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THEORETICAL CALCULATIONS OF MEAN POLARIZABILITY DERIVATIVES WITH RESPECT TO INTERNAL SYMMETRY COORDINATE

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The CNDO/2 calculation has been applied to the mean polarizability derivatives, $\alpha'(S_j)=\left(\frac{\partial \alpha}{\partial S_j}\right)_0$ and $\alpha''(S_j)=\left(\frac{\partial^2 \alpha}{\partial S_j^2}\right)_0$, where α is the mean polarizability and S_j an appropriate symmetry coordinate. The calculated (α')'s were proportional to the observed values. The α''/α' ratio increased with the energy-increase of the incident light.

The infrared absorption intensity of vibration band has been successfully discussed[1] by the dipole-moment derivatives, $\mu'=\left(\frac{\partial \mu}{\partial Q_j}\right)_0$ and $\mu''=\left(\frac{\partial^2 \mu}{\partial Q_j^2}\right)_0$, calculated by the CNDO/2 method,[2] where μ is the molecular dipole moment and Q_j an appropriate normal coordinate of molecular vibration. In the same way, it is interesting to discuss the intensity of Raman spectrum by the polarizability derivatives, $\alpha'=\left(\frac{\partial \alpha}{\partial Q_j}\right)_0$ and $\alpha''=\left(\frac{\partial^2 \alpha}{\partial Q_j^2}\right)_0$, calculated from the wave functions obtained by the CNDO/2 method. In a previous paper,[3] the approximate method of calculation for the molecular polarizability has been discussed in detail, this method being characterized by taking account of the energy of the incident light. Then, as the first step of this study, the polarizability derivatives calculated from this approximate method has been compared with those obtained from the experimental results. The bond polarizability derivatives calculated from the observed results for molecules by Schrötter and Bernstein[4] were available for the purpose of this work.

The molecular polarizabilities were calculated for the molecules distorted in the manner dictated by the symmetric stretching coordinate, S_j. The desired values were obtained by fitting the calculated polarizabilities to a cubic function with respect to the S_j coordinate and by taking the first and second derivatives at the equilibrium distance. The polarizability derivatives, α'(cal),

Table 1. Polarizability derivatives, α' and α''[a)]

Molecule		α'(cal) (Å^2)	α'(obs)[b)] (Å^2)	α''(cal) (Å)	$(\gamma')^2$ (Å^4)[c)]
CO_2		1.704		0.829	13.96
NH_3		0.991		0.953	1.616
CH_4		0.876	2.08	0.645	0.0
C_2H_2	S_{CH}	0.638	1.44	0.787	2.827
	S_{CC}	1.655	2.94	1.660	14.23
C_2H_4	S_{CH}	1.243	2.08	0.996	3.242
	S_{CC}	1.130	1.89	3.189	18.76
C_2H_6	S_{CH}	1.373	2.65	0.890	0.656
	S_{CC}	0.362[d)]	0.92	2.126	0.809

a) $\alpha' = \left(\frac{\partial \alpha}{\partial S_j}\right)_0$ and $\alpha'' = \left(\frac{\partial^2 \alpha}{\partial S_j^2}\right)_0$. Polarizabilities ($\alpha$) were calculated under the condition that the energy of incident light was equal to zero.

b) Calculated from bond polarizability derivatives reported in Ref. 4.

c) The anisotropy term. d) The absolute value of α'.

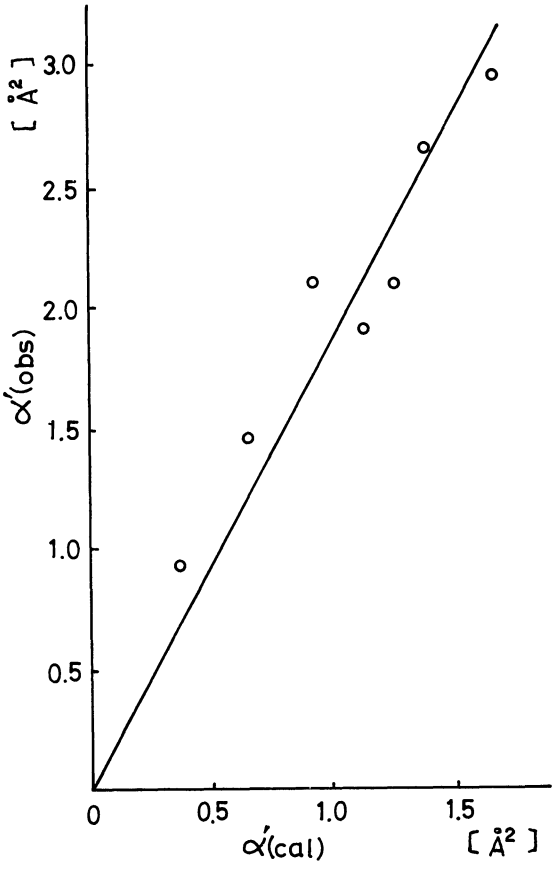

Fig. 1. The relation between α'(cal) and α'(obs)

obtained from this calculation are, in Table 1, listed and compared with those values, α'(obs), calculated from the bond polarizability derivatives estimated by Schrötter and Bernstein. As can be seen from Fig. 1, it has been recognized that α'(cal)'s are proportional to α'(obs)'s. The second derivatives of polarizability, α'', listed in Table 1 are important factors to discuss the Raman intensity referring to the first overtone. Generally, these values, α'', seem to be too small to bring about the Raman intensity of the first overtone equivalent to that of the fundamental. For the Raman intensity of the first overtone is affected by the integral $\langle \Psi_0 | Q^2 | \Psi_2 \rangle$ which is very small in comparison with the integral $\langle \Psi_0 | Q | \Psi_1 \rangle$ referring to the calculation of the

Table 2. Variations of polarizability derivatives with the energy of incident light, E_o.

	C_2H_2 (S_{CH})		C_2H_2 (S_{CC})	
E_o(eV)	α' (Å^2)	α'' (Å)	α' (Å^2)	α'' (Å)
2.0	0.647	0.805	1.685	1.681
4.0	0.676	0.864	1.782	1.915
6.0	0.730	0.978	1.969	2.326
8.0	0.822	1.187	2.305	3.163
10.0	0.985	1.596	2.938	5.077
12.0	1.343	2.684	4.381	11.04
13.0	1.789	4.416	6.072	20.90
14.0	3.195	12.31	10.57	62.57
14.5	5.796	34.07	17.57	169.1
15.0	19.04	230.3	49.11	1112
(15.540)[a]				

	C_2H_4 (S_{CH})		C_2H_4 (S_{CC})	
E_o (eV)	α' (Å^2)	α'' (Å)	α' (Å^2)	α'' (Å)
2.0	1.277	0.881	1.196	3.459
4.0	1.363	0.984	1.431	4.488
6.0	1.538	1.205	2.013	7.381
8.0	1.874	1.688	3.652	17.72
9.0	2.160	2.164	5.796	35.11
10.0	2.607	3.040	11.30	95.13
10.5	2.939	3.810	18.11	193.6
11.0	3.398	5.097	34.61	518.5
(12.190)[a]				

	C_2H_6 (S_{CH})		C_2H_6 (S_{CC})	
E_o (eV)	α' (Å^2)	α'' (Å)	α' (Å^2)	α'' (Å)
2.0	1.401	0.917	0.378	2.189
4.0	1.489	1.010	0.431	2.402
6.0	1.665	1.200	0.543	2.839
8.0	1.991	1.589	0.771	3.725
10.0	2.649	2.504	1.297	5.808
12.0	4.398	5.808	2.987	13.19
13.0	7.040	13.49	5.899	29.06
13.5	10.46	29.19	11.76	56.88
14.0	22.57	144.1	23.15	205.1
(14.530)[a]				

a) The lowest transition energy calculated by the CNDO/2-CI method.

Table 2. (continued)

	CH_4	
E_0(eV)	α' (Å^2)	α" (Å)
2.0	0.890	0.662
4.0	0.943	0.715
6.0	1.018	0.821
8.0	1.164	1.015
10.0	1.419	1.392
12.0	1.920	2.254
14.0	3.229	5.354
15.0	5.297	13.84
15.5	8.422	37.08
16.0	24.11	298.4
(16.466)[a]		

Raman intensity of the fundamental, where ψ_n is the wave function for the n-th state of the harmonic oscillator denoted by a normal coordinate Q. Also, the anisotropy terms, $(\gamma')^2$, which are effective factors for the theoretical calculation of the Raman intensity are listed in Table 1. These values which are used to calculate the depolarization ratio will be discussed in future study.

The variation of the polarizability derivatives, α' and α", with the energy-increase of the incident light have been calculated by the aid of the approximate method characterized in this work. The calculated α' and α" increased with the energy-increase of the incident light (see Table 2). These results explain the deviation of experimental results from the ν^4-law for the Raman intensity, the deviation being observed by Hoffman and Moser for CCl_4.[5] The closer the energy of the incident light to the transition energy for the lowest excited state, the greater the ratio α"/α'. These results of calculations suggest that the Raman line arising from the first overtone can be observed in the resonance and preresonance Raman measurements.

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