.197, while those for the B_{1g}-vibrations are 0.857, this value being expected in view of the group theory.

The values of the elements of the Raman tensors calculated with the force constants of Set 0 are shown in Table 3. From these values, the effective terms in the theoretical calculation of the Raman intensities can be discussed. For the A_{1g}-vibrations, the term A gives the main contribution to the intensities; no off-diagonal elements of the Raman tensor contribute to the intensities. Moreover, the mean part of the Raman tensor is more effective on the intensities of the A_{1g}-vibrations than is the anisotropy part, judging from the results on ρ_n shown in Table 2. Therefore, it can be said that the intensity of the A_{1g}-vibrations arises mainly from the mean part referring to the term A, $\bar{\alpha}_a'(A)$, which is written as followss

$$\begin{aligned}\bar{\alpha}_a'(A) &= \frac{1}{3}\sum_{\sigma}\sum_{r\neq g}\left[\frac{\langle g^\circ|R_\sigma|r^\circ\rangle\langle r^\circ|h_a|r^\circ\rangle\langle r^\circ|R_\sigma|g^\circ\rangle}{(\varepsilon_r{}^\circ-\varepsilon_g{}^\circ-E_0)^2}\right.\\ &\quad\left.+\frac{\langle g^\circ|R_\sigma|r^\circ\rangle\langle r^\circ|h_a|r^\circ\rangle\langle r^\circ|R_\sigma|g^\circ\rangle}{(\varepsilon_r{}^\circ-\varepsilon_g{}^\circ+E_0)^2}\right]\\ &= \frac{1}{3}\sum_{r\neq g}\left[\frac{1}{(\varepsilon_r{}^\circ-\varepsilon_g{}^\circ-E_0)^2}+\frac{1}{(\varepsilon_r{}^\circ-\varepsilon_g{}^\circ+E_0)^2}\right]\\ &\quad\times\frac{\langle r^\circ|h_a|r^\circ\rangle}{(\varepsilon_r{}^\circ-\varepsilon_g{}^\circ)}f_{rg},\end{aligned}$$

where f_{rg} is the oscillator strength of the electronic transition from the ground state to the r-th excited state. The value of f_{rg} calculated by the semi-empirical molecular orbital calculation is usually 2—3 times larger than the observed one.[13] This fact partly explains the overestimation of the $(d\sigma/d\Omega)_{//}$ of the A_{1g}-vibrations. In the calculated results for the non-totally symmetric vibrations, the contribution of the term C to the intensities is larger than that of the term B. This result is opposite to the usual conception that the contribution of the term C is small in comparison with that of the term B, because the energy separations between the electronic excited states appearing in the denominators of the term B are smaller than those between the electronic ground state and the excited states in the denominators of the term C. In the derivation of the terms B and C used in this work, there is only one approximation—the vibronic energy, E_{ri} in Eqs. 3 and 4 in Part I, is regarded as constant over the vibrational states. Therefore, if we want to determine the effective terms which contribute to the intensities of the non-totally symmetric vibrations, a theoretical calculation without the approximation described just above must be done.

The Raman intensities and the depolarization ratios of ethylene were calculated by the polarizability method with the force constants of Set 0 in order to compare these results with those obtained from the vibronic method. The polarizability method leads to undesirable results, as will be mentioned below (see Table 4). The intensity of the ν_4 vibration, the non-totally symmetric one, is stronger than that of the ν_2 vibration, the totally symmetric one. In the depolarization ratio, the value for the ν_3 vibration is larger than that generally found for the totally symmetric vibrations.

TABLE 4. RAMAN INTENSITIES, DEPOLARIZATION RATIOS, AND RAMAN TENSORS OF ETHYLENE CALCULATED BY THE POLARIZABILITY METHOD WITH SET 0

	$(d\sigma/d\Omega)_{//}$ $\times 10^{30}$ [cm^2]	ρ_n	$(\alpha_{\rho\sigma})'\times 10^4$[cm^2 g$^{-1/2}$]			
			$(\alpha_{xx})'$	$(\alpha_{yy})'$	$(\alpha_{zz})'$	$(\alpha_{xy})'=(\alpha_{yx})'$
$\nu_1(A_{1g})$	2.80	0.236	1.728	2.662	0.034	0.0
$\nu_2(A_{1g})$	0.345	0.194	0.049	0.573	0.381	0.0
$\nu_3(A_{1g})$	2.92	0.747	2.150	−0.917	0.007	0.0
$\nu_4(B_{1g})$	1.61	0.857	0.0	0.0	0.0	2.454
$\nu_5(B_{1g})$	0.0005	0.857	0.0	0.0	0.0	0.021

Conclusions

From the results in Tables 1—4, the following conclusions can be drawn;

(a) The conclusions in Part I are almost all confirmed in the present work.

(b) The Raman intensity calculated by the vibronic method is sensitive to the set of force constants used in the calculation.

(c) The *trans*-interaction in the modified Urey-Bradley force field introduced by Scherer and Overend plays an important role not only in the frequencies, but also in the Raman intensities.

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