PURE ROTATIONAL SPECTRA OF 1,2- AND 1,3-BENZENE-d₂ OBSERVED BY MICROWAVE FOURIER TRANSFORM SPECTROSCOPY*

M. OLDANI, R. WIDMER, G. GRASSI and A. BAUDER

Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich (Switzerland)

(Received 21 December 1987)

ABSTRACT

The pure rotational spectra of 1,2- and 1,3-benzene- d_2 have been measured over the 8-18 GHz range with a pulsed microwave Fourier transform spectrometer. Rotational constants have been determined from the measured transition frequencies. Structural information has been obtained from the moments of inertia of all measured isotopic species of benzene.

INTRODUCTION

The rotational spectra of highly symmetric molecules cannot be observed in the microwave region, because they lack a permanent electric dipole moment. Asymmetric deuteration of such molecules provides a small vibrationally induced dipole moment which lies in the range $10^{-2}-10^{-3}$ D. Very weak rotational spectra result as a consequence. Previous work in this field was recently reviewed by Hirota [1]. Rotational spectra of important but fairly small molecules, such as partially deuterated acetylene [2,3], ethylene [4], ethane [5-8], allene [9,10] and dimethylacetylene [11], have been observed. With the advent of pulsed microwave Fourier transform (MWFT) spectroscopy the investigations have been extended to other molecules like glyoxal [12] and cyclobutane [13]. Even the rotational spectrum of benzene- d_1 was recently measured with this technique [14]. The vibrationally induced dipole moment of benzene- d_1 was determined from the Stark effect and was found to be as small as 0.008 D [15].

Pulsed MWFT spectroscopy is at present the most sensitive technique for the observation of rotational transitions in the microwave range. It is capable of measuring transitions with absorption coefficients as low as 2.5×10^{-12} cm⁻¹ [16]. The method does not depend on the Stark modulation which is difficult to apply because of the high electric fields required for an appreciable modulation of molecules with very small dipole moments.

^{*}Dedicated to the memory of Professor Walter Gordy.

In the present work we report the assignment and analysis of rotational spectra which were measured for 1,2- and 1,3-benzene- d_2 . The position of a hydrogen nucleus with respect to the molecular center of benzene was derived in various ways from different combinations of the moments of inertia of isotopic species. For this purpose, the results from the microwave spectrum of benzene- d_1 [14] and from the high resolution IR spectrum of benzene [17] were combined with the results of the microwave spectra of the dideuterated benzenes. Several methods for determining the substitution coordinates are critically compared.

EXPERIMENTAL

Chemicals

A commercial sample of benzene-1,2- d_2 (MSD Isotopes, isotopic purity 95.4 at.% D) was used as received.

The synthesis of benzene-1,3- d_2 started from 1,3-dibromobenzene which was reacted with butyl-lithium at -80°C. The monolithium-substituted product was hydrolysed with CH₃OD to bromobenzene-3- d_1 [18]. The latter was then transformed with magnesium to the corresponding Grignard reagent in an ether solution. The Grignard reagent was hydrolysed with D₂SO₄ diluted in D₂O to form benzene-1,3- d_2 [19]. The raw product was purified by gas chromatography up to 99.9%.

MWFT spectrometer

The MWFT spectrometer of the Ekkers-Flygare type [20] covered the frequency range 8-18 GHz. Our design is similar to that described by Bestmann et al. [21]. Two 6 m long X- and P-band waveguide cells were used. The spectra were recorded with sample pressures around 25 mTorr and temperatures between -50° C and 20° C. Microwave pulses with a duration of 100-200 ns and a power of 10-20 W polarized the sample. The pulses were repeated at a rate of 50 kHz. The carrier frequency was offset by less than 4 MHz from a rotational transition frequency. The emission signals of each polarization decay were amplified, downconverted to the frequency band of 0-50 MHz and sampled with a 3-bit A/D converter at a rate of 100 MHz. The digitized signals for 512 channels were added in a multichannel analyzer and eventually in a LSI-11/73 processor. For the detection of the weaker transitions up to 720×10^{6} pulses were needed for an acceptable signal-to-noise ratio. The conventional power spectrum was calculated with the fast Fourier transform routine in the LSI-11/73.

Three or more independent measurements with carrier frequencies higher and lower than the transition frequency were performed for a given transition.



Fig. 1. Three deuterated species of benzene with their principal axes. The centers of the sixmembered rings are marked by a circle.

TABLE 1

Measured transition frequencies (MHz) of benzene-1,2- d_2

Transition	$\nu_{\rm obs}^{\ a}$	$\nu_{\rm obs} - \nu_{\rm calc}{}^{\rm b}$	
1(0,1)- 0(0,0)	7826.756(26)	0.013	
2(0,2) - 1(0,1)	13454.316(9)	-0.042	
2(1,2) - 1(1,1)	13151.802(26)	0.036	
4(4,1)- 4(2,2)	10177.938(26)	-0.004	
5(4,2) - 5(2,3)	13652.717(7)	-0.009	
6(4,3)-6(4,2)	11982.662(13)	-0.014	
7(5,2)-7(5,3)	11151.383(30)	-0.008	
8(6,3)- 8(6,2)	10126.312(10)	-0.013	
9(7,2)- 9(7,3)	8948.520(29)	0.028	
13(10,4)-13(10,3)	12447.221(31)	-0.003	
14(11,3)-14(11,4)	10784.073(40)	-0.039	
15(12,5)-15(12,4)	9062.379(34)	-0.003	
19(15,4)-19(15,5)	12068.307(19)	-0.001	
20(16,4)-20(16,5)	9977.475(14)	-0.007	
23(18,5)-23(18,6)	15355.310(20)	0.013	
24(19,5)-24(19.6)	12898.437(10)	0.008	
29(23,6)-29(23,7)	13347.208(8)	0.006	
30(24,6)-30(24,7)	10721.060(26)	0.011	
34(27,7)-34(27,8)	13475.747(16)	-0.026	
39(31,8)-39(31,9)	13338.903(160)	0.008	

^aStandard deviation from three different measurements in parentheses. ^bCalculated from the molecular constants of Table 3.

Accurate transition frequencies were obtained by fitting a parabola to the center of an absorption line and determining the peak frequency. The uncertainty of a frequency measurement was estimated from the standard deviation of the independent experiments.

34

Transition	$\nu_{\rm obs}^{\ \ a}$	$\nu_{ m obs} - \nu_{ m calc}{}^{ m b}$	
1(1,1)-0(0,0)	8163.049(70)	0.021	
2(0,2) - 1(1,1)	13098.672(36)	-0.011	
4(1,3)-4(2,2)	12963.879(47)	0.005	
5(3,2) - 5(2,3)	12575.506(40)	0.012	
6(3,3)-6(4,2)	12028.090(34)	-0.020	
7(5,3)-7(6,2)	14342.960(53)	-0.010	
8(7,2)-8(6,3)	14944.620(85)	-0.066	
9(5,4)- 9(6,3)	17204.019(03)	-0.013	
10(7,3)-10(6,4)	16446.621(11)	-0.013	
11(7,4)-11(8,3)	15564.033(13)	-0.015	
12(9,3)-12(8,4)	14667.368(34)	-0.033	
13(9,4)-13(10,3)	13900.586(18)	-0.031	
14(11,3) - 14(12,2)	13576.391(53)	-0.009	
15(11,4) - 15(12,3)	13320.006(35)	0.016	
16(13,3)-16(12,4)	13719.656(19)	0.027	
17(13,4)-17(14,3)	14660.565(14)	-0.025	
18(13,5)-18(14,4)	16781.295(28)	-0.006	
19(15,4)-19(14,5)	16409.645(17)	-0.002	
20(15,5)-20(16,4)	16555.606(12)	0.003	
21(17,4)-21(16,5)	17287.435(17)	-0.021	

Measured transition frequencies (MHz) of benzene $-1,3-d_2$

^aStandard deviation from three different measurements in parentheses.

^bCalculated from the molecular constants of Table 3.

ASSIGNMENT AND ANALYSIS

The shifts of the rotational constants between the dideuterated benzenes and benzene itself were calculated from a geometrical model with r(C-C)=1.395 Å and r(C-H)=1.082 Å. These shifts were added to the observed rotational constants of benzene [17]. In this way the low J transition frequencies of the rotational spectra were predicted with an accuracy of a few MHz. Because of the rotation of the principal axis system upon deuteration benzene- $1,2-d_2$ shows only μ_a -type transitions, whereas benzene- $1,3-d_2$ exhibits exclusively μ_b -type transitions. The orientation of the principal axis system is depicted in Fig. 1.

The low J transitions were located readily. After a preliminary adjustment of the rotational constants from the measured frequencies of the low J transitions, assignments of transitions were extended up to J=39 for benzene-1,2 d_2 and up to J=21 for benzene = 1,3- d_2 . The measured transition frequencies with their estimated uncertainties for the two dideuterated benzenes are listed in Tables 1 and 2.

Rotational constants and some of the quartic centrifugal distortion con-

TABLE 3

Parameter	Benzene- d_1^{c}	Benzene-1,2- d_2	Benzene-1,3- d_2
A (MHz)	5689.144(6)	5498.062(4)	5502.669(7)
B (MHz)	5323.934(6)	5164.242(4)	5152.057(6)
C (MHz)	2749.674(6)	2662.496(4)	2660.358(6)
Δ_J (kHz)	0.0^{d}	0.0^{d}	0.0^{d}
Δ_{JK} (kHz)	-1.2(1)	-1.52(3)	0.0^{d}
Δ_{K} (kHz)	-3.6(7)	0.0^{d}	0.55(3)
$\delta_J (kHz)$	0.019(3)	0.032(2)	0.218(6)
δ_{K} (kHz)	0.0^{d}	0.7(1)	0.409(2)
Ne	20	20	20
$\sigma ({ m kHz})^{ m f}$	30	23	27
I_a (uÅ ²)	88.8322(1)	91.9195(1)	91.8425(1)
I_b (uÅ ²)	94.9259(1)	97.8612(1)	98.0927(1)
I_c (uÅ ²)	183.7960(4)	189.8140(3)	189.9666(5)
⊿₀ (uŲ) ^g	0.0379(4)	0.0333(3)	0.0314(5)

Rotational constants, quartic centrifugual distortion constants and moments of inertia $^{\rm a}$ of deuterated species of benzene $^{\rm b}$

^aConversion factor of 505379.05 MHz uÅ². ^bNumbers in parentheses are standard deviations of the least squares fit. ^cRef. 14. ^dNot fitted, constrained to zero. ^eNumber of measured transitions in the least squares fit. ^fMean residual error of a measured transition frequency. ^gInertial defect, $\Delta_0 = I_c - I_a - I_b$.

stants were determined from the measured transition frequencies in a least squares fit. The results for the dideuterated benzenes and the previous results for benzene- d_1 [14] are collected in Table 3. The centrifugal distortion constants are defined according to Watson's asymmetric reduction in the III^r representation [22]. Those which showed standard deviations larger than their values were constrained to zero in the final fits. The determined centrifugal distortion constants act mainly as fitting parameters to improve the accuracy of the rotational constants but may not be physically relevant.

STRUCTURE DETERMINATION

As Table 3 reveals, the substituted benzenes as rigid planar molecules have a small positive inertial defect $\Delta_0 = I_c - I_a - I_b$. A slight decrease of the inertial defect is noticed for successive steps of deuterium substitutions in benzene. This trend may be extrapolated to the unsubstituted benzene to yield $\Delta_0 = 0.0434(15)$ uÅ². The rotational constant *C* of benzene has not yet been determined experimentally. It can now be calculated from the corresponding principal moment of inertia $I_c = 2I_b + \Delta_0 = 177.7150(19)$ uÅ². I_b was known from the rotational constant B = 5688.916(42) MHz which was obtained from the analysis of the high resolution IR spectra by Pliva and Pine [17]. The value C = 2843.784(30) MHz represents the best estimate for benzene.

TABLE 4

Substitution coordinates of the hydrogen nucleus from different deuterated species of benzene

Substituted species	Parent species	a _H (Å)	b _H (Å)	r _H ^a (Å)	Equation ^b
$\overline{d_1}$	d_0	2.4767	0.0	2.4767	(1a)
d_1	d_0	2.4759	0.0	2.4759	(2)
d_1	d_0	2.4741	0.0	2.4741	(3)
d_0	d,	2.4437	0.0	2.4752	(4a)
d_1	d_0	2.4754	0.0	2.4754	(5)
d	d_1	2.4426	0.0	2.4741	(6a)
$1,2-d_2$	d_1	1.2072	2.1456	2.4775	(4a), (4b)
$1, 2 - d_2$	d_1	1.2072	2.1446	2.4766	(6a), (6b)
$1,2-d_2$	d_0	2.1448	1.2379	2.4764	(7a), (7b)
$1,2-d_2$	d_0	2.1442	1.2368	2.4754	(8a), (8b)
$1, 3 - d_2$	d_1	1.2699	2.1457	2.4774	(4a), (4b)
$1,3-d_2$	d_1	1.2699	2.1441	2.4761	(6a), (6b)
$1, 3 - d_2$	d_0	2.1447	1.2380	2.4763	(7a), (7b)
$1,3-d_2$	d_0	2.1440	1.2367	2.4751	(8a), (8b)

^aDistance of a hydrogen nucleus from the center of the six-membered ring of benzene. The centerof-mass is shifted by 0.0315 Å between benzene and benzene- d_1 . ^bEquations used to calculate the substitution coordinates, see text.

The moments of inertia of the mono- and dideuterated benzenes listed in Table 3 and those of benzene were used to determine substitution coordinates of a hydrogen nucleus in benzene. Because of the high symmetry of benzene and the availability of several deuterated species, substitution coordinates were calculated in different ways. The results are collected in Table 4. For comparison the results were transformed to the distance $r_{\rm H}$ of the hydrogen nucleus from the center of the six-membered ring using the shift of the center-of-mass upon isotopic substitution.

The standard method originally proposed by Kraitchman [23] applies to the single substitution of a nucleus in a molecule. If the unsubstituted benzene is considered as a symmetric top the coordinates of the substituted nucleus which is not located on the symmetry axis are given by [23]

$$a^{2} = (I'_{b} - I'_{a}) (I'_{b} - I'_{c}) / \mu (I'_{b} - I'_{a} - I'_{c} + I_{a})$$
(1a)

and

$$c^{2} = (I'_{a} - I_{a})(I'_{c} - I_{a})/\mu(I'_{a} + I'_{c} - I'_{b} - I_{a})$$
(1b)

where the primed moments of inertia refer to the substituted molecule and $\mu = M \Delta m / M + \Delta m$ with M as the mass of the unsubstituted molecule and with Δm as the mass change upon isotopic substitution. A small negative value was obtained for c^2 which should vanish for a planar molecule such as benzene. This result is an indication of the incomplete suppression of the rovibrational interaction and was disregarded. However, if the distance of the substituted nucleus from the symmetry axis [23]

$$a^2 + c^2 = (I'_b - I_b)/\mu \tag{2}$$

is attributed to the coordinate a^2 alone in a planar molecule c^2 affects the final result as shown in Table 4. The equivalent distance was calculated with the equation for a substitution in a planar asymmetric top [23]

$$a^{2} + b^{2} = (I_{c}' - I_{c})/\mu$$
(3)

and assigned to a^2 alone. The corresponding equations for the individual coordinates [23]

$$a^{2} = (I'_{b} - I_{b})(I'_{a} - I_{b})/\mu(I_{a} - I_{b})$$
(4a)

and

$$b^{2} = (I'_{a} - I_{a})(I'_{b} - I_{a})/\mu(I_{b} - I_{a})$$
(4b)

could only be applied if benzene- d_1 was chosen as the parent molecule and benzene as the substituted one. Although b^2 should vanish for this case a small value of 0.0034 Å² was found which represents three times the propagated uncertainties of the moments of inertia. The marginally secured value was omitted.

Rudolph [24] recommended a different set of equations from those of Kraitchman [23] for the determination of substitution coordinates for nuclei on a principal plane or on a principal axis of inertia. The equations of Rudolph provide a unique solution. They use the planar second moments of inertia $P_x = (-I_x + I_y + I_z)/2$, x,y,z = a,b,c and cyclic permutations, instead of the moments of inertia. The coordinate of a nucleus substituted on the principal axis *a* is given by [24]

$$a^2 = (P'_a - P_a)/\mu \tag{5}$$

Corresponding to eqn. (4a) and (4b) with benzene- d_1 as parent molecule the coordinates of a nucleus substituted on the principal plane ab were calculated according to the equations of Rudolph [24] by

$$a^{2} = (P'_{a} - P_{a}) \left[1 + (P'_{b} - P_{b}) / (P_{b} - P_{a}) \right] / \mu$$
(6a)

and

$$b^{2} = (P'_{b} - P_{b}) \left[1 + (P'_{a} - P_{a}) / (P_{a} - P_{b}) \right] / \mu$$
(6b)

The value of b^2 was smaller than its uncertainty and was neglected. The eqns. (6a) and (6b) differ from those of Kraitchman [23] for a general substitution in an asymmetric top by the omission of the factor $[1 + (P'_c - P_c)/(P_c - P_a)]$ or $[1 + (P'_c - P_c)/(P_c - P_b)]$, respectively. The factors were numerically equal to one well within the accuracy which is required for the final results.

In addition, similar results for the position of a hydrogen nucleus were obtained from the dideuterated species of benzene. The eqns. (4a) and (4b) or (6a) and (6b) were applied for a single substitution starting from benzene- d_1 as parent molecule. Alternatively, the simultaneous substitutions of two equivalent nuclei in benzene-1,2- d_2 and benzene-1,3- d_2 were also evaluated as double substitution of benzene as parent molecule. Chutjian [25] derived the equations of the substitution coordinates for two nuclei in the principal plane xz which are related by the symmetry C_{2v} with the symmetry axis along z in the form

$$x^2 = (I'_z - I_z) / \Delta m' \tag{7a}$$

and

$$z^2 = (I'_x - I_x)/\mu'$$
 (7b)

where $\mu' = M \Delta m' / (M + \Delta m')$ and $\Delta m' = 2\Delta m$ refer to the total mass change upon double substitution. As shown in Fig. 1 the principal axis *a* represents the symmetry axis *z* for benzene-1,2-*d*₂ with the substituted nuclei in the plane *ab*. For benzene-1,3-*d*₂ the principal axis *b* is the symmetry axis.

Later, Nygaard [26] modified the equations of Chutjian [25] for double substitutions and introduced the planar second moments of inertia. The coordinates are then given by [26]

$$x^2 = (P'_x - P_x) / \Delta m' \tag{8a}$$

and

$$z^2 = (P'_z - P_z)/\mu'$$
 (8b)

Finally, 14 different ways were explored for the calculation of substitution coordinates of the same nucleus in benzene as shown in Table 4. The propagated uncertainties of the moments of inertia onto the substitution coordinates do not exceed 0.0002 Å. However, the systematic errors of the results due to the vibration-rotation interaction are much larger as revealed in Table 4.

DISCUSSION

The formulas for the calculation of substitution coordinates are correct equations only for the "equilibrium" moments of inertia. Since the "equilibrium" moments of inertia are not known for benzene and the isotopic species we were forced to insert the moments of inertia of the vibrational ground state. This procedure introduced systematic errors of the order of the inertial defects. Fortunately, benzene is a rather rigid molecule where the systematic errors are quite small.

Inspection of Table 4 shows two groups of results for $r_{\rm H}$ of 2.4753(2) Å and 2.4763(4) Å. Each group is consistent within the experimental uncertainties. Zero-point rovibrational interactions were compensated to a different extent in the two groups which reflect variants of the determinations of substitution

coordinates. The remaining results are spread over the range between 2.4741 Å and 2.4775 Å. The average of all results is 2.4759 ± 0.0018 Å. The total spread of the results is still small. However, the substitution structure deviates systematically from the equilibrium structure as demonstrated for a few small linear molecules by Costain [27]. It is difficult to estimate the deviation for a larger molecule like benzene.

The average of $r_{\rm H}$ determined in this work from the substitution coordinates is slightly smaller than the r_0 structure value of 2.4795(15) Å obtained by Cabana et al. [28] from the analysis of medium resolution IR spectra of C_6H_6 and C_6D_6 . Essentially the same result of 2.479(6) Å for the r_z structure was determined by Tamagawa et al. [29] from electron diffraction measurements.

The hydrogen nuclei are located at the corners of a regular hexagon. This fact followed directly from the angle between the position vector of a hydrogen nucleus and the principal axis a. The angle was calculated to be $30.0\pm0.03^{\circ}$ for both dideuterated species of benzene (see Fig. 1). In addition, it was found that the principal axis system was rotated by $29.99\pm0.01^{\circ}$ between benzene- d_1 and either benzene-1,2- d_2 and benzene-1,3- d_2 [30]. This result corroborates the six-fold symmetry of the position of the hydrogen nuclei.

Recently, Ermer [31] pointed out that the geometrical structure of benzene is not known at present with high reliability from direct X-ray, neutron, and electron diffraction measurements, in particular with respect to the $D_{\rm 6h}/D_{\rm 3h}$ symmetry problem. Our knowledge of the planar regular hexagon with symmetry D_{6h} for the carbon skeleton has been based mainly on vibrational selection rules. Ermer argued that a deviation in the direction of a planar D_{3h} structure with alternating single and double bonds would not have been detectable by the previous structure investigations. The substitution structure determined in our study fixes the hydrogens on a regular hexagon. However, if the carbon skeleton is distorted in the direction of the symmetry D_{3h} , two equivalent structures must exist which are separated by a potential barrier. For a low barrier, a rapid tunneling between two equivalent D_{3h} structures occurs which can safely by excluded, since no splitting or broadening of the rotational transitions of the deuterated benzenes was observed. A high barrier is not consistent with the accepted interpretation of the vibrational spectra as discussed by Ermer [31]. Thus, these experimental facts are in conflict with the hypothesis of a D_{3h} carbon skeleton.

ACKNOWLEDGMENTS

Financial support from the Schweizerischer Nationalfonds (project no. 2.223-0.84) is gratefully acknowledged. We thank Messrs. M. Andrist and W. Groth for their contributions during the construction of the MWFT spectrometer. One of us (A. B.) is indebted to Prof. W. Lüttke and Prof. O. Ermer for stimulating discussions on the structure of benzene.

REFERENCES

- 1 E. Hirota, in K.N. Rao (Ed.), Molecular Spectroscopy: Modern Research, Vol. III, Academic Press, New York, 1985, p. 297.
- 2 J.S. Muenter and V.W. Laurie, J. Am. Chem. Soc., 86 (1964) 3901.
- 3 K. Matsumura, T. Tanaka, Y. Endo, S. Saito and E. Hirota, J. Phys. Chem., 84 (1980) 1793.
- 4 E. Hirota, Y. Endo, S. Saito, K. Yoshida, I. Yamaguchi and K. Machida, J. Mol. Spectrosc., 89 (1981) 223.
- 5 E. Hirota and C. Matsumura, J. Chem. Phys., 55 (1971) 981.
- 6 E. Hirota, K. Matsumura, M. Imachi, M. Fujio, Y. Tsuno and C. Matsumura, J. Chem. Phys., 66 (1977) 2660.
- 7 E. Hirota, S. Saito and Y. Endo, J. Chem. Phys., 71 (1979) 1183.
- 8 E. Hirota, Y. Endo, S. Saito and J.L. Duncan, J. Mol. Spectrosc., 89 (1981) 285.
- 9 E. Hirota and C. Matsumura, J. Chem. Phys., 59 (1973) 3038.
- 10 B. Vogelsanger, M. Oldani and A. Bauder, J. Mol. Spectrosc., 119 (1986) 214.
- 11 J. Nakagawa, M. Hayashi, Y. Endo, S. Saito and E. Hirota, J. Chem. Phys., 80 (1984) 5922.
- 12 M. Rodler, M. Oldani, G. Grassi and A. Bauder, J. Chem. Phys., 86 (1987) 5365.
- 13 B. Vogelsanger, W. Caminati and A. Bauder, Chem. Phys. Lett., 141 (1987) 245.
- 14 M. Oldani and A. Bauder, Chem. Phys. Lett., 108 (1984) 7.
- 15 E. Fliege and H. Dreizler, Z. Naturforsch., Teil A, 42 (1987) 72.
- 16 M. Oldani, M. Andrist, A. Bauder and A.G. Robiette, J. Mol. Spectrosc., 110 (1985) 93.
- 17 J. Pliva and A.S. Pine, J. Mol. Spectrosc., 93 (1982) 209.
- 18 G. Bauer, K. Scheffler and H.B. Stegmann, Chem. Ber., 109 (1976) 2231.
- 19 D. Todd, J. Chem. Educ., 50 (1973) 366.
- 20 J. Ekkers and W.H. Flygare, Rev. Sci. Instrum., 47 (1976) 448.
- G. Bestmann, H. Dreizler, H. M\u00e4der and U. Andresen, Z. Naturforsch., Teil A, 35 (1980) 392.
- 22 J.K.G. Watson, in J.R. Durig (Ed.), Vibrational Spectra and Structure, Vol. VI, Elsevier, New York, 1977, p. 1.
- 23 J. Kraitchman, Am. J. Phys., 21 (1953) 17.
- 24 H.D. Rudolph, J. Mol. Spectrosc., 89 (1981) 460.
- 25 A. Chutjian, J. Mol. Spectrosc., 14 (1964) 361.
- 26 L. Nygaard, J. Mol. Spectrosc., 62 (1976) 292.
- 27 C.C. Costain, J. Chem. Phys., 29 (1958) 864.
- 28 A. Cabana, J. Bachand and J. Giguère, Can. J. Phys., 52 (1974) 1949.
- 29 K. Tamagawa, T. Iijima and M. Kimura, J. Mol. Struct., 30 (1976) 243.
- 30 H.D. Rudolph, J. Mol. Spectrosc., 89 (1981) 430.
- 31 O. Ermer, Angew. Chem., 99 (1987) 791.