

Production, Microwave Spectrum, Barrier to Internal Rotation, Dipole Moment and Molecular Models of Methylthioketene, $\text{CH}_3\text{—CH=C=S}$

BØRGE BAK,^a HENRIK SVANHOLT^a and ARNE HOLM^b

^a Chemical Laboratory V, The H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø and ^b Chemical Laboratory II, The H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

Hitherto not described methylthioketene, $\text{CH}_3\text{—CH=C=S}$, has been produced by pyrolysis of 4-methyl-1,2,3-thiadiazole and of 5-methyl-1,2,3-thiadiazole. The dominant (96 %) isotopic species, $\text{CH}_3\text{—CH=C=}^{32}\text{S}$, was identified by its ground state microwave spectrum and microwave spectra of five vibrationally excited species. *A*, *E* splittings due to internal methyl group rotation were observed and reproduced by a finally adopted structure and a barrier of 435 cm^{-1} . The experimental dipole moment of methylthioketene in its second torsionally excited level is 1.54 Debye (see text). Three slightly different rigid models of methylthioketene are presented based on stated assumptions and on experimental values of rotational constants *B* and *C* of $\text{CH}_3\text{—CH=C=}^{32}\text{S}$ and $\text{CH}_3\text{—CH=C=}^{34}\text{S}$. The calculated C—C=C valence angle and/or the calculated bond lengths are close to comparable geometric parameters in other molecules.

1,2,3-Thiadiazole (I, Fig. 1) pyrolyzes to thioketene (III, Fig. 1) under C(4) and C(5) scrambling and H(5) migration.^{1,2} We have investigated if the 4- and 5-methyl derivatives of (I), 4- and 5-methyl-1,2,3-thiadiazole (V and VI), will by analogy both convert to hitherto unknown methylthioketene (IV, Fig. 1). II (Fig. 1) was not observable by microwave product analysis¹ but its methyl derivative might be sufficiently stable. A search for microwave transitions from this species was, therefore, included.

EXPERIMENTAL

Preparation of V and VI was carried out following Refs. 3 and 4. Both samples were repeatedly distilled *in vacuo* until their vapor pressure at 0 and 20 °C was 0.5 and 1.0 Torr, respectively (L. K. B. instrument). Pyrolysis and subsequent analysis of polar dissociation products were performed as described for $(\text{CH}_3)_2\text{NH}$.⁵

In the present case vapors at *ca.* 50 mTorr were pumped through a hot (1000 K) 20 cm length of quartz tubing (i.d. 8 mm) directly into the cell of a conventional Stark-modulated microwave (m.w.) spectrometer operated in the 18.6–39.6 GHz region at room temperature. The entrance to exit pressure in the cell was of the order 25/10 mTorr (one-half of this being N_2).

M.w. frequencies were measured to ± 0.1 MHz. Our calculated r.m.s. deviations are larger than this. In part, this is due to near-coincidence of transition frequencies as to be expected from a near-prolate symmetric top such as IV. Also, low-lying vibrational levels cause coincidences. Stark lobes were frequently disturbing so that some transition fre-

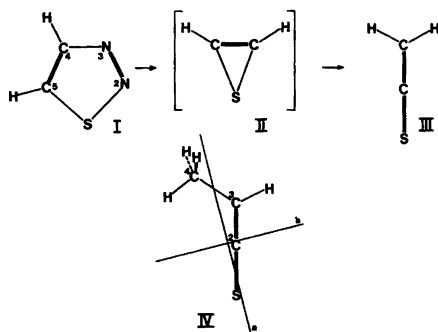


Fig. 1. Formulae and atom numbering in 1,2,3-thiadiazole (I), thi-irene (II), thioketene (III) and methylthioketene (IV). Heavy atoms of IV in plane of inertial axes, *a* and *b*.

Table 1. Notation and percentage, PERCENT, relative to methylthioetene (^{32}S) (IV) in its ground level (g.l.), of its first and second torsionally excited levels, $\nu_t(1)$ and $\nu_t(2)$, its first excited skeletal in-plane deformation level, $\nu_b(1)$, its second excited level, $\nu_b(2)$, its $\nu_b(1) + \nu_t(1)$ level, and of methylthioetene (^{34}S) in its ground level. Number of observed *A*-type, *R*-branch μ_a -transitions, *N*. Root-mean-square (r.m.s.) deviations as calculated by ROTFIT.¹² J_{max} (maximum rotational quantum number involved)=7. Experimental frequencies available on request.^a

NOTATION	PERCENT	<i>N</i>	r.m.s.
$\text{CH}_3\text{CH}=\text{C}=\text{}^{32}\text{S}$			
IV (g.l.)	100	37	0.2040
$\nu_t(1)$	51	18	0.2868
$\nu_t(2)$	29	23	0.4458
$\nu_b(1)$	47	39	0.3060
$\nu_b(2)$	22	20	0.1244
$\nu_b(1) + \nu_t(1)$	24	16	0.2499
$\text{CH}_3\text{CH}=\text{C}=\text{}^{34}\text{S}$			
(g.l.)	4	24	0.1475

^aTransitions of IV (g.l.) useful for analytical identification may be taken from Table 2.

Table 2. Observed frequencies F_A (MHz) of selected *A*-type transitions (TRANSITIONS) with experimental *A,E* splittings, $\nu_A - \nu_E$ (MHz), for methylthioetene (^{32}S) in its ground level, IV (g.l.) and its first torsionally excited level, $\nu_t(1)$, compared to splittings calculated by SEM 4.¹¹ Molecular model, see text. Barrier height = 435 cm^{-1} . Torsional frequency $\nu_t = 140 \text{ cm}^{-1}$.

TRANSITIONS	IV (g.l.)			$\nu_t(1)$		
	F_A	$\nu_A - \nu_E$ Exp.	Calc.	F_A	$\nu_A - \nu_E$ Exp.	Calc.
$3_{13} \rightarrow 4_{14}$	20734.00	-4.25	-3.42	20734.88	-260.22	-260.91
$3_{03} \rightarrow 4_{04}$	21039.90	0.60	0.54	21031.53	-12.34	-12.67
$3_{12} \rightarrow 4_{13}$	21355.30	5.30	4.42	21338.98	223.33	222.36
$4_{14} \rightarrow 5_{15}$	25916.14	-2.04	-1.56	25917.50	-283.91	-285.28
$4_{04} \rightarrow 5_{05}$	26295.46	0.46	0.66	26285.14	-15.50	-15.91
$4_{13} \rightarrow 5_{14}$	26693.14	3.38	2.82	26672.56	237.80	237.42
$5_{15} \rightarrow 6_{16}$	31097.77	-1.00	-0.72	31098.77	-286.86	-288.61
$5_{05} \rightarrow 6_{06}$	31548.43	0.85	0.79	31536.01	-18.74	-19.20
$5_{14} \rightarrow 6_{15}$	32030.02	2.64	2.23	32005.33	231.68	231.64
$6_{16} \rightarrow 7_{17}$	36278.47	-0.38	-0.27	36278.82	-272.62	-274.23
$6_{06} \rightarrow 7_{07}$	36797.69	0.94	0.92	36783.54	-21.82	-22.52
$6_{15} \rightarrow 7_{16}$	37365.89	2.40	2.03	37337.16	207.98	208.39

frequencies are slightly erroneous, although $<1 \text{ MHz}$.

Adopting the generally accepted idea of taking over structural and dynamic data from a related molecule to foresee what is to be expected from the microwave spectrum of IV we have applied data from methylketene,^{6,7} thioetene⁸ and methylisothiocyanate.⁹

Assuming a $\text{C}=\text{S}$ distance of 1.554 \AA from thioetene and taking the remaining geometric parameters from methylketene a rigid model of IV with rotational constants $A, B, C = 34768, 2736$ and

2576 MHz was obtained. Thus, groups of lines separated by $B+C = 5312 \text{ MHz}$ are anticipated. When V and VI were pyrolyzed, identical dense groups of lines ca. 5260 apart, separated by almost "empty" $3000\text{--}4000 \text{ MHz}$ regions were observed. Further, replacing the $\text{C}=\text{O}$ force-constant of methylketene (161.7 nN/\AA)⁷ by a $\text{C}=\text{S}$ force-constant of 81.0 nN/\AA ⁹ and using the remaining force-constants for methylketene,⁷ produced predicted in-plane normal vibration frequencies at $168, 573, 803 \dots \text{ cm}^{-1}$. Omitting CH_3 -group torsion, out-of-plane

normal vibration frequencies at 418, 517, 1019... cm^{-1} were estimated (program VIBROT).¹⁰ When considering the great spectral density of the observed m.w. spectra we estimated that assignment of transitions to levels less than 20% populated relative to the ground level (g.l.) would be ambiguous. This means an upper limit of 335 cm^{-1} for the energy of vibrational levels to be considered. Taking the first torsionally excited level at $\nu_t(1) = 140 \text{ cm}^{-1}$ (to be derived) and the lowest non-torsionally excited level at $\nu_b(1) = 157 \text{ cm}^{-1}$ (*vide infra*) we must be prepared to find 7 m.w. spectra: an intense spectrum assignable to IV in the g.l.; two spectra of molecules in states $\nu_t(1)$ and $\nu_b(1)$, one-half as intense; three spectra of molecules in states $\nu_b(2)$, $\nu_t(1) + \nu_b(1)$ and $\nu_t(2)$, all about equally intense and ca. 20% as intense as the g.l. spectrum. Outside the dense spectral regions one can expect the microwave spectrum of isotopic $\text{CH}_3\text{CH}=\text{C}=\text{S}^{34}\text{S}$ (4% abundance) to be observable without difficulty. Nomenclature and abundances are summarized in Table 1.

Moreover, the CH_3 group in IV is expected to cause *A,E* doublets due to hindered internal rotation. Therefore, recordings at widely different square-wave voltage amplitudes are necessary. For transitions of type $J_{K_{-1},K_1} \rightarrow (J+1)_{K_{-1},K_1+1}$ all *E*-components (except for $K_{-1}=0$) and *A*-components for which $K_{-1} > 2$ show first-order Stark effect. They were recorded at 5–10 V/cm or lower. *A*-components of transitions for which $K_{-1} \leq 2$, and *E*-components for which $K_{-1}=0$ show quadratic Stark effect and were usually recorded at several hundred V/cm. The assignments to follow agree with the intensity and Stark effect relations outlined above.

Vapors of V and VI started to break down by pyrolysis at the same oven temperature (700 K), producing identical m.w. spectra at increasing temperature.

ASSIGNMENT

A- and *E*-type, μ_a (Fig. 1) transitions of IV (g.l.) were easily assigned due to their intensity. *A,E* splittings turned out to be small (Table 2) except for $K_{-1}=2$. The IV (g.l.) spectrum is partly overlapped by the weaker spectrum of IV in the $\nu_t(1)$ state in which the *A,E* splittings are much larger (Table 2). The observed *A,E* splittings of these two spectra were reproduced by using an available program¹¹ SEM-4, assuming a barrier to internal rotation of 435 cm^{-1} with $\nu_t(1) = 140 \text{ cm}^{-1}$ and $\nu_t(2) = 256 \text{ cm}^{-1}$. The assumed geometry of IV was as above except for a small change of CH_3 group geometry, necessary to introduce when using SEM-4 (assumed C–H distances 1.083 \AA , assumed C(3)C(4) H angles = 111.1° (Fig. 1), inertial moment about C(3)–C(4) = 3.087 u \AA^2).

Rotational and distortion constants for IV (g.l.) and $\nu_t(1)$ as obtained by an available ROTFIT program¹² are given in Table 3. An estimated value of the inertial defect, I.D. = $I_c - I_b - I_a = -2.867 \text{ u \AA}^2$ was used throughout, based on a vibrational contribution of 0.220 u \AA^2 from the vibrational calculation above,⁷ taking I.D. = -3.087 (methyl group contribution) + $0.220 = -2.867 \text{ u \AA}^2$. Within limits ($\pm 0.3 \text{ u \AA}^2$) this *ad hoc* choice of I.D. has practically no influence on *B,C*, Δ_{JK} and Δ_J , but it fixes *A* under stated conditions. The value of *A* is of some interest to the final molecular models of IV, but of highest importance for precise predictions of possible μ_b transitions in the m.w. spectrum.

Likewise, the $\nu_b(1)$ spectrum is partly overlapped by the weaker spectrum $\nu_b(1) + \nu_t(1)$. It turned out that the *A,E* splittings for the $\nu_b(1)$ spectrum were of the same order of magnitude as for IV (g.l.) and that the *A,E* splittings for the $\nu_b(1) + \nu_t(1)$ spectrum were of the same order of magnitude as for $\nu_t(1)$. Also, the

Table 3. Rotational constants *A*, *B* and *C* (MHz) and distortion constants Δ_J and Δ_{JK} (kHz) of methylthioketene (^{32}S) in its ground level, IV (g.l.), of 5-vibrationally excited levels (as defined in Table 1) and of methylthioketene (^{34}S) in its ground level, IV* (g.l.), all based on *A*-type μ_a -transitions.

	<i>A</i> ^a	<i>B</i>	<i>C</i>	<i>B</i> + <i>C</i>	Δ_J	Δ_{JK}
IV (g.l.)	35528(7)	2708.362(21)	2552.969(22)	5261.331	0.39(14)	–46.55(30)
$\nu_t(1)$	36303(11)	2705.158(35)	2554.038(36)	5259.196	0.91(29)	–134.7(1.9)
$\nu_b(1)$	34819(7)	2717.566(24)	2557.390(24)	5274.956	0.24(20)	–46.79(42)
$\nu_b(1) + \nu_t(1)$	35736(7)	2713.904(28)	2558.964(31)	5272.868	0.82(28)	–134.6(1.4)
$\nu_b(2)$	34158(3)	2726.599(14)	2561.738(16)	5288.337	0.22(13)	–34.09(30)
$\nu_t(2)$	31932(8)	2732.985(44)	2553.994(43)	5286.979	–0.86(41)	340.0(9)
IV* (g.l.)	35449(4)	2639.524(20)	2491.327(20)	5130.851	1.08(18)	–45.79(21)

^a Inertial defect $I_c - I_a - I_b = -2.867 \text{ u \AA}^2$ assumed. Absolute values of the *A* constants dependent on this assumption.

m.w. spectra of molecules in states $v_b(2)$ and $v_t(2)$ are partly overlapping. The A, E splittings for $v_b(2)$ were small. The lines of $\text{CH}_3\text{CH}=\text{C}=\text{}^3\text{S}$ were observed in-between dense regions and were easy to assign. Rotational and distortion constants of the seven species investigated are summarized in Table 3. There is good consistence between the distortion constants Δ_{JK} and Δ_J for IV (g.l.), $v_b(1)$, $v_b(2)$ and $\text{CH}_3\text{CH}=\text{C}=\text{}^3\text{S}$, all without torsional excitation. Further, a calculation by the force-constant method⁷ gave $\Delta_{JK} = -49.8$ kHz and $\Delta_J = 0.86$ kHz in fair agreement with the m.w. determination. The agreement between the distortion constants for $v_t(1)$ and $v_t(1) + v_b(1)$ is noteworthy, both states involving one torsional quantum. A change of sign of Δ_{JK} occurs for the $v_t(2)$ state. An interpretation will not be given here.

The quoted value of $v_b(1) = 157 \text{ cm}^{-1}$ was determined by relative intensity measurements of two E -type transitions ($4_{13} \rightarrow 5_{14}$) of IV (g.l.) at 26689.76 MHz and of molecules in the $v_b(1)$ state at 26769.76 MHz using a rarely occurring opportunity to compare spectral lines with controlled and experimentally quite similar Stark patterns. An average of 6 intensity measurements for each transition gave $v_b(1) = 157 \pm 5 \text{ cm}^{-1}$ consistent with the value of 168 cm^{-1} obtained by the force-field method.⁷

DIPOLE MOMENT. μ_b -TRANSITIONS

The dipole moment (DPM) of IV was estimated as reported here and measured to support the identification of IV as methylthio ketene and to provide information on the orientation of the DPM in the molecular frame.

For ketene and methylketene the size and direction of their DPM's, \bar{P}_K and \bar{P}_{MK} , are known. $\bar{P}_K = 1.414$ Debye (D),¹³ forming an angle of 0° , $\bar{P}_{MK} = 1.79 \text{ D}$ ⁶ forming an angle of 8° with the $>\text{C}=\text{C}=\text{O}$ chain. Thus, the equation $\bar{P}_K + \bar{P}_M = \bar{P}_{MK}$ is easily solved for $\bar{P}_M = 0.44 \text{ D}$, forming an angle of 35° with the $>\text{C}=\text{C}=\text{O}$ chain. Our final

model (*vide infra*) of IV was now placed in its inertial system (Fig. 1). $\bar{P}_M = 0.44 \text{ D}$ was taken over forming an angle of 35° with the (supposed) linear $>\text{C}=\text{C}=\text{S}$ chain. The known DPM of thio ketene, $\bar{P}_{TK} = 1.02 \text{ D}$,⁸ is inserted along the $>\text{C}=\text{C}=\text{S}$ chain of IV. \bar{P}_{MTK} , the DPM of IV, follows from $\bar{P}_{MTK} = \bar{P}_M + \bar{P}_{TK} = 1.40 \text{ D}$ with inertial axes components $\mu_a = 1.40 \text{ D}$ and $\mu_b = 0.10 \text{ D}$.

In our microwave spectra lines suitable for Stark lobe measurements are rare. For example, all A -type lines from IV (g.l.) have nearby E -type components. An A -type, Stark identified $3_{12} \rightarrow 4_{13}$ transition at 21050.56 MHz associated with $v_t(2)$ was finally chosen because of its isolated position with no nearby E -components and no irrelevant Stark lobes. As documented in Table 4, $\mu_a[v_t(2)] = 1.54 \text{ D}$. The ground level DPM must be close to this since vibrational excitation is unlikely to change the DPM substantially.¹⁵ The agreement between estimated and measured DPM is satisfactory.

Regions with few, scattered lines such as 32.6–36.3 GHz and 37.6–39.6 GHz were scanned in search of μ_b -transitions. A Q -line series of dominant intensity for a predicted μ_b spectrum within 20–40 GHz is expected ($J_{OJ} \rightarrow J_{1,J-1}$; $J = 1-12$), independent of the adopted value of the rotational constant.

A of Table 3, the spacing of these transitions, but not their precise positions can be precalculated, taking B and C from Table 3. None of our experimental "scattered" lines could be fitted with the predicted spacings in agreement with our estimate of $\mu_b/\mu_a = 0.07$, the μ_b transitions being too weak to be observed by us.

MOLECULAR MODELS

The well-defined rotational constants B and C of IV (g.l.) and of $\text{CH}_3\text{CH}=\text{C}=\text{}^3\text{S}$ (Table 3) contain structural information under stated assumptions. Throughout, we shall assume a methyl group

Table 4. Stark lobe shifts $\Delta\nu$ (MHz) of A -type transition $3_{12} \rightarrow 4_{13}$ at 21501.56 MHz assigned to the 2nd torsionally excited level, $v_t(2)$ of methylthio ketene. Field F in V/cm. M = 'magnetic' quantum number. Computer program STARK.¹⁴ Calculated dipole moment μ_a (Debye units).

F	645	699	753	806	860	914	968	1032	1290	1419	1548
M	3	3	2	2	2	2	2	2	1	1	1
$-\Delta\nu$	10.6	11.7	6.7	7.5	8.7	9.4	10.5	11.7	5.7	6.7	7.7
μ_a	1.55	1.51	1.56	1.54	1.56	1.52	1.52	1.51	1.56	1.54	1.51
$\langle \mu_a \rangle$						1.54					

Table 5. Calculated geometric parameters for 3 rigid models common to $\text{CH}_3\text{CH}=\text{C}=\text{}^{32}\text{S}$ and $\text{CH}_3\text{CH}=\text{C}=\text{}^{34}\text{S}$ compared to experimental rotational constants ${}^{32}\text{A}_0$, ${}^{32}\text{B}_0$, ${}^{32}\text{C}_0$ and ${}^{34}\text{A}_0$, ${}^{34}\text{B}_0$, ${}^{34}\text{C}_0$ (MHz). Distances in Å, angles in degrees.

Species	Geometric parameters			
	C=S	C=C	C-C	$\angle(\text{C}-\text{C}=\text{C})$
M_1	1.5576	1.3163	1.518 ^a	122.97
M_2	1.5520	1.3321	1.508	122.60 ^a
M_3	1.5627	1.3140 ^b	1.515	122.90
Calculated rotational constants				
	A	B	C	
$\text{CH}_3\text{CH}=\text{C}=\text{}^{32}\text{S}$				
M_1	34992	2708.3396	2552.9733	
M_2	34989	2708.2733	2552.9023	
M_3	34992	2708.3196	2552.9830	
${}^{32}\text{A}_0, {}^{32}\text{B}_0, {}^{32}\text{C}_0$	35528	2708.362	2552.969	
$\text{CH}_3\text{CH}=\text{C}=\text{}^{34}\text{S}$				
M_1	34911	2639.5249	2491.3293	
M_2	34911	2639.4545	2491.2636	
M_3	34912	2639.4073	2491.2277	
${}^{34}\text{A}_0, {}^{34}\text{B}_0, {}^{34}\text{C}_0$	35449	2639.524	2491.327	

^aTaken from the 'r_s' structure of methylketene. ^bTaken from the 'r_s' structure of thioketene.⁸

geometry as indicated under ASSIGNMENT and oriented as shown in Fig. 1. One further, assumed geometric parameter will fix the three remaining geometric parameters of IV, reproducing *B* and *C* and leaving *A* with a so far acceptable error (Table 5). None of the calculated bond lengths and the valence angle of the new molecule are of unexpected magnitude.

DISCUSSION

The carbon atom scrambling which occurs when thioketene is formed from 1,2,3-thiadiazole has, therefore, its possible analogue when methylthioketene is formed from either 4- or 5-methyl-1,2,3-thiadiazole supporting the view that a three-membered ring intermediate, $\text{CH}_3-\text{C}=\text{CH}-\text{S}$, or methyl-thi-irene(VII), might exist. Since we know that our weak, unidentified lines are not μ_b -lines of methylthioketene we cannot exclude that these lines are due to VII. On the other hand, it has proved impossible for us to confirm it on the existing rather thin evidence. The same type of argument holds for VIII, IX and X, but not for XI (Fig. 2) for which ground-state rotational constants have been given.¹⁶ A rigid rotor spectrum was calculated and shown to be unable to explain the weak lines not attributable to methylthioketene.

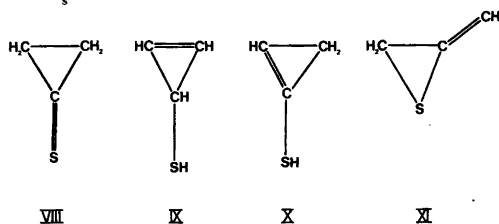


Fig. 2. Three-membered ring isomers of acyclic methylthioketene, VIII–XI. Only XI is known experimentally.¹⁶

In addition to the cyclic isomers of Fig. 2 there are several (XII–XVI) acyclic isomers of methylthioketene such as $\text{CH}_3-\text{S}-\text{C}\equiv\text{CH}$ (XII),¹⁷ $\text{CH}_3-\text{C}\equiv\text{C}-\text{SH}$ (XIII), $\text{CH}_2=\text{CH}-\text{CH}=\text{S}$ (XIV),⁸ $\text{CH}_2=\text{C}=\text{CHSH}$ (XV) and $\text{CH}\equiv\text{C}-\text{CH}_2\text{SH}$ (XVI).¹⁸ It followed from Refs. 17, 8 and 18 that our weak, non-assigned lines could not be associated with XII, XIV or XVI. The expected m.w. spectra of XIII and XV would be of near-prolate top type. For both molecules an appreciable μ_a DPM component must exist which would result in accumulation of m.w. lines as for methylthioketene. This was not observed.

During pyrolysis two hydrogens at adjacent atoms are often lost.⁵ Thus, $\text{CH}_2=\text{C}=\text{C}=\text{S}$ and $\text{CH}\equiv\text{C}-\text{CH}=\text{S}$ might be formed, but these species are not among our products for the reason given for XIII and XV.

Acknowledgements. Thanks are due to G. O. Sørensen, N. W. Larsen and Th. Pedersen of this laboratory for permission to use their computer programs ROTFREKVEN, ROTFIT, VIBROT, STARK (G.O.S.) and SEM-4. The Danish Research Council for Natural Sciences has supported this work. Stud.scient. Niels Arnt Kristiansen was helpful in part of this work.

REFERENCES

1. Bak, B., Nielsen, O. J., Svanholt, H., Holm, A., Toubro, N. H., Krantz, A. and Lauren, J. *Acta Chem. Scand. A* 33 (1979) 161.
2. Krantz, A. and Lauren, J. *J. Am. Chem. Soc.* 99 (1977) 4842.
3. Raap, R. and Micetich, R. G. *Can. J. Chem.* 46 (1968) 1057.
4. Wolff, L. *Justus Liebigs Ann. Chem.* 333 (1904) 1.
5. Bak, B., Larsen, N. W. and Svanholt, H. *Acta Chem. Scand. A* 31 (1977) 755.
6. Bak, B., Christiansen, J. J., Kunstmann, K., Nygaard, L. and Rastrup-Andersen, J. *J. Chem. Phys.* 45 (1966) 883.
7. Nicolaisen, F. *Unpublished result. This laboratory.*
8. Georgiou, K., Kroto, H. W. and Landsberg, B. M. *J. Mol. Spectrosc.* 77 (1979) 365.
9. Lett, R. G. and Flygare, W. H. *J. Chem. Phys.* 47 (1967) 4730.
10. Sørensen, G. O. *Program VIBROT* (available). *This laboratory.*
11. Larsen, N. W. and Pedersen, T. *Program SEM-4* (available). *This laboratory.*
12. Sørensen, G. O. *Program ROTFIT* (available). *This laboratory.*
13. Johnson, H. R. and Strandberg, M. W. P. *J. Chem. Phys.* 20 (1952) 687.
14. Sørensen, G. O. *Program STARK* (available). *This laboratory.*
15. Gordy, W. and Cook, R. L. *Microwave Molecular Spectra*, Wiley, New York 1970.
16. Block, E., Penn, R. E., Ennis, M. D., Owens, T. A. and Shin-Liang Yu, *J. Am. Chem. Soc.* 100 (1978) 7436.
17. den Engelsen, D. *J. Mol. Spectrosc.* 22 (1967) 426; 30 (1969) 474.
18. Mirri, A. M., Scappini, F., Cervellati, R. and Favero, P. G. *J. Mol. Spectrosc.* 63 (1976) 509.

Received April 30, 1980.