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THE STRUCTURE OF TRICARBON OXIDE SULFIDE, O=C=C=C=S, AS A FUNCTION OF THE VIBRATIONAL QUANTUM NUMBER v_7, DETERMINED BY THE ISOTOPIC SUBSTITUTION METHOD*

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The molecular structure of tricarbon oxide sulphide (3-thioxo-1,2-propadiene-1-one), has been determined by the substitution method using the rotational constants of five isotopic species. Since the lowest-lying bending mode ν_7 in C_3OS is at 82.6 cm^{-1} the vibrational dependence of the molecular structure on this particular mode could be determined. By removing the vibrational dependence of the molecular structure on ν_7 an effective equilibrium structure was obtained:

$$\mathrm{O} \overset{}{=\!=\!=} \mathrm{C} =\!=\!= \mathrm{C} =\!=\!= \mathrm{C} =\!=\!= \mathrm{S}$$
$$1.1343\ \text{Å} \quad 1.2696\ \text{Å} \quad 1.2540\ \text{Å} \quad 1.5825\ \text{Å}.$$

An interpretation of the pronounced vibrational dependence of the molecular structure on the excitation of the bending mode ν_7 is presented in the light of the stretch-bend interaction introduced by Bunker in the semi-rigid bender analysis of the quasilinear molecule carbon suboxide, O=C=C=C=O.

1. Introduction

The molecule 3-thioxo-1,2-propadiene-1-one, O=C=C=C=S, has seven fundamental vibrational modes [1]. The four stretching vibrations ν_1, ν_2, ν_3 and ν_4 belong to the symmetry species Σ^+, while the three bending modes ν_5, ν_6, and ν_7 are twofold degenerate and belong to the symmetry species Π. Originally O=C=C=C=S was investigated in order to determine whether it belongs to the group of linear molecules or to the exotic group of quasilinear molecules such as O=C=C=C=O [2]. Microwave experiments revealed beyond doubt that O=C=C=C=S has a spectrum typical of a linear molecule with the lowest-lying bending mode ν_7 at 82.6 cm^{-1} [2, 3, 4]. This bending mode is well separated from all the other normal modes [1] and can be described successfully by the model of a harmonic two-dimensional isotropic oscillator [4]. This finding was of course in sharp contrast to the complex spectral behaviour of O=C=C=C=O which is almost half-way between a linear and a bent molecular model [5, 6].

The energy levels of the ν_7 vibrational manifold are highly populated at room temperature and the rotational lines arising from molecules in these vibrational levels

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* Dedicated to Prof. I. Kovács on his 70th birthday

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can be observed for the various isotopic species in natural abundance except for the species containing ^{18}O. In this paper we report measurements on these isotopic species and a molecular structure derived using Kraitchman's substitution method. This method has been used to determine the molecular structure as a function of the excitation of the lowest-lying bending mode ν_7. Therefore, an approximate equilibrium configuration of the O=C=C=C=S molecule can be derived by eliminating the effects of ν_7 upon the molecular structure.

2. Experimental procedures

Samples of C_3OS were prepared by the reaction of C_3O_2 with P_4S_{10} as described by Winnewisser et al [2, 3]. Measurements of rotational transitions for the various isotopically substituted species in natural abundance were carried out with a Hewlett-Packard microwave spectrometer model MRR 8460 A. All measurements were conducted in the frequency band from 26.5 GHz to 40 GHz. The following isotopic species of tricarbon oxide sulfide have been measured:

$^{16}O{=}^{12}C{=}^{12}C{=}^{12}C{=}^{32}S$	92.26%
$^{16}O{=}^{12}C{=}^{12}C{=}^{12}C{=}^{34}S$	4.22%
$^{16}O{=}^{12}C{=}^{12}C{=}^{13}C{=}^{32}S$	1.107%
$^{16}O{=}^{12}C{=}^{13}C{=}^{12}C{=}^{32}S$	1.107%
$^{16}O{=}^{13}C{=}^{12}C{=}^{12}C{=}^{32}S$	1.107%.

The lines of the ^{18}O-substituted species could not be observed in natural abundance. The relative intensities of the observed rotational lines of the above-mentioned isotopic species relative to some lines arising from excited vibrational states of the main species are shown in Fig. 1 for the ^{34}S-containing species and in Fig. 2 for the ^{13}C-containing species. All measurements were carried out at room temperature and at a pressure of 0.010 mbar. Since C_3OS is rather sensitive to the presence of water vapour in the absorption cell, we conditioned the cell for several hours with C_3O_2, a procedure which removed all traces of water very effectively.

3. Spectral data and their reduction to the molecular structure

a) Spectral data and molecular constants

In a previous communication [3] the reduction of the spectral data for the main isotopic species $^{16}O{=}^{12}C{=}^{12}C{=}^{12}C{=}^{32}S$ to the rotational and centrifugal distortion constants was discussed in detail. The Hamiltonian used there was originally derived by Nielsen [7, 8] and Amat and Nielsen [9]. It rests on three assumptions:

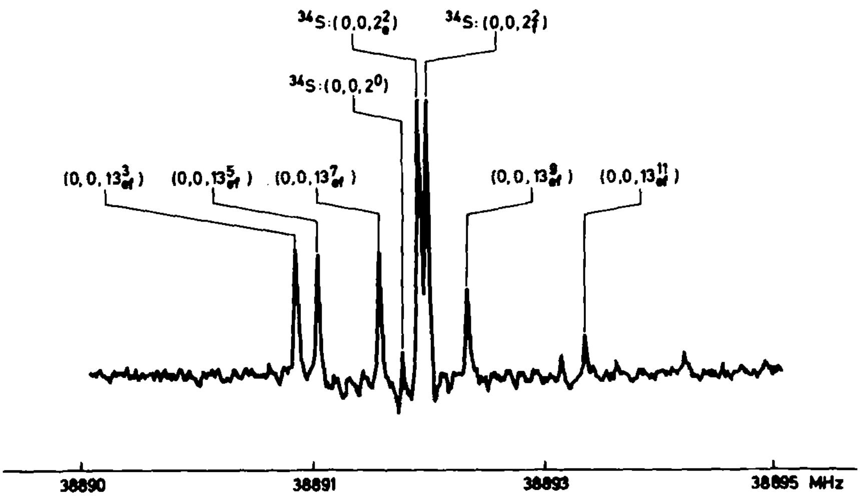

Fig. 1. Recorder trace of rotational lines of the $J=14 \leftarrow 13$ transition of $^{16}O=^{12}C=^{12}C=^{12}C=^{34}S$ molecules in the vibrational state $v_7=2$ in the region of highly excited vibrational satellite lines of the parent species

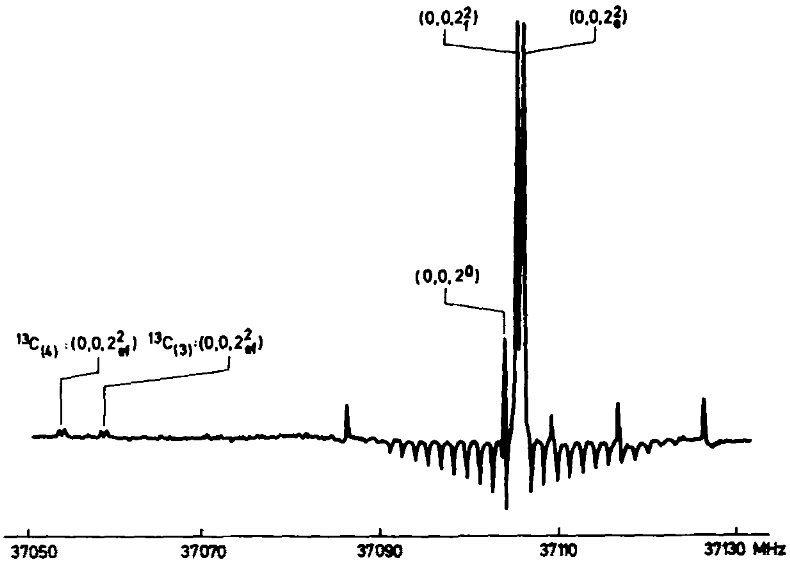

Fig. 2. Recorder trace of part of the $J=13 \leftarrow 12$ rotational transition showing absorption lines from vibrational state $v_7=2$ of the $^{16}O_{(1)}=^{12}C_{(2)}=^{12}C_{(3)}=^{13}C_{(4)}=^{32}S_{(5)}$ and $^{16}O_{(1)}=^{12}C_{(2)}=^{13}C_{(3)}=^{12}C_{(4)}=^{32}S_{(5)}$ isotopic species and of the parent species

1) The equilibrium structure of the molecule is linear. 2) The amplitudes of the normal modes of vibration are small and 3) the potential function associated with each of the bending modes of the molecule may be presented by a two-dimensional isotropic harmonic oscillator with slight anharmonicity. It was found that all these assumptions hold well for C_3OS [3]. Therefore, the spectroscopic constants of all the isotopic species were determined by using the well-known relationship for the rotational energies [3].

$$E_{Rot}/hc = [B_v + \gamma_{l_t l_t} l_t^2] [J(J+1) - l^2] - D_v [J(J+1) - l^2]^2 , \tag{1}$$

with

$$B_v = B_e^* - \alpha_t (v_t + 1) + \gamma_{tt} (v_t + 1)^2 , \tag{2}$$

$$D_v = D_e^* + \beta_t (v_t + 1) , \tag{3}$$

where

B_v = rotational constant for a given vibrational state;
D_v = centrifugal distortion constant;
$\alpha_t, \beta_t, \gamma_{tt}$ = rovibrational interaction constants for the t-th normal mode;
$\gamma_{l_t l_t}$ = rovibrational interaction constant;
B_e^*, D_e^* = effective equilibrium spectroscopic constants which include the zero point vibrational contributions of all normal modes except ν_7;
v_t = vibrational quantum number of the t-th normal mode;
l = sum of the vibrational angular momentum quantum numbers which is in this case $l = l_t$;
J = quantum number of the total angular momentum.

It should be pointed out that only the well separated low-lying bending mode ν_7 is considered in the above expansion. Therefore, only effective equilibrium spectroscopic constants which include the zero point vibration contributions of the other six normal modes can be determined, and hence an effective equilibrium structure. When the ν_7 vibrational mode is considered, the rotational constants can be determined by

$$B_v = \frac{\nu_{obs}}{2(J+1)} + 2D_v [(J+1)^2 - l^2] - \gamma_{l_7 l_7} l_7^2 . \tag{4}$$

The effects of l-type resonance can be accounted for by using the effective centrifugal distortion constant, D_{vl}, obtained for each component separately, as discussed in [4]. Most of the constants appearing in Eqs. (1—3) can be determined for the isotopic species using the frequencies summarized in Table I, which also includes the B_v values. The expansion coefficients are given in Table II. However, for four isotopic species only one rotational transition could be observed due to experimental difficulties. Therefore, the D_v values were assumed to be equal to those of the parent species (3). In the case of incomplete experimental data for some of the isotopic species the higher order

Table I

Observed frequencies and the corresponding rotational constants O=C=C=C=S isotopic species in various states of the bending mode ν_7 as well as the rotational and centrifugal distortion constants of the parent molecule

Isotopic species (1) (2) (3) (4) (5)	(v_5^l, v_6^l, v_7^l)		$(0,0,0^0)$	$(0,0,1_e^1)$	$(0,0,1_f^1)$	$(0,0,2^0)$	$(0,0,2_e^2)$	$(0,0,2_f^2)$
$^{16}O={}^{12}C={}^{12}C={}^{12}C={}^{32}S$	J:	$D_{vl}/Hz^{a)}$	43.98(91)	53.71(1.12)	56.15(1.30)	142.28(91)	−14.49(1.32)	71.5(1.76)
	3, . . ., 13	B_v/MHz$^{b)}$	1413.9124(3)	1420.5481(4)		1427.1457(3)$^{c)}$	1427.1448(5)$^{c)}$	
$^{16}O={}^{12}C={}^{12}C={}^{12}C={}^{34}S$	$J+1\leftarrow J$	ν_{obs}/MHz	38559.312	38716.298	38762.954	38917.648	38919.966	38919.240
	$14\leftarrow 13$	B_v/MHz$^{b)}$	1377.1355	1383.5737		1389.9717$^{c)}$	1389.9718$^{c)}$	
$^{16}O={}^{13}C={}^{12}C={}^{12}C={}^{32}S$	$J+1\leftarrow J$	ν_{obs}/MHz	39202.689	39262.940	39411.006	——	39571.110	39570.326
	$14\leftarrow 13$	B_v/MHz$^{b)}$	1400.1133	1406.6932			1413.2256	
$^{16}O={}^{12}C={}^{13}C={}^{12}C={}^{32}S$	$J+1\leftarrow J$	ν_{obs}/MHz	36719.990	36865.972	——	37058.442	37060.392	37059.712
	$13\leftarrow 12$	B_v/MHz$^{b)}$	1412.3222	1418.8709$^{d)}$		1425.3728$^{c)}$	1425.3726$^{c)}$	
$^{16}O={}^{12}C={}^{12}C={}^{13}C={}^{32}S$	$J+1\leftarrow J$	ν_{obs}/MHz	36717.194	36864.588	——	37053.636	37055.792	37054.994
	$13\leftarrow 12$	B_v/MHz$^{b)}$	1412.2146	1418.7935$^{d)}$		1425.1879$^{c)}$	1425.1874$^{c)}$	

a) Effective centrifugal distortion constants taken from Table 3 in Ref. [4].

b) Determined from the frequencies listed and the D_{vl} values of the parent species according to Eq. (4). The $\gamma_{l_7 l_7}$ values were taken from Table II.

c) For the structural calculations the average value of the reported B_v has been used.

d) l-type doubling constant of parent molecule assumed.

Table II

Rotational constant B_e^* (see Text) and the rovibrational interaction constants used to derive it for the parent molecule and isotopic species of O—C—C—C—S

Isotopic species (1) (2) (3) (4) (5)	B_e^*/MHz[a]	α_7/MHz	γ_{77}/MHz	$\gamma_{l_7 l_7}(v_7=1)$/MHz	$\gamma_{l_7 l_7}(v_7=2)$/MHz
^{16}O—^{12}C—^{12}C—^{12}C—^{32}S	1407.2133	−6.7202	−0.02506	0.00580	0.00635
	±0.0070	±0.0041	±0.00050	±0.00006	±0.00011
^{16}O—^{12}C—^{12}C—^{12}C—^{34}S	1370.6572	−6.4984	−0.02005	0.00545	0.00625
^{16}O—^{12}C—^{12}C—^{13}C—^{32}S	1405.6531	−6.5866	[−0.02506]	[0.00580]	0.00730
^{16}O—^{12}C—^{13}C—^{12}C—^{32}S	1405.7219	−6.6254	[−0.02506]	[0.00580]	[0.00585]
^{16}O—^{13}C—^{12}C—^{12}C—^{32}S	1393.4780	−6.6577	[−0.02506]	[0.00580]	[0.00635]

[a] In calculating the effective equilibrium rotational constants B_e^* only a second order polynomial for the parent molecule data was used in order to be consistent with the limited data available for the isotopic species. Therefore, the entries for the parent species deviate slightly from the values reported in Tables 3 and 4 in Ref. [3].

expansion coefficients were also taken to be equal to those of the parent species (3). They are indicated in square brackets in Table II. The B_v values in Table I were determined accordingly.

b) Molecular structure

Since neither experimental nor theoretical evidence suggest nonlinearity of the $O_{(1)}=C_{(2)}=C_{(3)}=C_{(4)}=S_{(5)}$ molecule, a linear molecular structure was assumed. The standard substitution coordinates $z_s(i)$ [10, 11, 12] for four of the five atoms, $C_{(2)}$, $C_{(3)}$, $C_{(4)}$ and $S_{(5)}$ could be directly determined by the use of Kraitchman's equation [10]

$$[z_s(i)]^2 = \frac{I'_z - I_z}{\mu_i}, \tag{5}$$

where i represents the index of the individual nuclei, and I'_z and I_z are the effective moments of inertia in a given vibrational state for the isotopically substituted species and the parent species, respectively. The reduced mass is expressed by

$$\mu_i = \frac{M \Delta m_i}{M + \Delta m_i}, \tag{6}$$

where Δm_i is the change of mass of the i-th nucleus induced by the isotopic substitution, and $M = \Sigma_i m_i$.

The substitution coordinate $z_s(i)$ relative to the principal axis system in the parent species for the atoms substituted seem to be well determined using the criteria of Watson [12] and are given in Table III. However, due to the nearly equal magnitude of the coordinates of the carbon atoms $C_{(3)}$ and $C_{(4)}$ relative to the center of mass, additional information is needed to unambiguously assign the two ^{13}C species to the observed spectrum. This information can be supplied by two methods.

The first method was used successfully in the structure determination of fulminic acid, HCNO, by Winnewisser and Bodenseh [13]. It consists of using the substitution coordinates of the other nuclei and the moment of inertia of the parent molecule to determine the oxygen coordinate in the ground state, which is found to be −3.0249 Å in O=C=C=C=S. Together with the substitution coordinates of the remaining nuclei the center-of-mass condition can be used to discriminate between the two assignment possibilities of the carbon atoms $C_{(3)}$ and $C_{(4)}$. The possible sign combinations of the coordinates give

$O_{(1)}$=	$C_{(2)}$=	$C_{(3)}$=	$C_{(4)}$=	$S_{(5)}$	$\Sigma_i m_i z_i$/amuÅ
−	−	−	+	+	−0.5796
−	−	+	−	+	−0.9204

Since the center of mass condition requires $\sum_i m_i z_i = 0$, the first sign combination fulfills this condition more satisfactorily. Therefore, the assignment of the ^{13}C spectra to the proper ^{13}C isotopic species has been made with the first sign combination.

In view of the fact that the second sign combination is within a factor of two of the first sign combination as far as $\sum_i m_i z_i$ is concerned, it seems advisable to invoke a second method of determining the proper assignment of the ^{13}C-spectra of C_3OS. Therefore, the first moment equation or center-of-mass condition was introduced directly to determine $z_5 \simeq z_s(5)$ as has been found reliable in the structure determination of many molecules:

$$\sum_i m_i z_s(i) = 0 . \tag{7}$$

Depending which sign combination was chosen for the carbon nuclei $C_{(3)}$ and $C_{(4)}$, two oxygen center-of-mass coordinates were obtained designated with Roman numerals I and II in Table III. From these coordinates two slightly different molecular structures can be calculated. For the first set the coordinates of the nuclei in the principle axis system of the parent species are given in Fig. 3, for the effective equilibrium state and the ground vibrational state. The internuclear distances are also entered in Fig. 3. The second set of coordinates leads to a different molecular structure with a pronounced change in the carbon-oxygen internuclear distance to $r(CO) = 1.1130$ Å. Such a short carbon-oxygen internuclear distance has not previously been reported in the literature [14]. The shortest internuclear distance for the carbon-oxygen bond is found in CO with $r(CO) = 1.1282$ Å as can be seen from Fig. 4. Furthermore, it is expected that the carbon-oxygen bond in C_3OS is similar to that in $O{=}C{=}S$ for which an internuclear distance $r(CO)$ of 1.1572 Å has been reported [14]. From that we conclude that in C_3OS the oxygen-carbon internuclear distance of 1.1343 Å given in Fig. 3 is physically

Table III

Coordinates of the nuclei in $O{=}C{=}C{=}C{=}S$ derived by the substitution method and the center-of-mass condition in various vibrational states of v_7[a)]

	$O_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$S_{(5)}$
$z^*(i)_e/\text{Å}$	I) -3.0238 II) -3.0025	-1.8895	∓ 0.6199	± 0.6341	$+2.2166$
$z(i)_{v_7=0}/\text{Å}$	I) -3.0249 II) -2.9931	-1.8849	∓ 0.6371	± 0.6583	$+2.2128$
$z(i)_{v_7=1}/\text{Å}$	I) -3.0151 II) -2.9929	-1.8799	∓ 0.6513	± 0.6661	$+2.2084$
$z(i)_{v_7=2}/\text{Å}$	I) -3.0241 II) -2.9731	-1.8756	∓ 0.6664	± 0.7004	$+2.2041$

a) The conversion factor $(B \times I)$ was taken to be 5.0539098×10^5 MHz amu Å^2 according to the fundamental constants given in Ref. [18]. The isotopic masses were taken from appendix V in Ref. [19].

more reasonable and hence the molecular structure of C_3OS presented here, derived from the coordinates of set I in Table III, is the most probable and physically meaningful geometrical structure of the molecule.

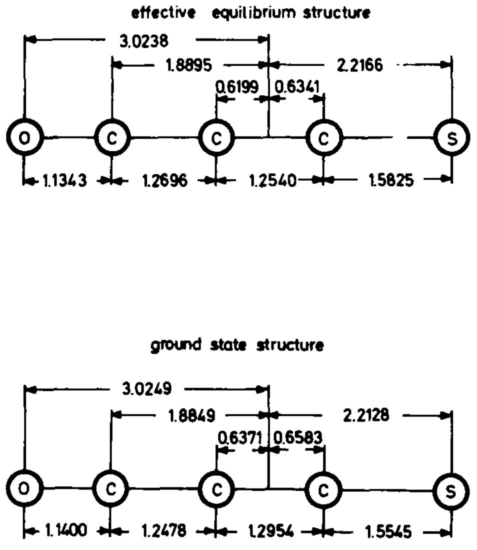

Fig. 3. r_s-coordinates of the nuclei in $O{=}C{=}C{=}C{=}S$ and the internuclear distances in the principle axis system of the parent species given for the effective equilibrium state and the ground vibrational state. Entries in Å units

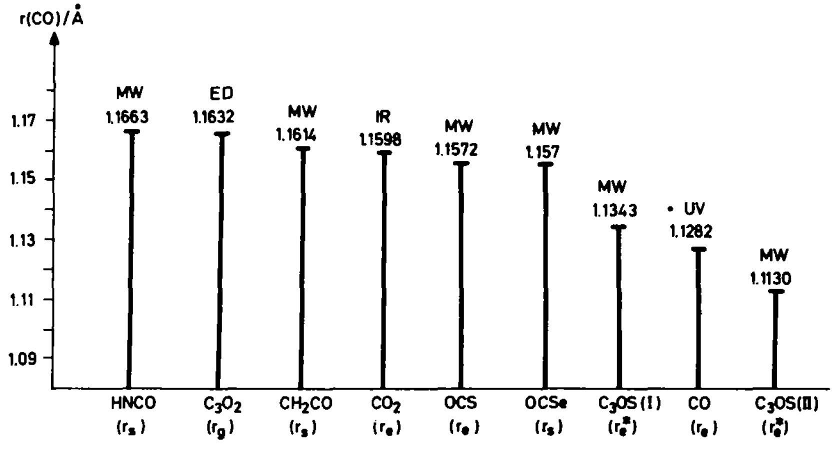

Fig. 4. Comparison of CO internuclear distances determined by various methods in eight selected molecules [14]. The shortest internuclear distance for a carbon-oxygen bond is found in CO. Therefore. the C_3OS structure (I) is assumed to be the physically more meaningful one

4. Discussion

The structures obtained and displayed in Fig. 3 are in a generalized sense r_s structures, which can be assumed to be a good approximation of the r_e structure [15]. This holds especially for the effective equilibrium structure r_e^* where the vibrational contributions of the lowest-lying bending mode $\nu_7 = 82.6\ \mathrm{cm}^{-1}$ could be removed. The zero-point vibrational contributions of the four stretching vibrations and the remaining two bending modes could not be determined due to lack of experimental data. The influence, however, of the dominant bending mode ν_7 upon the structure of the C_3OS molecule in three vibrational states can be seen from the comparison of the structural data and the total length of the molecule. The r_s-structures for the states $v_7 = 0$, $v_7 = 1$ and $v_7 = 2$ must be considered to be projections of the positions of the five nuclei onto the axis of least moment of inertia, the a or z-axis, which will pass through all atoms in the equilibrium configuration. The overall projected length of the molecule decreases slightly from 5.2404 Å in the effective equilibrium state to 5.2282 Å in the second excited state of ν_7. The shrinkage of $\Delta\left[\sum_i r_s(i)\right] = 0.0122$ Å is within the limits predicted by the Morino—Bastiansen shrinkage effect [16] for larger molecules. It is remarkable that $r_s(C_{(3)} - C_{(4)})$ increases as a function of v_7 while the two adjacent internuclear distances $r_s(C_{(2)} - C_{(3)})$ and $r_s(C_{(4)} - S_{(5)})$ decrease in value as can be seen by inspecting Table IV and Fig. 5. The increase of $r_s(C_{(3)} - C_{(4)})$ by $\Delta r_s(C_{(3)} - C_{(4)}) = 0.1128$ Å from the effective equilibrium state to the second excited state must be considered a consequence of ρ-dependence, where ρ is the complement of the bending angle [6]. This ρ-dependence in the form $r_{CC} = r_{CC}^{\mathrm{lin}} + Y_{CC}\rho^2$ was used by Bunker [6] with the coefficient Y_{CC} as an adjustable parameter in his semirigid-bender Hamiltonian treatment of carbon suboxide. He found that the coefficient Y_{CC} is positive so that r_{CC} increases as a function of vibrational excitation of ν_7. In the unsymmetrical molecule O═C═C═C═S the displacement coordinates for the nuclei $C_{(3)}$ and $C_{(4)}$ describing the deformation of the molecule in the ν_7 normal mode are large and antiparallel to the amplitudes for oxygen and sulfur [1]. The amplitude of $C_{(2)}$ is negligibly small. The relatively small changes in the projection of the $r_s(C_{(2)} - O_{(1)})$ internuclear distances as

Table IV
Internuclear distances and total molecular length in Å units of O—C—C—C═S derived using the coordinates in Table III

Vibrational state	$r_s(O_{(1)}—C_{(2)})$	$r_s(C_{(2)}—C_{(3)})$	$r_s(C_{(3)}—C_{(4)})$	$r_s(C_{(4)}—S_{(5)})$	$R = \sum_i r_s(i)$
$v_7 = e^*$	1.1343	1.2696	1.2540	1.5825	5.2404
$v_7 = 0$	1.1400	1.2478	1.2954	1.5545	5.2377
$v_7 = 1$	1.1352	1.2286	1.3174	1.5423	5.2235
$v_7 = 2$	1.1485	1.2092	1.3668	1.5037	5.2282

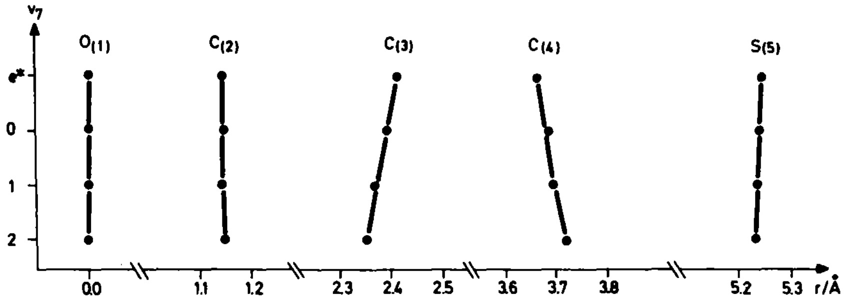

Fig. 5. Dependence of the r_s-coordinates and hence the internuclear distances in C_3OS on the excitation of ν_7. The over-all length of the molecule decreases slightly while the internuclear distance $r(C_{(2)}—C_{(3)})$ decreases and $r(C_{(3)}—C_{(4)})$ increases noticeably as a function of v_7. This effect can be explained by a stretch-bend interaction affecting the two bonds adjacent to the central carbon atom

a function of v_7 indicate that this internuclear distance does not change significantly with the excitation of ν_7. A similar behaviour was found empirically by Bunker [6] for the C—O internuclear distances in carbon suboxide.

From the present data we can conclude that the molecular structure of C_3OS in the excited states of ν_7 is bent with a strong stretch-bend interaction affecting the two bonds about the central carbon atom. If we assume as in C_3O_2 [6] that the two carbon bonds $r(C_{(2)}-C_{(3)})$ and $r(C_{(3)}—C_{(4)})$ are equal in length, then as v_7 and r(C—C) increase, the projection obtained for the corresponding internuclear distance $r_s(C_{(2)}—C_{(3)})$ must decrease and the projection of $r_s(C_{(3)}—C_{(4)})$ onto the linear axis must increase, while the overall length of the molecule shrinks only slightly. This at first surprising result can be shown to be simply due to the mass asymmetry of the molecule.

In Fig. 6 the present effective equilibrium structure of C_3OS is compared with the reported structures of C_3O_2 [14, 6] and C_3S_2 [17].

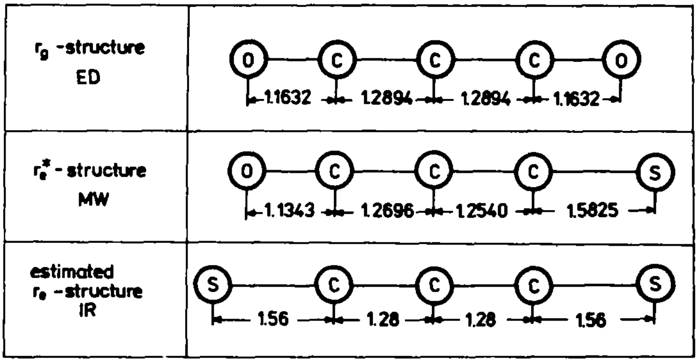

Fig. 6. Comparison of the available molecular structures for C_3O_2 [14], C_3OS and C_3S_2 [17]. Only the effective equilibrium structure of C_3OS is based on the substitution method. Entries in Å units

Some comment should be made concerning the accuracy of the above results. In deriving the molecular constants in Table I the assumption was made that the centrifugal distortion constants for all isotopic species are equal to those of the parent molecule. Due to the smallness of the centrifugal distortion term, this assumption can be safely made. Furthermore the effective r_e^*-structure of C_3OS is probably a good approximation of the real equilibrium structure since the rotation-vibration interaction constants α_s are proportional to $1/\omega_s$ and $\omega_7 \ll \{\omega_5, \omega_6\}$ as well as $\{\omega_5, \omega_6\} \ll \omega_1, \omega_2, \omega_3, \omega_4\}$ [1]. Thus, the larger part of the rotational-vibrational interaction is described by considering the lowest-lying bending mode. The most reasonable estimate of the zero-point contributions of the remaining vibrations is given by the Costain error estimate $\delta r = \pm 0.0012/b_K$ Å where b_K is the value of the Kraitchman coordinate [15]. The errors estimated in this way for the coordinates in Table III range from ±0.0005 Å for the sulfur atom to ±0.002 Å for the central carbon atoms. If we assume that the errors of the coordinates are added or the squares of the errors are added in forming the bond length then the internuclear distances in Table IV have errors of about ±0.0020 Å to ±0.0050 Å.

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References

1. F. M. Nicolaisen and J. Johs. Christiansen, J. Mol. Struct., *52*, 157, 1979.
2. M. Winnewisser and J. Johs. Christiansen, Chem. Phys. Letters, *37*, 270, 1976.
3. M. Winnewisser, E. W. Peau, K. Yamada and J. Johs. Christiansen, Z. Naturforsch., *36a*, 819, 1981.
4. M. Winnewisser and E. W. Peau, Chem. Phys. *71*, 377, 1982.
5. K. Yamada and M. Winnewisser, Z. Naturforsch., *31a*, 139, 1976.
6. P. R. Bunker, J. Mol. Spectr., *80*, 422, 1980.
7. H. H. Nielsen, Phys. Rev., *60*, 794, 1941.
8. H. H. Nielsen, "Molecular Spectra" in Handbuch der Physik 37/1, 173—313, 1959.
9. G. Amat and H. H. Nielsen, J. Mol. Spectr., *2*, 152, 1958; *2*, 163, 1958.
10. J. Kraitchman, Am. J. Phys., *21*, 17, 1953.
11. C. C. Costain, J. Chem. Phys., *29*, 864, 1958.
12. J. K. G. Watson, J. Mol. Spectr., *48*, 479, 1973.
13. M. Winnewisser and H. K. Bodenseh, Z. Naturforsch., *22a*, 1724, 1967.
14. Landolt-Börnstein, "Structure Data of Free Polyatomic Molecules" in Numerical Data and Functional Relationships in Science and Technology, Group II, Volume 7 Springer Verlag, Berlin, 1976.
15. C. C. Costain, Trans. Amer. Cryst. Assoc., *2*, 157, 1966.
16. G. Nagarajan and E. R. Lippincott, J. Chem. Phys., *42*, 1809, 1965.
17. A. O. Diallo, Can. J. Chem., *46*, 2641, 1968.
18. B. N. Taylor, W. H. Parker and D. N. Langenberg, Revs. Mod. Phys., *41*, 375, 1969.
19. W. Gordy and R. L. Cook, "Microwave Molecular Spectra" in Chemical Applications of Spectroscopy, Ed. N. West, Interscience Publishers, John Wiley & Sons, New York, 1970.