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Force Field of Allene

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The force constants based on the simple or modified Urey-Bradley, and the general force fields have been determined from the observed fundamental frequencies, Coriolis coupling constants and centrifugal distortion constants of allene C_3H_4, C_3D_4 and $C_3H_2D_2$ by the damped least-squares method. It is concluded that the simple or modified UBFF is not suitable for reproducing the observed data. In order to attain the best fit between the observed and calculated values, new bond-angle interaction constants q(CH, CCC) and q(CC, HCH) as well as the bond-bond and angle-angle interaction constants p and l should be added to the simple UBFF.

The intramolecular force field of an allene molecule is of interest in connection with the electronic structure of the adjacent double bond system in the molecule. Although there are many papers on the measurements and analysis of infrared or Raman spectra,[1-19] calculation of the force constants for the allene molecule has not yet been thoroughly accomplished.

Shuler and Fletcher[8] observed the infrared spectrum of allene-d_2 and calculated the force constants from the observed frequencies of allene-h_4 and -d_4 to support the assignment of the fundamental frequencies of allene-d_2. Sverdlov and Borisov[20,21] determined the force constants and calculated the normal frequencies allene-h_4, -d_1, -1,1-d_2, -1,3-d_2, -d_3 and -d_4 in order to to elucidate the peculiarity of the vibrational spectra of compounds with cumulated double bonds. Venkateswarlu and Pillai[22] determined the force constants from the observed Raman and infrared data, and compared these results with those of molecules having similar chemical bonds. Cyvin,[23] and Andersen *et al.*[24] determined the force constants in order to evaluate the mean amplitudes of vibration for allene-h_4, -d_1, -1,1-d_2, -1,3-d_2, -d_3, -d_4 and -t_4. Fletcher and Thompson[25] applied the Hybrid Orbital Force Fiele (HOFF) to the allene molecule, and determined the force constants from the vibrational frequencies and Coriolis coupling constants of allene-h_4, -d_4 and -1,1-d_2.

However, according to latest studies, some of the observed vibrational frequencies or Coriolis coupling constants used in these papers are proved to be based on erroneous assignment. Nemes *et al.*[26] determined the force constants from the observed data of the fundamental frequencies and the Coriolis zeta constants of allene-h_4, -d_4 and -d_2, but their analysis was made only on the E species vibrations of the allene molecule.

Very recently, the centrifugal distortion constants of allene-d_2 has been obtained from the analysis of microwave spectrum.[27] For allene-h_4 and -d_4, Maki and Toth[17] measured the vibration-rotation spectra with a high resolution, and obtained the values of D_J and D_{JK}. Inclusion of these centrifugal distortion constants into the calculation of the force constants will lead to a better determination of the force field of the allene molecule.

We have determined the force constants of the allene molecule in order to attain the best fit between the observed and calculated values of the thirty-seven fundamental frequencies, ten Coriolis coupling constants and five centrifugal distortion constants of allene-h_4, -d_4 and -1,1-d_2. From the values of the force constants based on the simple or modified Urey-Bradley, and the more general force field, the intramolecular force field of the allene molecule has been discussed in relation to the electronic structure of the adjacent double bond system in the molecule.

Calculation

The observed data of the fundamental frequencies, the Coriolis coupling constants and the centrifugal distortion constants of allene-h_4, -d_4, and -d_2 have been taken from the literature where the correct band assignment was made. Since the ν_7 and ν_{10} bands of allene-d_2 have not been observed in the spectra, their frequencies have roughly been estimated by the frequency product rule.[5,26] For the ν_{11} and ν_{15} bands of allene-d_2, the frequencies estimated from the combination bands have been adopted.[8]

In calculating the force constants from the observed data of the fundamental frequencies, the Coriolis coupling constants and the centrifugal distortion constants, the statistical weights for these data are of much significance in the least-squares determination. The final results are very sensitive to the allocation of the statistical weights for the observed data. We have taken the statistical weight of a given observed datum as the squared reciprocal of its experimental uncertainty, in accordance with Nemes *et al.*[26] and Aldous and Mills.[23]

For the experimental uncertainty of a fundamental frequency, 1% of the observed wave number has been taken, the vibrational anharmonicity or any resonance effect being taken into consideration. The value 0.02 has been taken for the uncertainty of a Coriolis coupling constant. The uncertainty of a centrifugal distortion constant has been taken from the experimental error given in the literature.[17,27] The uncertainty for the estimated vibrational frequencies of allene-d_2 (ν_7, ν_{10}, ν_{11} and ν_{15}) has been taken to be 15 cm^{-1} according to Nemes *et al.*[26] The observed data and their uncertainties used in the least squares calculation are summarized in Table 1.

The computation of normal frequencies by means of Wilson's GF matrix method and the refinement of force constants by the least squares method have been carried out using a FACOM Model 270-30 electronic computer system. The molecular structure parameters used in the computations are taken from the work of Maki and Toth[17] as follows: $r(\text{C–H})=1.087(\text{A})$, $R(\text{C=C})=1.308$, and $\angle\text{HCH}=118°10'$. The internal

TABLE 1(a). OBSERVED AND CALCULATED VALUES OF ALLENE-h_4

		Obsd	$\delta^{a)}$	Ref.$^{b)}$	UBFF		MUBFF		GFF	
					Calcd	$\Delta\nu^{c)}$	Calcd	$\Delta\nu^{c)}$	Calcd	$\Delta\nu^{c)}$
A_1	ν_1	3015	30	R.G. (12)	3020	−5	3016	−1	3017	−2
	ν_2	1443	14	R.G. (12)	1461	−18	1468	−26	1453	−10
	ν_3	1073	11	R.G. (12)	1048	25	1060	12	1081	−9
B_1	ν_4	865	9	R.L. (1)	867	−2	867	−2	867	−2
B_2	ν_5	3407	30	I.G. (17)	3020	−13	3012	−5	3016	−9
	ν_6	1957	20	I.G. (3)	1984	−27	1973	−16	1957	0
	ν_7	1398	14	I.G. (3)	1410	−12	1405	−7	1398	−0
E	ν_8	3486	31	I.G. (16)	3107	−21	3145	−20	3121	−36
	ν_9	999	10	I.G. (16)	1037	−38	1037	−38	994	5
	ν_{10}	841	8	I.G. (16)	801	40	801	40	846	−5
	ν_{11}	355	4	I.G. (16)	347	9	347	8	351	4
	ζ_8	0.002	0.02	I.G. (16)	0.001	0.001	0.001	0.001	−0.007	0.009
	ζ_9	0.137	0.02	I.G. (16)	0.251	−0.114	0.250	−0.113	0.169	−0.032
	ζ_{10}	0.017	0.02	I.G. (16)	−0.159	0.176	−0.157	0.174	−0.008	0.025
	ζ_{11}	0.814	0.02	I.G. (16)	0.877	−0.063	0.877	−0.063	0.816	−0.002
	$\lvert\zeta_{9,10}\rvert$	0.563	0.02	I.G. (16)	0.530	0.033	0.524	0.039	0.562	0.001
$D_J{}^{d)}$		0.116	0.02	I.G. (17)	0.090	0.026	0.088	0.028	0.084	0.032
$D_{JK}{}^{d)}$		4.60	1.8	I.G. (17)	4.29	0.31	4.34	0.26	5.14	−0.54

a) Experimental uncertainty. b) R: Raman, I: infrared, G: gas, L: liquid. c) Error (=Obsd−Calcd). d) In units of $10^{-6}\,\mathrm{cm}^{-1}$.

TABLE 1(b). OBSERVED AND CALCULATED VALUES OF ALLENE-d_4

		Obsd	δ	Ref.	UBFF		MUBFF		GFF	
					Calcd	$\Delta\nu$	Calcd	$\Delta\nu$	Calcd	$\Delta\nu$
A_1	ν_1	2195	22	R.L. (1)	2199	−5	2205	−10	2205	−10
	ν_2	1228	12	R.L. (1)	1216	12	1231	−3	1227	1
	ν_3	874	9	R.L. (1)	865	9	865	9	877	−3
B_1	ν_4	615	6	R.L. (1)	613	2	613	2	613	2
B_2	ν_5	2229	22	I.G. (17)	2217	12	2232	−3	2218	11
	ν_6	1920	19	I.G. (17)	1944	−24	1915	5	1917	3
	ν_7	1034	10	I.G. (3)	1029	6	1025	9	1019	15
E	ν_8	2330	23	I.G. (16)	2308	22	2309	21	2296	34
	ν_9	825	8	I.G. (16)	845	−21	845	−20	822	2
	ν_{10}	666	7	I.G. (16)	643	23	643	23	662	4
	ν_{11}	307	3	I.G. (16)	299	7	299	7	309	−3
	ζ_8	0.013	0.02	I.G. (16)	0.002	0.011	0.002	0.011	−0.014	0.027
	ζ_9	0.354	0.02	I.G. (16)	0.434	−0.080	0.432	−0.078	0.350	0.003
	ζ_{10}	−0.122	0.02	I.G. (16)	−0.276	0.154	−0.274	0.152	−0.086	−0.036
	ζ_{11}	0.707	0.02	I.G. (16)	0.791	−0.084	0.791	−0.084	0.702	0.005
	$\lvert\zeta_{9,10}\rvert$	0.534	0.02	I.G. (16)	0.448	0.086	0.442	0.092	0.521	0.014
D_J		0.041	0.02	I.G. (17)	0.055	−0.014	0.054	−0.013	0.052	−0.011
D_{JK}		—	—		2.42	—	2.44	—	2.82	—

coordinates and the symmetry coordinates of the allene molecules are given in Tables 2 and 3, respectively.

The force constants have been adjusted by the damped least-squares method by the equation

$$\Delta K = (\tilde{J}WJ)^{-1}\tilde{J}W\Delta\nu,$$

where J and W are the Jacobian and weight matrices, respectively, and ΔK and $\Delta\nu$(obsd−calcd) are the column matrices. The standard deviations of the force constants have been evaluated by the equations

$$\sigma(K) = (\sigma_1{}^2 + \sigma_2{}^2)^{1/2},$$

$$\sigma_1 = \left[\frac{N}{N-k}(\tilde{J}WJ)^{-1}\right]_{ii}^{1/2},$$

and

$$\sigma_2 = \left[\frac{N}{N-k}\widetilde{(\tilde{J}WJ)^{-1}(\tilde{J}W\Delta\nu)}(\tilde{J}W\Delta\nu)(\tilde{J}WJ)^{-1}\right]_{ii}^{1/2},$$

where N, k denote the numbers of the available observed data and the adjusted force constants, respectively.[29)]

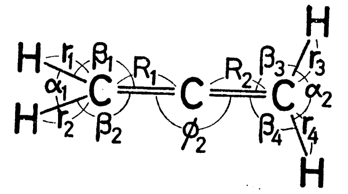
Table 1(c). Observed and calculated values of allene-d_2

		Obsd	δ	Ref.	UBFF		MUBFF		GFF	
					Calcd	$\Delta\nu$	Calcd	$\Delta\nu$	Calcd	$\Delta\nu$
A_1	ν_1	3013	30	I.G. (10)	3020	−7	3002	11	3017	−4
	ν_2	2227	22	I.G. (10)	2209	18	2212	14	2212	15
	ν_3	1940	19	I·G. (10)	1964	−24	1964	−24	1937	3
	ν_4	1418	14	I.G. (8)	1438	−20	1420	−2	1428	−10
	ν_5	1176	12	I.G. (8)	1158	18	1149	27	1171	5
	ν_6	924	9	R.L. (5)	918	6	933	−9	928	−4
A_2	ν_7	750	15	Est. (5)[a]	751	−1	751	−1	751	−1
B_1	ν_8	2318	23	I.G. (10)	2308	10	2309	9	2296	22
	ν_9	841	8	I.G. (15)	862	−21	862	−21	846	−5
	ν_{10}	812	15	Est. (26)[a]	776	36	776	36	822	−10
	ν_{11}	336	15	Est. (8)[b]	318	18	319	17	317	19
B_2	ν_{12}	3084	31	I.G. (10)	3107	−22	3105	−21	3121	−37
	ν_{13}	996	10	I.G. (16)	1036	−40	1036	−40	994	2
	ν_{14}	667	7	I.G. (16)	656	11	656	11	663	4
	ν_{15}	327	15	Est. (8)[b]	325	2	325	2	343	−16
D_J		0.080	0.01	Mw. (27)[c]	0.070	0.010	0.068	0.012	0.066	0.014
D_{JK}		4.33	0.17	Mw. (27)[c]	3.40	0.93	3.49	0.84	4.05	0.28

a) Estimated from the frequency product rule. c) Estimated from the combination bands. c) Microwave spectrum.

Table 2. Internal coordinates of allene

Symbol	Description
r_1, r_2, r_3, r_4	CH stretching
R_1, R_2	CC stretching
α_1, α_2	HCH scissoring
β_1, β_2, β_3, β_4	HCC bending (in-plane)
γ_1, γ_2	CH_2 wagging (out-of-plane)
ϕ_1, ϕ_2	CCC bending
τ	Torsion



Results and Discussion

First, in order to confirm the validity of the simple Urey-Bradley force field (UBFF),

$$2V = \sum K_i(\Delta r_i)^2 + \sum H_{ij}r_ir_j(\Delta\phi_{ij})^2 + 2\sum F'_{ij}q^\circ_{ij}(\Delta q_{ij})$$
$$+ \sum F_{ij}(\Delta q_{ij})^2 + \sum\pi(\Delta\gamma)^2 + Y(\Delta\tau)^2,$$

where K, H, F, π, Y are the stretching, bending, repulsive, out-of-plane bending, and torsional force constants, respectively, we determined these force constants by the least-squares method using the observed data. The converged values and their standard deviations of the UBFF force constants are given in Table 4. The calculated values of the normal frequencies, the Coriolis coupling constants and the centrifugal distortion constants of the allene molecules are given in Table 1 in comparison with the observed data.

Although the nine UBFF force constants were de-

Table 3. Symmetry coordinates of allene

h_4, d_4	A_1	S_1 : $(r_1+r_2+r_3+r_4)/2$	d_2	A_1	S_1' : S_1
		S_2 : $(2\alpha_1-\beta_1-\beta_2+2\alpha_2-\beta_3-\beta_4)/\sqrt{12}$			S_2' : S_2
		S_3 : $(R_1+R_2)/\sqrt{2}$			S_3' : S_3
	B_1	S_4 : τ			S_4' : S_5
	B_2	S_5 : $(r_1+r_2-r_3-r_4)/2$			S_5' : S_6
		S_6 : $(R_1-R_2)/\sqrt{2}$			S_6' : S_7
		S_7 : $(2\alpha_1-\beta_1-\beta_2-2\alpha_2+\beta_3+\beta_4)/\sqrt{12}$		A_2	S_7' : S_4
	E	S_8 : $(r_1-r_2)/\sqrt{2}$		B_1	S_8' : S_8
		S_9 : γ_2			S_9' : S_9
		S_{10} : $(\beta_1-\beta_2)/\sqrt{2}$			S_{10}' : S_{10}
		S_{11} : ϕ_1			S_{11}' : S_{11}
				B_2	S_{12}' : $(r_3-r_4)/\sqrt{2}$
					S_{13}' : γ_1
					S_{14}' : $(\beta_3-\beta_4)/\sqrt{2}$
					S_{15}' : ϕ_2

TABLE 4. CONVERGED VALUES AND STANDARD DEVIATIONS OF THE UBFF AND MUBFF FORCE CONSTANTS

	UBFF	MUBFF	From GFF
K(CH)$^{a)}$	4.77 (0.09)	4.81 (0.04)	4.21 (1.09)
K(CC)$^{a)}$	8.62 (0.26)	8.86 (0.29)	7.84 (0.65)
H(HCH)$^{a)}$	0.33 (0.03)	0.33 (0.03)	0.26 (0.25)
H(HCC)$^{a)}$	0.19 (0.04)	0.22 (0.05)	−0.03 (0.13)
H(CCC)$^{a)}$	0.27 (0.01)	0.27 (0.01)	0.31 (0.03)
F(HH)$^{a)}$	0.01 (0.07)	−0.01 (0.08)	0.23 (0.74)
F(HC)$^{a)}$	0.57 (0.12)	0 49 (0.13)	1.22 (0.42)
$\pi^{b)}$	0.04 (0.00)	0.04 (0.00)	0.05 (0.00)
$\mathrm{Y}^{b)}$	0.39 (0.01)	0.39 (0.01)	0.39 (0.01)
p(CH, CH)$^{a)}$		0.01 (0.07)	−0.25 (0.56)
p(CH, CC)$^{a)}$		−0.09 (0.07)	−0.53 (0.33)
p(CC, CC)$^{a)}$		0.24 (0.21)	0.45 (0.16)
l(HCC, CCC)$^{b)}$			−0.05 (0.02)
l(CCC, γ)$^{b)}$			0.05 (0.01)
q(CH, CCC)$^{c)}$			−0.22 (0.03)
q(CC, HCH)$^{c)}$			0.24 (0.17)

a) In units of mdyn/Å. b) In units of mdyn·Å. c) In units of mdyn.

termined (Table 4), the agreement between the observed and calculated values is not satisfactory as a whole. In particular, the disagreement in the normal frequencies ν_9 and ν_{10} of allene-h_4 and -d_4, ν_{13} and D_{JK} of allene-d_2, and the Coriolis coupling constants ζ_9, ζ_{10}, ζ_{11}, $|\zeta_{9,10}|$ is much larger than experimental uncertainty. The weighted sum of squared errors, a residual 389 in this case indicates the average difference between the observed and calculated values

$$\sqrt{389/52} = 2.7$$

is about three times larger than the experimental uncertainty. A disagreement to this extent cannot be ignored. Therefore, in order to reduce it, several other interaction force constants have been added to the above simple UBFF.

Shimanouchi[30] introduced several new interaction force constants for the purpose of revising the simple Urey-Bradley force field, and determined their values for various molecules:

$p : p(\Delta r_i)(\Delta r_j)$	bond-bond interaction (SiX_4)
$\rho : \rho(\Delta r_i)(\Delta r_j)$	resonance interaction (CO_3^{--})
$t : t(\Delta\phi_{ij})(\Delta\phi_{kl})$	trans interaction (CH_3CH_3)
$g : g(\Delta\phi_{ij})(\Delta\phi_{kl})$	gauche interaction (CH_3CH_3)
$l : l(\Delta\phi_{ij})(\Delta\phi_{ik})$	angle-angle interaction (CH_2X_2).

The bond-bond interaction force constants p(CH,CH), p(CH,CC), and, in particular, p(CC,CC) are considered to take important roles in the force field of the allene molecule. Thus we added the three force constants p to the UBFF, and determined the twelve MUBFF force constants by the least-squares method. Converged values are compared with those of the simple UBFF in Table 4, the calculated values of ν, ζ, D being given in Table 1.

Although the new interaction force constants p converged to have appreciable values (Table 4), the effect of introducing such force constants on the calculated values (Table 1) is not striking. The residual in this case is 376, and thus the average difference

$$\sqrt{376/52} = 2.7$$

is about three times larger than experimental uncertainty. This agreement is slightly better than in the case of the above simple UBFF. However, the disagreement cannot be overlooked, and the force field sould be improved.

For this purpose, we determined the force constants based on the more general force field (GFF), and transformed the converged values of the GFF force constants into the UBFF force constants. A modification of the Urey-Bradley force field was discussed.

The twenty-three force constants based on the general force field were adjusted by the least-squares method from the total fifty-two observed data. A refinement of all the GFF force constants led to large standard deviations for some force constants. Hence, in order to reduce them, and to determine individual force constants definitely, the number of adjusted force constants was reduced, on the assumption that interaction between non-adjacent bonds in the allene molecule can well be neglected.

Though the force constant $F(3,3)$ in the A_1 symmetry species of allene-h_4 or -d_4 still differs from $F(6,6)$ in B_2, the other five force constants in B_2 are equal to those in A_1, and the two force constants $F(8,9)$ and $F(9,10)$ in the E species are equal to zero. Thus the sixteen independent GFF force constants were adjusted by the least squares method from the observed ν, ζ, D data. The converged values and standard deviations of the GFF force constants are listed in Table 5.

The agreement between the observed and calculated values in this case is satisfactory as a whole. The residual is 34.1, hence the average difference between the observed and calculated values

$$\sqrt{34.1/52} = 0.81$$

is even smaller than experimental uncertainty. The disagreement between the observed and calculated

Table 5. Converged values and standard deviations of the GFF force constants

A_1	$F(1, 1)$[a]	5.13 (0.19)
	$F(2, 2)$[b]	0.44 (0.04)
	$F(3, 3)$[a]	10.20 (0.32)
	$F(1, 2)$[c]	−0.19 (0.37)
	$F(1, 3)$[a]	0.58 (0.42)
	$F(2, 3)$[c]	−0.24 (0.04)
B_1	$F(4, 4)$[a]	0.39 (0.01)
B_2	$F(5, 5)$[a]	5.13 (0.19)[d]
	$F(6, 6)$[a]	9.28 (0.19)
	$F(7, 7)$[b]	0.44 (0.04)[d]
	$F(5, 6)$[a]	0.58 (0.42)[d]
	$F(5, 7)$[c]	−0.19 (0.37)[d]
	$F(6, 7)$[c]	−0.24 (0.04)[d]
E	$F(8, 8)$[a]	5.28 (0.10)
	$F(9, 9)$[b]	0.05 (0.00)
	$F(10, 10)$[b]	0.51 (0.03)
	$F(11, 11)$[b]	0.41 (0.04)
	$F(8, 9)$[c]	0.00[d]
	$F(8, 10)$[c]	0.52 (0.20)
	$F(8, 11)$[c]	−0.31 (0.47)
	$F(9, 10)$[b]	0.00[d]
	$F(9, 11)$[b]	0.07 (0.01)
	$F(10, 11)$[b]	−0.06 (0.03)

a) In units of mdyn/Å. b) In units of mdyn·Å. c) In units of mdyn. d) See text.

values mentioned above in the case of UBFF and MUBFF is now well resolved in terms of the GFF force constants (Table 1). The agreement is satisfactory, and the GFF force constants (Table 5) are qualified as pertinent to the representation of the force field of the allene molecule.

They were thus converted into the UBFF force constants, and several interaction constants which should be added to the Urey-Bradley force field were determined. (See Table 4 for a comparison with force constants of UBFF and MUBFF). Some remarks are given concerning the results obtained for the MUBFF force constants derived from the GFF.

As new interaction force constants which should be added to the UBFF, in addition to the bond-bond interaction term p and the angle-angle interaction term l proposed by Shimanouchi, the necessity of introducing the bond-angle interaction term q should be stressed. The constant q(CC, HCH) is important for describing the normal frequencies of the A_1 and B_2 type vibrations.

The bond-angle interaction term q(CH,CCC) as well as the angle-angle interaction term l(HCC,CCC) and l(CCC,γ) are important for describing the normal frequencies and the Coriolis coupling constants of the E type vibrations. The necessity of introducing the term l was stressed by Shimanouchi for molecules such as methylene halides. The fact that the term l is also of significance in molecules containing double bonds such as allene is interesting in relation to the intramolecular force field.

The bond-bond interaction terms p(CH,CH), p(CH, CC) and p(CC,CC) suggest an electronic interaction between the bonds in the allene molecule. The strong electronic interaction between the adjacent double bonds in the allene molecule may give rise to the effectiveness of the value for p(CC,CC).

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References

1) R. C. Lord and J. Ocampo, *J. Chem. Phys.*, **19**, 260 (1951).
2) J. de Heer, *ibid.*, **20**, 637 (1952).
3) R. C. Lord and P. Venkateswarlu, *ibid.*, **20**, 1237 (1952)
4) K. N. Rao and E. D. Palik, *ibid.*, **23**, 2112 (1955).
5) J. C. Evans, J. K. Wilmshurst, and H. J. Bernstein, *Can. J. Chem.*, **34**, 1139 (1956).
6) J. Overend and H. W. Thompson, *Trans. Faraday Soc.*, **52**, 1295 (1956).
7) K. N. Rao and E. D. Palik, *J. Mol. Spectrosc.*, **1**, 24 (1957).
8) W. E. Shuler and W. H. Fletcher, *ibid.*, **1**, 95 (1957).
9) K. N. Rao, A. H. Nielsen, and W. H. Fletcher, *J. Chem. Phys.*, **26**, 1572 (1957).
10) D. R. Eaton and H. W. Thompson, *Proc. Roy. Soc., Ser. A*, **250**, 39 (1959).
11) J. Overend and B. Crawford Jr., *J. Chem. Phys.*, **29**, 1002 (1958).
12) S. Brodersen and E. H. Richardson, *J. Mol. Spectrosc.*, **4**, 439 (1960).
13) J. Blanc, C. Brecher, and R. S. Halford, *J. Chem. Phys.*, **36**, 2654 (1962).
14) I. M. Mills and J. L. Duncan, *J. Mol. Spectrosc.*, **9**, 244 (1962).
15) I. M. Mills, *Mol. Phys.*, **8**, 363 (1964).
16) I. M. Mills, W. L. Smith, and J. L. Duncan, *J. Mol. Spectrosc.*, **16**, 349 (1965).
17) A. G. Maki and R. A. Toth, *ibid.*, **17**, 136 (1965).
18) N. Van Thanh, *Ann. Phys. (Paris)*, **1967**, 241.
19) J. M. R. Stone, *J. Mol. Spectrosc.*, **38**, 503 (1971).
20) L. M. Sverdlov, *Opt. Spectrosc.*, **2**, 540 (1957).
21) L. M. Sverdlov and M. G. Borisov, *ibid.*, **9**, 227 (1961).
22) K. Venkateswarlu and M. G. K. Pillai, *Z. Phys. Chem.*, **18**, 396 (1958).
23) S. J. Cyvin, *J. Chem. Phys.*, **29**, 583 (1958).
24) B. Andersen, R. Sølevik, J. Brunvoll, S. J. Cyvin, and G. Hagen, *Acta Chem. Scand.*, **21**, 1759 (1967).
25) W. H. Fletcher and W. T. Thompson, *J. Mol. Spectrosc.*, **25**, 240 (1968).
26) L. Nemes, J. L. Duncan, and I. M. Mills, *Spectrochim. Acta*, **23A**, 1803 (1967).
27) E. Hirota and C. Matsumura, *J. Chem. Phys.*, **59**, 3038 (1973).
28) J. Aldous and I. M. Mills, *Spectrochim. Acta*, **18**, 1073 (1962).
29) T. Ogawa and T. Mayazawa, *ibid.*, **20**, 557 (1964).
30) T. Shimanouchi, *Pure Appl. Chem.*, **7**, 131 (1963).