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Microwave Spectra of *o*-Difluorobenzene in the Excited Vibrational States[*1]

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The microwave spectra of *o*-difluorobenzene in various excited vibrational states have been measured in the frequency region from 10- to 30-GHz. The R- and Q-branch transitions of the a-type have been assigned. The rotational constants for the $v_1=1$ state are $A=3254.77$, $B=2226.85$, and $C=1324.67$ MHz, and those for the $v_2=1$ state are $A=3269.76$, $B=2220.48$, and $C=1322.94$ MHz. The inertial defects in the excited states have been used in order to make vibrational assignments. It is very probable that the v_1 and the v_2 mode are the out-of-plane vibration of A_2 and the in-plane vibration of A_1 respectively.

Previous studies[1,2] of the microwave spectrum of *o*-difluorobenzene in the ground vibrational state have shown that the molecule is planar and that the angle made by two C–F bonds is probably

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1) A. Hatta, C. Hirose and K. Kozima, This Bulletin, **41**, 1088 (1968).

2) L. Nygaard, E. R. Hansen, R. L. Hansen, J. Rastrup-Andersen and G. O. Søensen, *Spectrochim. Acta*, **23A**, 2813 (1967).

TABLE 1. TRANSITION FREQUENCIES (in MHz) FOR THE EXCITED VIBRATIONAL STATES OF *o*-DIFLUOROBENZENE

Transition	$v_1=1$ Observed*	$\nu_{\mathrm{obsd}}-\nu_{\mathrm{calcd}}$	$v_1=2$ Observed*	$\nu_{\mathrm{obsd}}-\nu_{\mathrm{calcd}}$	$v_1=3$ Observed*	$\nu_{\mathrm{obsd}}-\nu_{\mathrm{calcd}}$
$2_{11}\rightarrow 3_{12}$	11685.0	+0.2	11680.8	+0.3	—	
$3_{13}\rightarrow 4_{14}$	11858.6	−0.2	11861.6	+0.2	—	
$3_{12}\rightarrow 4_{13}$	14873.4	−0.2	14866.7	+0.2	—	
$3_{21}\rightarrow 4_{22}$	16079.3	+0.2	—		—	
$4_{14}\rightarrow 5_{15}$	14550.9	+0.2	14554.7	+0.2	14558.7	+0.2
$4_{04}\rightarrow 5_{05}$	14591.2	+0.1	14594.0	−0.3	—	
$4_{23}\rightarrow 5_{24}$	16911.1	+0.2	—		—	
$4_{13}\rightarrow 5_{14}$	17548.3	+0.1	17539.7	0.0	—	
$5_{15}\rightarrow 6_{16}$	17212.8	−0.1	—		—	
$5_{05}\rightarrow 6_{06}$	17223.8	−0.1	17229.0	+0.1	—	
$5_{14}\rightarrow 6_{15}$	20039.2	+0.1	20032.5	+0.1	—	
$5_{23}\rightarrow 6_{24}$	23082.0	+0.1	—		—	
$5_{41}\rightarrow 6_{42}$	23155.6	0.0	23159.5	0.0	23163.7	0.0
$6_{25}\rightarrow 7_{26}$	22479.9	+0.1	—		—	
$6_{15}\rightarrow 7_{16}$	22581.6	−0.2	22577.8	−0.3	22574.2	−0.2
$6_{34}\rightarrow 7_{35}$	24771.2	0.0	24765.2	0.0	24759.1	0.0
$6_{24}\rightarrow 7_{25}$	25719.7	0.0	25702.7	0.0	25685.6	+0.1
$6_{33}\rightarrow 7_{34}$	28089.0	−0.2	28077.6	0.0	28065.6	0.0
$7_{35}\rightarrow 8_{36}$	27668.0	−0.2	27661.3	+0.4	—	
$6_{15}\rightarrow 6_{34}$	11923.7	−0.2	—		—	
$8_{36}\rightarrow 8_{35}$	11723.0	+0.3	11710.0	+0.1	—	
8_{26}—8_{45}	14326.8	−0.3	14268.2	−0.4	14209.0	+0.2

Transition	$v_2=1$ Observed*	$\nu_{\mathrm{obsd}}-\nu_{\mathrm{calcd}}$	$v_1=1+v_2=1$** Observed*	$\nu_{\mathrm{obsd}}-\nu_{\mathrm{calcd}}$	$v_3=1$ Observed*
$2_{02}\rightarrow 3_{03}$	9416.8	+0.3	—		—
$2_{21}\rightarrow 3_{22}$	10630.5	+0.2	—		—
$2_{11}\rightarrow 3_{12}$	11662.0	−0.1	—		—
$3_{13}\rightarrow 4_{14}$	11844.5	+0.1	—		—
$3_{03}\rightarrow 4_{04}$	11981.1	+0.4	—		—
$3_{22}\rightarrow 4_{23}$	13865.0	−0.3	—		—
$3_{12}\rightarrow 4_{13}$	14861.1	+0.4	—		—
$3_{21}\rightarrow 4_{22}$	16031.5	+0.1	—		—
$4_{23}\rightarrow 5_{24}$	16877.8	+0.2	—		—
$4_{13}\rightarrow 5_{14}$	17545.9	+0.1	—		17541.5
$5_{15}\rightarrow 6_{16}$	17194.2	+0.1	17201.0	−0.1	—
$5_{05}\rightarrow 6_{06}$	17205.7	−0.3	—		—
$5_{14}\rightarrow 6_{15}$	20034.5	+0.1	—		—
$5_{23}\rightarrow 6_{24}$	23064.8	−0.1	23050.0	−0.2	—
$5_{41}\rightarrow 6_{42}$	23055.8	0.0	23058.5	0.0	—
$6_{25}\rightarrow 7_{26}$	22459.4	−0.1	—		—
$6_{15}\rightarrow 7_{16}$	22570.0	+0.3	—		—
$6_{34}\rightarrow 7_{35}$	24736.4	−0.2	24730.5	+0.1	—
$6_{24}\rightarrow 7_{25}$	25722.6	−0.3	25705.3	+0.1	—
$6_{33}\rightarrow 7_{34}$	28031.4	+0.2	—		28106.6
$8_{26}\rightarrow 8_{45}$	14393.9	−0.1	—		($v_3=2$; 28112.2)

* Maximum experimental uncertainty in the frequency measurements is ±0.2 MHz.

** Combination tone of the v_1 and the v_2 mode.

larger than 60°.

The infrared and Raman spectra of *o*-difluorobenzene have been investigated by Green *et al.*,[3] Scott *et al.*,[4] and Nonnenmacher and Mecke.[5] However, the vibrational assignments by these authors in the far-infrared region ($<$400 cm^{-1}) are different from each other. The present study has been carried out in order to investigate the microwave spectra of *o*-difluorobenzene in the excited vibrational states and to obtain information about their vibrational assignments.

Experimental

The spectra were measured over the frequency range from 10- to 30-GHz with a conventional Stark modulation microwave spectrometer, employing 110-kHz square-wave or sine-wave modulation. The absorption-line frequencies were measured by the same method as has been previously reported by the present authors.[1]

All the measurements were made at room temperature. The sample of *o*-difluorobenzene was prepared from commercial *o*-fluoroaniline by the method of Schiemann and Pillarsky.[6]

Results

The rotational spectra were obtained for six excited vibrational states. The states will be designated hereafter by using the vibrational quantum numbers of v_i.

Assignments of the microwave spectra for the excited states were difficult because of the weakness of the lines and the complexity of the spectra. Because the spectra of the low-J R-branch transitions for the excited states, particularly for the $v_1=1$ state, overlap with the corresponding ground-state lines, an analysis for the low-J transitions was not easy. The lines of the excited states with the relatively high-J values, however, are well separated, and little overlapping occurs. The observations of the qualitative Stark patterns of the spectra were very helpful in the assignments. A least-squares procedure was used to get the best fit between the observed and the calculated frequencies. Agreement is as good as in the case of the ground state. A FACOM 222 digital computer was used in carrying out these calculations. For the $v_3=1$ state, only two transitions are assigned on the basis of their Stark effects and the relative intensities. The rotational constants were obtained for the states of the over-tones ($v_1=1$, 2, and 3, and $v_2=1$) and for that of the combination tone ($v_1=1+v_2=1$). The observed frequencies and the assignments in the excited states are listed in Table 1, together with the differences between the observed frequencies and those calculated by the use of the rigid rotor rotational constants given in Table 2.

As may be seen in Table 1, the centrifugal distortion effect is not important in the transitions studied. The rotational constants and the asymmetry parameters obtained are listed in Table 2. The principal moments of inertia derived from the rotational constants and the resulting inertial defects are listed in Table 3. As is shown in Tabel 3, the inertial defect, $\Delta_{v_1}(=I_c-I_a-I_b)$, becomes progressively more negative as the vibration is excited to higher over-tone states. For the $v_2=1$ state, $\Delta_{v_2=1}$ is also negative, though less in magnitude than $\Delta_{v_1=1}$.

The difference in the inertial defects between the first excited state and the ground state of v_1, $\delta\Delta_1$, is -0.757 amu·Å^2. That of v_2, $\delta\Delta_2$, is -0.197 amu·Å^2.

The measurements of relative intensity were made on the selected transitions of the ground and the first two excited states of v_1 and the first excited state of v_2.

Because of the richness of the spectrum, there were only a few transitions for which reliable measurements could be made. By the use of isolators the relative intensities were obtained by a direct comparison of the line heights on a recorder. The lines are so closely spaced that the variations in the microwave powder were limited to about 10% during these measurements. The results are shown in Table 4.

Discussion

Because the molecule of *o*-difluorobenzene, $^{12}C_6H_4F_2$, has a C_{2v} (or C_2) symmetry, the total wave-function should change in sign under the effect of the rotation operation of 180° about the two-fold axis of symmetry. Since the ratio of the number of the symmetric spin functions to that of the antisymmetric spin functions is 36 : 28, the antisymmetric rotational states (with K_{-1} odd) are more populated than the symmetric rotational states (with K_{-1} even) by this ratio for the ground vibrational state.

In the first vibrationally-excited state the value of the ratio must change to its inverse only for the vibrational mode of B_1 or B_2. As can be seen from Table 4, the relative intensities of the rotational transitions for the same vibrationally-excited state do not depend upon whether K_{-1} is even or odd. Therefore, it can be concluded that the vibration of the v_1 or the v_2 mode belongs to the A_1 or the A_2 type. In this paper the letters representing the frequencies and the relating quantities for different

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[3] J. H. S. Green, W. Kynaston and H. M. Paisley, *J. Chem. Soc.*, **1963**, 473.

[4] D. W. Scott, J. F. Messerly, S. S. Todd, I. A. Hossenlopp, A. Osborn and J. P. McCullough, *J. Chem. Phys.*, **38**, 532 (1963).

[5] G. Nonnenmacher and R. Mecke, *Spectrochim. Acta*, **17**, 1049 (1961).

[6] G. Schiemann and R. Pillarsky, *Chem. Ber.*, **62**, 3035 (1929).

TABLE 2. ROTATIONAL CONSTANTS FOR THE EXCITED STATES OF *o*-DIFLUOROBENZENE

	Ground state	$v_1=1$	$v_1=2$	$v_1=3$	$v_2=1$	$v_1=1+v_2=1$
A (MHz)	3263.55	3254.77	3246.04	3237.10	3269.76	3260.12
B (MHz)	2227.91	2226.85	2225.82	2224.77	2220.48	2219.21
C (MHz)	1323.87	1324.67	1325.48	1326.33	1322.94	1323.96
κ	−0.06785	−0.06515	−0.06241	−0.05960	−0.07794	−0.07523

TABLE 3. MOMENTS OF INERTIA* AND INERTIAL DEFECTS FOR THE EXCITED STATES OF *o*-DIFLUOROBENZENE

	Ground state	$v_1=1$	$v_1=2$	$v_1=3$	$v_2=1$	$v_1=1+v_2=1$
I_a (amu·Å^2)	154.854	155.272	155.690	156.120	154.560	155.017
I_b (amu·Å^2)	226.838	226.946	227.051	227.158	227.597	227.727
I_c (amu·Å^2)	381.741	381.510	381.277	381.033	382.009	381.715
Δ_{v_s} (amu·Å^2)	+0.049	−0.708	−1.464	−2.245	−0.148	−1.029

* Conversion factor: 5.05375×10^5, corresponding to ^{12}C=12 atomic weight scale.

TABLE 4. RELATIVE INTENSITIES* OF THE EXCITED STATE TRANSITIONS

Transition	$v_1=1$ ν cm^{-1}**	$v_1=2$ ν cm^{-1}**	$v_2=1$ ν cm^{-1}**	$v_3=1$ ν cm^{-1}**
$3_{12}\to4_{13}$	0.36 (206)	0.17 (364)	0.29 (250)	—
$4_{14}\to5_{15}$	0.33 (224)	0.14 (400)	—	—
$4_{32}\to5_{33}$	—	—	0.28 (260)	—
$4_{31}\to5_{32}$	—	—	0.26 (274)	—
$3_{21}\to4_{22}$	0.36 (206)	—	0.29 (250)	—
$3_{22}\to4_{23}$	—	—	0.30 (244)	—
$4_{23}\to5_{24}$	—	—	0.29 (250)	—
$4_{04}\to5_{05}$	0.37 (200)	0.15 (384)	—	—
$6_{24}\to7_{25}$	0.38 (194)	0.13 (406)	—	—
$6_{25}\to7_{26}$	0.34 (216)	—	0.28 (260)	—
$6_{33}\to7_{34}$	—	—	—	0.18 (298)
Mean value (in cm^{-1})	$\nu_{v_1=0\to1}$ =208	$\nu_{v_1=0\to2}$ =389	$\nu_{v_2=0\to1}$ =255	

* Referred to that the same rotational transition of the ground state.
** The estimated frequencies are shown in the parentheses.

TABLE 5. COMPARISON OF OUR VIBRATIIONAL ASSIGNMENTS WITH OTHER AUTHORS'

	This study ν_{obsd} cm^{-1}	Green *et al.*[3)] ν_{obsd} cm^{-1}	Scott *et al.*[4)] ν_{obsd} cm^{-1}	Nonnenmacher and Mecke.[5)]* ν_{obsd} cm^{-1}
ω_1	208 A_2	196 (R) A_1 and A_2	197 (R) B_2	197 (R) A_2
ω_2	255 A_1	—	240 (R) A_2	240 (R) B_2
ω_3	~300 B_2	298 (R) B_2	296 (R) A_1	—
ω_4	—	441 (IR) B_1	436 (R) B_1	—
ω_5	—	451 (IR) B_2	451 (IR) B_2	451 (IR) B_2

* Assignments for out-of-plane vibrations.

vibrational modes are designated by the numerical suffixes which number the vibrations from lower to higher. From the data of the intensities, the mean values of the vibrational frequencies of ω_1 and ω_2 were calculated to be 208 cm^{-1} and 255 cm^{-1} respectively. In view of the experimental error for the intensity measurements, these results are in agreement with those obtained by means of the Raman spectra,[4,5)] as is shown in Table 5. For the v_3 mode, only two rotational transitions could be observed, as is shown in Table 1. The relative intensity of the $4_{13}\to5_{14}$ transitions could not be accurately measured because of the overlapping of the other band.

The relative intensity of the $6_{33} \rightarrow 7_{34}$ transitions for the $v_3 = 0$ and 1 states is shown in Table 4. From this value, the frequency of ω_3 is calculated to be 298 cm^{-1} if the v_3 mode is of the B_1 or the B_2 type. On the other hand, the value is calculated to be 348 cm^{-1} if the v_3 mode is of the A_1 or the A_2 type. As the value of 298 cm^{-1} is in good agreement with that of the Raman spectrum, the former assignment seems to be correct. Therefore, it is reasonable that the v_3 mode is of the B_2 type, according to the assignment given by Green *et al.*[3)]

Until now three different assignments for the vibrational type have been reported. However, only for the v_4 and v_5 modes the assignments agree with each other, as is shown in Table 5. Let us, then, proceed to assign the v_1 and v_2 modes by assuming that the assignments for the v_4 and v_5 modes are correct. For this purpose the values of the inertial defect are useful. For a planar molecule a general formula for inertial defect, $\varDelta$, has been given by Oka and Morino[7)] as follows:

$$\varDelta = \varDelta_{\mathrm{vib}} + \varDelta_{\mathrm{cent}} + \varDelta_{\mathrm{elec}}$$

$$\varDelta_{\mathrm{vib}} = \sum_r (v_r + 1/2)\varDelta_r = \sum_r \frac{\boldsymbol{h}}{\pi^2 \boldsymbol{c}} (v_r + 1/2) \times \sum_s{}' \frac{\omega_s{}^2}{\omega_r(\omega_r{}^2 - \omega_s{}^2)} \{(\zeta_{rs}^{(a)})^2 + (\zeta_{rs}^{(b)})^2 - (\zeta_{rs}^{(c)})^2\} + \sum_t \frac{\boldsymbol{h}}{\pi^2 \boldsymbol{c}} \cdot \frac{3}{2\omega_t} (v_t + 1/2) \tag{1}$$

where ω_r and ω_s are the wave numbers of different modes of vibrations, ζ's are Coriolis coupling constants, and the last term is taken into account only when the modes of r belong to the out-of-plane vibrations. The superscripts refer to the molecular fixed principal axes along which a vibrational angular momentum is produced. From this equation the difference between the total values of the inertial defect for two adjacent vibrational states can be expressed as follows:

$$\varDelta v_{r+1} - \varDelta v_r = \frac{\boldsymbol{h}}{\pi^2 \boldsymbol{c}} \left[\sum_s{}' \frac{\omega_s{}^2}{\omega_r(\omega_r{}^2 - \omega_s{}^2)} \{(\zeta_{rs}^{(a)})^2 + (\zeta_{rs}^{(b)})^2 - (\zeta_{rs}^{(c)})^2\} + \frac{3}{2\omega_t} \right] \tag{2}$$

In Eq. (2) the difference between the values for $\varDelta_{\mathrm{cent}}$ are negligibly small and can be omitted, together with the difference in $\varDelta_{\mathrm{elec}}$.

From the character table for C_{2v}, it can be seen that the nonvanishing elements of the Coriolis coupling constants for this molecule are $\zeta_{A_1A_2}^{(a)}$, $\zeta_{B_1B_2}^{(a)}$, $\zeta_{A_1B_2}^{(b)}$, $\zeta_{A_2B_1}^{(b)}$, $\zeta_{A_1B_1}^{(c)}$, and $\zeta_{A_2B_2}^{(c)}$, where the subscripts refer to the vibrational modes. The C_2 axis of symmetry is the a-axis, and the axis perpendicular to the molecular plane is the c-axis.

Equation (2) shows that the vibrational modes and their frequencies directly affect the inertial defect through the Coriolis interactions and that the interactions fall off with an increase in the frequency difference because of the $(\omega_r{}^2 - \omega_s{}^2)$ terms in the denominator. Hence, we can assume that the higher vibrations ($s > 5$) are not important in these discussions.

It is very probable that the v_1 and v_2 modes are mainly due to the C–F deformation vibrations. Since it is clear, from symmetry considerations, that the out-of-plane vibrational modes belong to the A_2 and B_2 species and that the in-plane modes belong to the A_1 and B_1 species, the possibility that both the v_1 and v_2 modes belong to A_1 or A_2 can be excluded.

Additional evidence for this can also be obtained from the considerations based on Eq. (2). Therefore, there remain only the following two possibilities:

	ω_1	ω_2	ω_3	ω_4	ω_5
Case (1)	A_2	A_1	B_2	B_1	B_2
Case (2)	A_1	A_2	B_2	B_1	B_2

For Case (1), the following equations can be written on the basis of Eq. (2):

$$\frac{\boldsymbol{h}}{\pi^2 \boldsymbol{c}} \left[\frac{\omega_2{}^2}{\omega_1(\omega_1{}^2 - \omega_2{}^2)} (\zeta_{12}^{(a)})^2 - \frac{\omega^2{}_3}{\omega_1(\omega_1{}^2 - \omega^2{}_3)} (\zeta_{13}^{(c)})^2 + \frac{3}{2\omega_1} \right] = \delta\varDelta_1$$

$$\frac{\boldsymbol{h}}{\pi^2 \boldsymbol{c}} \left[\frac{\omega_1{}^2}{\omega_2(\omega_2{}^2 - \omega_1{}^2)} (\zeta_{12}^{(a)})^2 + \frac{\omega_3{}^2}{\omega_2(\omega_2{}^2 - \omega_3{}^2)} (\zeta_{23}^{(b)})^2 \right] = \delta\varDelta_2$$

where the terms containing $(\zeta_{14}^{(b)})^2$ and $(\zeta_{15}^{(c)})^2$ in the former equation and the terms containing $(\zeta_{25}^{(b)})^2$ and $(\zeta_{24}^{(c)})^2$ in the latter equation could be considered to be approximately cancelled out, because the value of ω_4 is not very different from that of ω_5. By using the wave numbers reported by Scott *et al.*,[4)] the possible values of the squares of the Coriolis coupling constants could be estimated as follows:

$$(\zeta_{12}^{(a)})^2 = 1.0 - 0.85, \quad (\zeta_{13}^{(c)})^2 = 0.26 - 0.0,$$
$$(\zeta_{23}^{(b)})^2 = 0.83 - 0.72$$

where the conversion factor of $\boldsymbol{h}/\pi_2 \boldsymbol{C} = 134.8599$ amu·Å^2·cm^{-1} was used. These values seem to be reasonable. On the other hand, for Case (2) no reasonable values of the squares of the Coriolis coupling constants could be obtained.

Therefore, it can be concluded that the assignments of Case (1) are correct. The assignments obtained are analogous to those obtained for *o*-dichlorobenzene by Nonnenmacher and Mecke[5)] and by Scherer.[8)]

[7)] T. Oka and Y. Morino, *J. Mol. Spectrosc.*, **6**, 472 (1961).

[8)] J. R. Scherer, *Spectrochim. Acta*, **20**, 345 (1964).