The Microwave Spectrum of 3,3,3-Trifluoropropene

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The microwave spectra of normal, 2-^{13}C, and three monodeuterated isotopic species of 3,3,3-trifluoropropene have been studied. The combined structure of r_0 and r_s was obtained from the rotational constants observed. It has been necessary to take account of a tilt angle of the symmetry axis of the trifluoromethyl group. The following structural parameters have been determined: r(C–C)=1.489±0.002 Å, r(C=C)=1.312±0.010 Å, r(C–H_1)=1.085±0.011 Å, r(C–H_2)=1.092±0.009 Å, r(C–H_3)=1.109±0.003 Å, ∠F–C–F=106.8±0.3°, ∠C–C=C=124.8±0.4°, ∠C=C–H_1=120.6±1.0°, ∠C=C–H_2=122.8±1.0°, ∠C=C–H_3=121.2±1.0°, and θ_t=1.0±0.8° on the assumption that r(C–F)=1.345±0.003 Å, where θ_t denotes the tilt angle of the CF_3 top axis relative to the C–C bond away from the double bond of the vinyl group. The components of the electric dipole moment have been determined to be μ_a=2.331±0.014 D and μ_b=0.698±0.025 D; these values give a total dipole moment of 2.433±0.020 D at an angle of 7±1° with the symmetry axis of the trifluoromethyl group. The relative intensity between the rotational transitions in the ground state and in the first torsionally-excited state has been measured. The torsional frequency has been determined to be 88±25 cm^{-1}.

When a trifluoromethyl group, CF_3, is substituted in a molecule, a significant structural change can be expected because fluorine is the most electronegative element. There have been several studies of the structural determination of molecules containing the trifluoromethyl group by means of microwave spectroscopy or other methods. The results thus far have not, however, shown definitely the trend of the structural change upon trifluoromethyl substitution. Hilderbrandt *et al.*[1] studied hexafluoroacetone, hexafluoropropylimine, and hexafluoroisobutene by means of the electron-diffraction method and revealed that, upon fluorine substitution, the C-C bond length of the molecules studied increased, contrary to the trend previously observed in pairs of ethane[2] and 1,1,1-trifluoroethane,[3] ethylene[4] and 1,1-difluoroethylene,[5] and so on.

The real structural change upon fluorine substitution should be extractable from the accurately-determined structures of the fundamental and simplest molecules, in which such other effects as steric repulsion are not conspicuous. The pair of propene and 3,3,3-trifluoropropene is a good example for study. Recently, Tokue, Fukuyama and Kuchitsu[6] studied both the molecules by the electron-diffraction method. Making a joint analysis using the electron-diffraction intensities and the results of our microwave spectroscopic study which we will report in this paper, they determined the average structure of 3,3,3-trifluoropropene and found that the molecule follows the trend previously observed. The infrared spectrum of 3,3,3-trifluoropropene has been observed in the gas phase and assigned except for the torsional mode of the CF_3 top.[7] The dipole moment of this molecule in the gas phase was determined to be 2.45 D by the dielectric-constant method.[8]

In this paper we will report the microwave spectrum of 3,3,3-trifluoropropene, including one ^{13}C isotopic species and three monodeuterated species, and the determination of the molecular structural parameters, the dipole moment, the torsional frequency, and the barrier to internal rotation. While this work was in progress, Mukhtarov and Kuliev[9] reported the rotational constants of 3,3,3-trifluoropropene in the ground and torsionally-excited states, and its dipole moment.

Experimental

The spectra were observed with a conventional 110 KHz Stark-modulation spectrometer.[10] The measurements were carried out at the temperature of dry ice. The accuracy of the frequencies measured was estimated to be better than 0.1 MHz. Normal 3,3,3-trifluoropropene was obtained from the K & K Co. and was used without further purification. A mixture of three monodeuterated isotopic species was kindly provided by Y. Nakano. A deuterated sample was prepared by a hydrogen-exchange reaction of normal species with the deuterium gas on a powdered nickel catalyst. The product was purified by gas chromatography.

Microwave Spectrum

The spectra of the normal 3,3,3-trifluoropropene observed in the X to K bands consisted of a strong *a*-type *R*-branch and weak *b*-type *R*- and *Q*-branch transitions, characteristic of a nearly prolate symmetric top. Their assignment was made on the basis of the Stark effect on each transition. The weak *b*-type *R*-branch transitions were measured by means of a recorder. The frequencies of the observed transitions are listed in Table 1. The rotational constants of the normal species were determined by a least-squares fitting of the lowest fifteen transitions, as is shown in Table 4. The centrifugal distortion effect was discarded in the analysis, because only low-J transitions were measured.

The strong satellite lines in the vicinity of the ground-state transitions and showing similar Stark effect behavior were found at slightly higher frequencies with regularly varying intensities. These were assigned to the transitions in the first and second torsionally-excited states, since their intensities indicated that the states belong to the vibrations of very low frequencies which were not observed in the infrared spectrum.[7] The frequencies of the observed transitions are listed in Table 2. The rotational constants in the torsionally-excited states were obtained in the same way as those of the ground state. These results are also given in Table 4. The obtained B and C rotational constants in the ground and torsionally-excited states are nearly equal to those reported by Mukhtarov and Kuliev.[9]

Table 1. Rotational transitions of the normal 3,3,3-trifluoropropene in the ground state (MHz)

Transition	ν_{obsd}[a]	$\nu_{obsd}-\nu_{calcd}$[c]
a type		
$2_{12} \leftarrow 1_{11}$	11562.94	0.07
$2_{02} \leftarrow 1_{01}$	11631.77	0.04
$2_{11} \leftarrow 1_{10}$	11703.55	0.04
$3_{13} \leftarrow 2_{12}$	17343.50	0.10
$3_{03} \leftarrow 2_{02}$	17444.04	0.10
$3_{22} \leftarrow 2_{21}$	17449.58	−0.21
$3_{21} \leftarrow 2_{20}$	17455.55	−0.09
$3_{12} \leftarrow 2_{11}$	17554.30	−0.05
$4_{14} \leftarrow 3_{13}$	23122.87	−0.01
$4_{04} \leftarrow 3_{03}$	23251.87	0.08
$4_{23} \leftarrow 3_{22}$	23265.24	−0.01
$4_{32} \leftarrow 3_{31}$	23269.37[b]	0.11
$4_{31} \leftarrow 3_{30}$		0.00
$4_{22} \leftarrow 3_{21}$	23279.48	−0.36
$4_{13} \leftarrow 3_{12}$	23404.00	−0.05
b type[b]		
$1_{11} \leftarrow 0_{00}$	8315.90	0.09
$2_{02} \leftarrow 1_{01}$	9132.67	0.15
$2_{12} \leftarrow 1_{01}$	14062.10	0.02
$2_{20} \leftarrow 1_{11}$	19272.87	−0.06
$3_{13} \leftarrow 2_{02}$	19773.65	−0.11
$3_{21} \leftarrow 2_{12}$	25165.36	−0.33
$3_{31} \leftarrow 2_{20}$	30121.76	0.09
$3_{30} \leftarrow 2_{21}$	30122.54	−0.03

a) Accuracy better than ±0.1 MHz, unless otherwise indicated, b) ±0.2 MHz. c) Calculated frequencies were obtained using the rotational constants in Table 4.

Their values of the A rotational constants are quite different from ours. This difference is due to the fact that we have observed both the *a*- and *b*-type spectra in the ground and torsionally-excited states.

Though all three ^{13}C isotopically-substituted species were searched for in their natural abundances (1.1%), most of the lines were masked or disturbed by other strong lines. Only the *a*-type spectrum of the 2-^{13}C species was assigned and measured, as is shown in Table 3.

Table 2. Rotational transitions of the normal 3,3,3-trifluoropropene in the torsionally-excited states (MHz)

Transition	$v_t=1$		$v_t=2$	
	ν_{obsd}[a]	$\nu_{obsd}-\nu_{calcd}$[c]	ν_{obsd}[a]	$\nu_{obsd}-\nu_{calcd}$[c]
a type				
$2_{12} \leftarrow 1_{11}$			11610.53	0.17
$2_{02} \leftarrow 1_{01}$	11646.83	0.07	11661.91	0.12
$2_{11} \leftarrow 1_{01}$	11709.10	−0.20	11714.70	−0.15
$3_{13} \leftarrow 2_{12}$	17379.04	0.05	17414.83	−0.21
$3_{03} \leftarrow 2_{02}$	17467.44	0.10	17490.69	0.04
$3_{22} \leftarrow 2_{21}$	17471.72	−0.10	17493.83	−0.08
$3_{21} \leftarrow 2_{20}$	17476.25	−0.05	17497.01	−0.16
$3_{12} \leftarrow 2_{11}$	17563.22	−0.02	17571.72	−0.04
$4_{14} \leftarrow 3_{13}$	23170.83	0.12	23219.08	−0.04
$4_{04} \leftarrow 3_{03}$	23284.75	0.18	23317.22	0.13
$4_{23} \leftarrow 3_{22}$	23294.93	0.04	23324.55	−0.03
$4_{32} \leftarrow 3_{31}$	23297.58[b]	−0.38	23326.31[b]	−0.51
$4_{31} \leftarrow 3_{30}$		−0.46		−0.56
$4_{22} \leftarrow 3_{21}$	23305.77	−0.30	23332.57	−0.14
$4_{13} \leftarrow 3_{12}$	23416.29	−0.03	23428.01	−0.04
b type[b]				
$1_{11} \leftarrow 0_{00}$	8317.91	0.09	8319.97	0.19
$3_{03} \leftarrow 2_{12}$	15033.91	0.16	15053.86	0.25
$3_{13} \leftarrow 2_{02}$	19812.54	−0.03	19852.13	0.05
$3_{22} \leftarrow 2_{11}$	24953.36	−0.11	23959.34	0.00
$3_{21} \leftarrow 2_{12}$	25143.28	−0.06		
$3_{31} \leftarrow 2_{20}$	30094.48	0.12		
$3_{30} \leftarrow 2_{21}$	30095.50	0.00		

a) Accuracy better than ±0.1 MHz, unless otherwise indicated. b) ±0.2 MHz. c) Calculated frequencies were obtained using the rotational constants in Table 4.

There are three isotopic isomers of monodeuterated species. For the sake of simplicity, each isomer is designated by the number of the substituted atom, as given in Fig. 1. Also, only *a*-type *R*-branch transitions were observed for these species because of the low enrichment of the deuterium atom. The results are shown in Table 3. The rotational constants of the 2-^{13}C and monodeuterated species were determined

Table 3. Observed rotational transition of 2-^{13}C and monodeuterated 3,3,3-trifluropropene (MHz)[a,b,c]

Transition	2-^{13}C	D_1	D_2	D_3
$2_{12} \leftarrow 1_{11}$	11467.56(0.00)	11201.53(0.00)	10932.97(0.00)	11344.58(0.00)
$2_{02} \leftarrow 1_{01}$		11282.89(−0.09)		11457.62(−0.07)
$2_{11} \leftarrow 1_{10}$	11620.15(0.00)	11368.29(0.00)	11064.96(0.00)	11579.61(0.00)
$3_{13} \leftarrow 2_{12}$		16801.32(0.21)	16398.57(−0.15)	
$3_{03} \leftarrow 2_{02}$		16919.51(−0.14)	16493.70(0.00)	17175.54(0.00)
$3_{22} \leftarrow 2_{21}$		16927.42(0.05)		
$3_{21} \leftarrow 2_{20}$		16934.92(−0.17)		
$3_{12} \leftarrow 2_{11}$		17051.09(−0.13)	16596.99(0.30)	17366.99(0.33)
$4_{14} \leftarrow 3_{13}$	22931.53(0.31)			
$4_{32} \leftarrow 3_{31}$	23091.93(0.41)			
$4_{31} \leftarrow 3_{30}$	(0.22)			

a) Accuracy better than ±0.2 MHz. b) Designation of isotopic species is given in Fig. 1. c) Differences between observed and calculated frequencies are shown in parentheses after observed values. Calculated values were obtained using the rotational constants listed in Table 4.

Table 4. Rotational constants (MHz) and moments of inertia (amu Å^2)[a] for 3,3,3-trifluoropropene

	Normal	$v_t=1$	$v_t=2$	2-^{13}C
A	5442.67±0.10	5436.56±0.10	5430.25±0.10	5122 ±170
B	2943.47±0.03	2942.68±0.03	2941.77±0.03	2924.11±0.05
C	2873.14±0.03	2881.26±0.03	2889.53±0.03	2847.82±0.05
I_a	92.855±0.002	92.959±0.002	93.067±0.002	
I_b	171.695±0.002	171.740±0.002	171.793±0.002	172.831±0.003
I_c	175.897±0.002	175.401±0.002	174.899±0.002	177.461±0.003
ΔI[b]	88.653±0.005	89.298±0.005	89.961±0.005	

	D_1	D_2	D_3
A	5520 ±70	5500 ±140	5213 ±50
B	2862.92±0.05	2782.74±0.05	2924.28±0.05
C	2779.54±0.05	2716.74±0.05	2806.77±0.05
I_a			
I_b	176.525±0.003	181.611±0.003	172.821±0.003
I_c	181.820±0.003	186.023±0.003	180.056±0.003
ΔI[b]			

a) Conversion factor=505376 MHz amu Å^2. b) $\Delta I=I_a+I_b-I_c$.

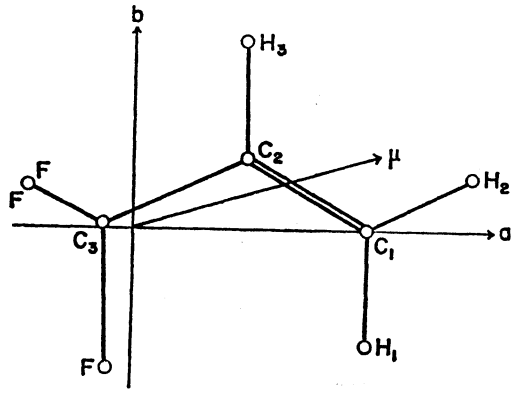

Fig. 1. Numbering of the hydrogen atoms in 3,3,3-trifluoropropene: the c principal axis is perpendicular to the paper.

from a few adequate transitions. The observed rotational constants and moments of intertia are given in Table 4. The large errors associated with the A rotational constants for the 2-^{13}C and monodeuterated species resulted from a lack of observation on b-type transitions.

Dipole Moment

The second-order Stark effect was measured for four transitions, as is shown in Table 5. The electrode spacing was calibrated using the $J=1\leftarrow0$ transition of OCS.[11] From the Stark coefficients, μ_a was determined to be 2.331±0.014 D, and μ_b, to be 0.698±0.025 D; these values gave a value of 2.433±0.020 D for the total dipole moment, where the error quoted was 2.5 times the standard deviation. The total dipole moment made an angle of 16°40′±40′ with the a principal axis. The orientation of the dipole moment relative to the molecular framework is not uniquely determined. It is reasonable to consider that the dipole moment

Table 5. Stark coefficients and dipole moment of 3,3,3-trifluoropropene

Transition	$\|M\|$	$\Delta\nu/E^2$[a] obsd	$\Delta\nu/E^2$[a] obsd−calcd
$2_{02}\leftarrow1_{01}$	0	-3.46_2	−0.015
	1	3.85_0	0.004
$2_{11}\leftarrow1_{10}$	0	2.98_1	0.009
$2_{12}\leftarrow1_{11}$	0	2.68_6	−0.023

$\mu_a=2.331\pm0.014$ D $\quad\mu_b=0.698\pm0.025$ D
$\mu_{total}=2.433\pm0.020$ D $\quad\angle\mu_{total}$ CF_3-axis=7±1°

a) Values in 10^{-5} MHz(V/cm)$^{-2}$

of 3,3,3-trifluoropropene is mainly made up of the group moment of the CF_3 top. The angle between the direction of μ_{total} and the symmetry axis of the CF_3 top was determined to be 7±1° on the basis of the structure determined in the following section. The dipole moment obtained in this study is in agreement with the value (μ=2.45 D) obtained by the dielectric-constant measurement.[8] Mukhtarov and Kuliev[9] gave slightly different values for the components of the dipole moment: $\mu_a=2.17\pm0.05$ D and $\mu_b=0.42\pm0.05$ D.

Molecular Structure

When the symmetry axis of the trifluoromethyl group is assumed to be colinear with the C–C single bond, there are eleven independent parameters specifying the structure of 3,3,3-trifluoropropene. As 2-^{13}C and three monodeuterated species were observed, the r_s coordinates of the center carbon atom and three hydrogen atoms were calculated to be as listed in Table 6. Three moments of inertia for the normal species are not enough to determine the remaining six parameters. We assume that the C–F bond distance is 1.345±0.003 Å,

Table 6. The r_s coordinates of atoms in 3,3,3-trifluoropropene (Å)

Atom	a_s	b_s
2-C	1.0655±0.0023	0.6605±0.0039
H_1	2.2022±0.0011	−1.0868±0.0025
H_2	3.1732±0.0007	0.4899±0.0056
H_3	1.0499±0.0023	1.7699±0.0015

the value obtained by the electron-diffraction method[6] and the most precise among the observed parameters. Moreover, we made full use of two moments of intertia for the 2-^{13}C species. Assuming the proper values for the parameters concerning three hydrogen atoms, four skeletal parameters, r(C–C), r(C=C), ∠F–C–F, and ∠C–C=C, were calculated by using three moments of inertia for the normal species and the I_b and I_c of the 2-^{13}C species. The results thus obtained were unreasonable, however, even if the effect of the zero-point vibrations was assumed to be rather large. It was found that five moments of inertia were never reconciled to the parameters of the vinyl group within any reasonable range, because the structure of the CF_3 group was strictly conditioned by the assumed value of the r(C–F) bond and the following equation;

$$\Delta I = I_a + I_b - I_c = 4m_F r_{CF}^2 \sin^2 \theta_{FCF}/2 + \Delta_0 \qquad (1)$$

This means that it is necessary to consider a relative configuration between the trifluoromethyl group and the vinyl group. Therefore, we recalculated the structure by taking account of the tilt of the symmetry axis of the trifluoromethyl group relative to the C–C single bond. About a one-degree tilt of the symmetry axis from the C–C single bond outward from the C–C=C angle was enough to explain five moments of inertia. The results are shown in Table 7. The remaining six parameters concerning the three hydrogen atoms were fitted to give their r_s coordinate as is given in Table 6. The obtained structural parameters are also shown in Table 7. The a and b coordinates of the C_2 atom in the molecular structure determined were calculated to be 1.0667 Å and 0.6613 Å respectively; these values were in agreement with the r_s coordinates given in Table 6.

Table 7. Molecular structure of 3,3,3-trifluoropropene

r(C–C)	1.489±0.002 Å
r(C=C)	1.312±0.010 Å
r(C–H_1)	1.085±0.011 Å
r(C–H_2)	1.092±0·009 Å
r(C–H_3)	1.109±0.003 Å
∠F–C–F	106.8±0.3°
∠C–C=C	124.8±0.4°
∠C=C–H_1	120.6±1.0°
∠C=C–H_2	122.8±1.0°
∠C=C–H_3	121.2±1.0°
θ_t[a]	1.0±0.8°
Assumed[b]	
r(C–F)	1.345±0.003 Å

a) For the defininition, see the text. b) Ref. 6.

Internal Rotation

No splitting due to internal rotation was observed in any of the spectral lines in the torsionally-excited states up to $v=2$. The frequency of the torsional vibration was obtained from the relative intensities of the transitions in the ground state and in the first torsionally-excited state by the use of the method of Esbitt and Wilson.[12] Nine transitions of $J=2\leftarrow1$, $3\leftarrow2$, and $4\leftarrow3$ with $K_{-1}=0$ and 1 were investigated, but only three were suitable for measurement. The difficulties arose from the richness of the lines. The results for the three transitions which had the least interference are shown in Table 8. From the average

Table 8. Relative intensities of the transitions in the ground state and the $v_t=1$ torsional state of 3,3,3-trifluoropropene at 294 K

Transition	$I(v_t=1)/I(G.S.)$
$3_{03} \leftarrow 2_{02}$	0.66±0.01
$3_{12} \leftarrow 2_{11}$	0.72±0.03
$4_{04} \leftarrow 3_{03}$	0.57±0.03
Average	0.65±0.08

relative intensity, the torsional frequency was found to be:

$$v_t = 88 \pm 25 \text{ cm}^{-1}.$$

This value is in good agreement with the frequency reported by Mukhtarov and Kuliev.[9] After the well-known method of the internal rotation analysis[13,14] and the molecular structure obtained, the three-fold barrier to the internal rotation of the trifluoromethyl top with respect to the vinyl group was calculated to be:

$$V_3 = 1640 \pm 800 \text{ cm}^{-1}.$$

The large uncertainty is due to the experimental error.

Discussion

The molecular structure of 3,3,3-trifluoropropene is conspicuous in a tilted trifluoromethyl group. Methyl group tilt has been found in several molecules from an analysis of the internal rotation or by structural analysis.[15] Tilted trifluoromethyl groups have not been reported since splittings due to the internal rotation are scarcely observed, and the detailed structures of the molecules containing a CF_3 top have rarely been determined. Though the magnitude of the tilt observed in this study is small, the heavy mass of the CF_3 top causes the effect to be noticeable, shifting the total moments of inertia. As has been described above, the moments of inertia including these shifts can never be explained within the plausible values of other skeletal parameters.

The tilt of the methyl group attached to an unsaturated carbon atom has not shown any definite direction,

such as is observed in propene,[16] acetone,[17] and methylketene.[18] It is not easy to find why the tilt of 3,3,3-trifluoropropene is away from the double bond of the vinyl group. In this connection, though, it should be noted that the distance between the H_1 atom and the fluorine atom in the plane of symmetry is 2.45 Å, slightly less than the sum of the atomic van der Waals radii, 2.55 Å.[19]

Tokue *et al.*[6] determined the average structure of 3,3,3-trifluoropropene by a joint analysis using the electron-diffraction intensities and our rotational constants. Their results agree with ours within the range of experimental error except for the C=C–H angle. The three C=C–H angles of 3,3,3-trifluoropropene have been determined separately in this study; their average is 121.5±1.0°. The corresponding value obtained by Tokue *et al.* is significantly small, 111.3±4.0°. Tokue *et al.* noticed that the C=C–H angle obtained in the joint analysis always became small if the weight of the rotational constants was increased relative to the diffraction intensities, while, inversely, if this angle was fixed to the $r_\alpha°$ parameter, 119.0°, some of the skeletal parameters were shifted appreciably. A similar situation was encountered in our structural analysis when the tilt of CF_3 top was not considered. It will be interesting to carry out the joint analysis with a tilted trifluoromethyl top.

When compared with the structures of related molecules, the partial structure of the CF_3 group of 3,3,3-trifluoropropene is very similar to those of analogous compounds.[3,20] The vinyl group of $CF_3CH=CH_2$ is slightly different from those of propene[21] and *cis*-3-fluoropropene.[22] The C–C single and C=C double bonds of 3,3,3-trifluoropropene are compared with those of related molecules in Table 9, which shows a systematic change in the bond distances upon trifluoromethyl substitution; a change in the C–C single bond connecting the methyl group and the rest of the molecule, which is brought about by the trifluoromethyl substitution, depends inversely on the electron-withdrawing force of the rest of the molecule. The molecules studied by Hilderbrandt *et al.*[1] may not act thus or may be influenced by other kinds of forces.

Table 9. Comparison of structures (Å)

Molecule	r(C–C)	r(C=C), r(C≡C) or r(C≡N)	Ref.
CH_3–CH_3	1.531_9±0.002		a)
CF_3–CH_3	1.492		b)
CH_3–CH=CH_2	1.501 ±0.004	1.336±0.004	c)
CF_3–CH=CH_2	1.489 ±0.002	1.312±0.010	This work
CH_3–C≡CH	1.4589	1.2062	d)
CF_3–C≡CH	1.46_4 ±0.002	1.201±0.002	e)
CH_3–C≡N	1.458_8	1.157_1	d)
CF_3–C≡N	1.46_1	1.15_3	b)

a) Ref. 2. b) Ref. 3. c) Ref. 21. d) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958). e) Ref. 20.

References

1) R. L. Hilderbrandt, A. L. Andreassen, and S. H. Bauer, *J. Phys. Chem.*, **74**, 1586 (1970).
2) K. Kuchitsu, *J. Chem. Phys.*, **49**, 4456 (1968).
3) L. F. Thomas, J. S. Heeks, and J. Sheridan, *Z. Electrochem.*, **61**, 935 (1957).
4) L. S. Bartell and R. H. Bonham, *J. Chem. Phys.*, **27**, 1414 (1957).
5) V. W. Laurie and D. T. Pence, *ibid.*, **38**, 2693 (1963).
6) I. Tokue, T. Fukuyama, and K. Kuchitsu, *J. Mol. Structure*, **17**, 207 (1973).
7) G. A. Crowder and N. Smyrl, *J. Chem. Phys.*, **53**, 4102 (1970).
8) J. J. Conradi and N. C. Li, *J. Amer. Chem. Soc.*, **75**, 1785 (1953).
9) I. A. Mukhtarov and V. A. Kuliev, *Izv. Akad. Nauk Azerb. SSR.*, **1970**, 146.
10) S. Saito, *J. Mol. Spectrosc.*, **30**, 1 (1969).
11) J. S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).
12) A. S. Esbitt and E. B. Wilson, Jr., *Rev. Sci Intsr.*, **34**, 901 (1963).
13) C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.*, **31**, 841 (1959).
14) M. Hayashi and L. Pierce, Tables for the Internal Rotation Problem, University of Notre Dame, 1961.
15) L. Piece and M. Hayashi, *J. Chem. Phys.*, **35**, 479 (1961).
16) E. Hirota, *ibid.*, **45**, 1984 (1966).
17) R. Nelson and L. Pierce, *J. Mol. Spectrosc.*, **18**, 344 (1965).
18) B. Bak, J. J. Christiansen, K. Kunstmann, L. Nygaard, and J. Rastrup-Andersen, *J. Chem. Phys.*, **45**, 883 (1966).
19) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York (1960).
20) J. N. Shoolery, R. G. Shulman, W. F. Sheehan, Jr., V. Schomaker, and D. M. Yost, *J. Chem. Phys.*, **19**, 1364 (1951).
21) D. R. Lide, Jr., and D. Christensen, *ibid.*, **35**, 1374 (1961).
22) E. Hirota, *ibid.*, **42**, 2071 (1965).