Microwave Spectrum of s-Trioxane

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The microwave spectrum of formaldehyde in the ground vibrational state has been extensively studied.[1,2] In order to analyze the microwave spectrum of formaldehyde in the excited vibrational states, however, it is necessary to observe weak spectral lines. *s*-Trioxane is the cyclic trimer of formaldehyde; microwave investigation of this molecule was first started because it was suspected to exist as an impurity in the sample of formaldehyde evolved by heating paraformaldehyde vapor. After making some measurements, this possibility has been eliminated. No trace of *s*-trioxane line was observed in the formaldehyde sample. However, rather strong spectral lines were observed for pure *s*-trioxane, and the spectroscopy has been continued to determine the molecular structure, the dipole moment and the vibration-rotation constants in the excited vibrational states of this molecule.

A preliminary report on the microwave spectrum of this molecule was published by Amble in 1951,[3] but no other work seems to have been reported. The molecular structure of *s*-trioxane has been examined by electron diffraction.[4] There are also vibrational and dipole moment studies of this molecule.[5] These previous works report that the *s*-trioxane molecule is a chair-form symmetric top both COC and OCO angles nearly tetrahedral.

Experimental

s-Trioxane was prepared by heating paraformaldehyde and dilute sulfuric acid in an oil bath.[6] The product was purified by sublimation. A commercially-available sample was also used. Purified *s*-trioxane is a colorless crystalline compound and is stable. The vapor pressure is large enough to observe the spectral lines at room temperature, but measurement at dry-ice temperature was impossible because of the low vapor pressure of the sample. The spectrograph used was a conventional one, with 100 kc. Stark modulation.

Spectrum

s-Trioxane is an oblate symmetric top, and the R-branch transitions, $J=1\leftarrow0$, $2\leftarrow1$ and $3\leftarrow2$, fall in the centimeter-wave region. Although this molecule is rather heavy and has low frequency vibrations, it gives fairly strong spectral lines because of the large dipole moment and so the spectral lines of ^{13}C isotopic species could be observed in the natural abundance. The dipole moment is directed along the axis with the largest moment of inertia, and c-type transitions are observed for the isotopic species.

TABLE I. OBSERVED FREQUENCIES OF *s*-TRIOXANE (IN Mc./sec.)

Transition	Observed frequency
$(^{12}CH_2{}^{16}O)_3$	
$J=1\leftarrow0$	10546.46 ± 0.05
$J=2\leftarrow1$	21092.97
$J=3\leftarrow2$	31639.36
$(^{12}CH_2{}^{16}O)_2(^{13}CH_2{}^{16}O)$	
$3_{30}\leftarrow2_{20}$	31354.0 ± 0.2
$3_{21}\leftarrow2_{11}$	31203.0 ± 1

The observed frequencies are listed in Table I. The assignment of the $3_{30}-2_{20}$ transition was confirmed by the Stark behavior of the line. The $3_{21}-2_{11}$ transition was measured with rather large uncertainty because of the weakness and the large Stark shift of the line. The $3_{31}-2_{21}$ transition could not be separated from the excited vibrational lines of the normal

TABLE II. ROTATIONAL CONSTANTS OF *s*-TRIOXANE

$(^{12}CH_2{}^{16}O)_3$	
$B=$	5273.23 ± 0.01 Mc./sec.
$(^{12}CH_2{}^{16}O)_2(^{13}CH_2{}^{16}O)$	
$A=$	5270.76 ± 0.4 Mc./see.
$B=$	5176.68 ± 0.4 Mc./sec.

1) T. Oka, H. Hirakawa and K. Shimoda, *J. Phys. Soc. Japan*, **15**, 2265 (1960); T. Oka, ibid., **15**, 2274 (1960). T. Oka, and Y. Morino, ibid., **16**, 1235 (1961).
2) K. Takagi and T. Oka, ibid., **18**, 1174 (1963).
3) E. Amble, *Phys. Rev.*, **83**, 210A (1951).
4) M. Kimura and K. Aoki, *J. Chem. Soc. Japan, Pure. Chem. Sec. (Nippon Kagaku Zassi)*, **72**, 169 (1951); W. Shand, *Acta Cryst.*, **3**, 54 (1950); O. Hassel and H. Viervoll, *Acta Chem. Scand.*, **1**, 149 (1947); L. E. Sutton and L. O. Brockway, *J. Am. Chem. Soc.*, **57**, 473 (1935).
5) S. T. Stair, Jr., and J. R. Nielsen, *J. Chem. Phys.*, **27**, 402 (1957); J. C. Decius, W. C. Steele and R. G. Snyder, ibid., **19**, 806 (1951); D. A. Ramsay, *Trans. Faraday Soc.*, **44**, 289 (1948); A. A. Maryott and S. F. Acree, *J. Research Natl. Bur. Standards*, **33**, 71 (1944).
6) J. F. Walker, "Formaldehyde," Reinhold Publishing Corporation, New York (1953).

TABLE III. MOLECULAR STRUCTURE OF *s*-TRIOXANE

	Present work	Amble	Kimura and Aoki	Shand
r(C-O), Å	1.411 ±0.01	1.41	1.42±0.02	1.40±0.02
∠COC	108°10′±1°	109°	110°±2°	112°±3°
∠OCO	111°10′±1°	109°	110°±1°	112°±3°

species. Weak lines with $K=2$ were not observed. The rotational constants have been determined from these frequencies, as Table II shows.

Molecular Structure

If the position of the six hydrogen atoms relative to the carbon atoms and the C_{3v} symmetry are assumed, the molecular structure of *s*-trioxane is expressed by three independent parameters. They have been determined by using the rotational constant, B, of the normal species and A and B of the ^{13}C isotopic species. It was assumed that the hydrogen atoms are attached to the carbon atoms at the tetrahedral angle, with three hydrogen-carbon bonds parallel to the symmetry axis. The carbon-hydrogen distance was assumed to be 1.09±0.005 Å. The coordinate system are taken so that the symmetry axis coincides with the z axis and one carbon atom (C_1) lies in the xz plane (Fig. 1).

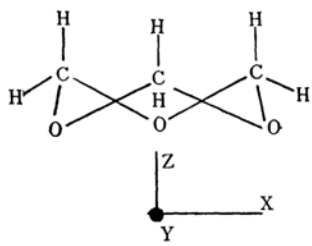

Fig. 1. The *s*-trioxane molecule.

The x and z coordinates of the carbon atom, C_1, have been determined by the substitution method[7] from the formula:

$$z^2_{C_1}=\frac{\Delta I_{aa}}{\mu}\left[1-\frac{\Delta I_{bb}-\Delta I_{aa}}{I_{aa}-I_{cc}}\right]$$

$$x^2_{C_1}=\frac{\Delta I_{bb}-\Delta I_{aa}}{\mu}\left[1+\frac{\Delta I_{aa}}{I_{aa}-I_{cc}}\right] \quad (1)$$

where ΔI_{aa} and ΔI_{bb} are the changes in the moments of inertia due to the isotopic substitution and $\mu=M\Delta C/(M+\Delta C)$, with M the total mass and ΔC the difference between the masses of ^{12}C and ^{13}C. There is no experimental data for I_{cc}, but, since the latter term in the bracket of Eq. 1 is much smaller than one, the value of I_{cc} calculated from a reasonable structure was used.

The z coordinates of the oxygen atoms have been determined from the condition of the center of gravity;

$$m_C z_C+m_O z_O+m_H(2z_C+2/3r)=0 \quad (r=1.09) \quad (2)$$

The x coordinate of the oxygen atom, O_1, is determined from the moment of inertia of the normal species by the formula:

$$I_{bb}=3\,[m_C(x^2_{C_1}/2+z^2_{C_1})+m_O(x^2_{O_1}/2+z^2_{O_1}) +m_H(x^2_{C_1}+2\sqrt{2x_{C_1}}r/3+2z^2_{C_1} +4z_{C_1}r/3+14r^2/9)] \quad (3)$$

The molecular structure thus determined is shown in Table III, together with the previous results.

The uncertainty of the molecular structure was estimated from the probable error of the experimental rotational constants and the uncertainty in the assumed hydrogen parameters. Although the uncertainty in the z coordinate is rather large, it is reduced in the C–O bond length and COC and OCO angles. The COC angle is smaller than the OCO angle by about 3 degrees. The C–O distance is shorter than the corresponding distances in trimethylene oxide (1.449±0.002 Å[8]) and methanol (1.434 Å[9]), but it is close to that of dimethyl ether (1.410±0.003 Å[10]).

Excited Vibrational States

In addition to the spectral lines of *s*-trioxane in the ground vibrational state, many vibrational satellites were observed, as shown in Table IV and Fig. 2. They were found to be the rotational lines of molecules in the excited states of four normal vibrations. Two of them were assigned to the degenerate E species, since they clearly showed l-type doubling. The l-type doubling constants, q_l, were determined from the splitting, as is shown in Table V. These two vibrations come from the COC and OCO bending vibrations, with a strong coupling with the torsional motion. They are named $\nu_E(1)$ and $\nu_E(2)$, as shown in Fig. 2. Since the frequency of $\nu_E(1)$ is

7) J. Kraitchman, *Am. J. Phys.*, 21, 17 (1953).
8) S. I. Chan, J. Zinn and W. D. Gwinn, *J. Chem. Phys.*, 34, 1319 (1961).
9) E. V. Ivash and D. M. Dennison, ibid., 21, 1804 (1953).
10) U. Blukis, P. H. Kasai and R. J. Myers, *J. Chem. Phys.*, 38 2753 (1963).

TABLE IV. OBSERVED FREQUENCIES OF *s*-TRIOXANE IN THE EXCTED VIBRATIONAL STATES (IN Mc./sec.)

Vibrational assignment	$J=1\leftarrow0$	$J=2\leftarrow1$	$J=3\leftarrow2$
$v_E(2)=1$	10553.76	21108.28	31699.4* 31661.95 31623.8*
Ground state	10546.46	21092.97	31639.36
$v_E(1)=1$	10536.17	21086.47* 21072.67 21057.47*	31633.1* 31609.4 31582.8*
$v_E(1)=2$	10526.46	21052.97	31579.3
$v_E(1)=3$	10517.21	21033.65	31550.0
$v_A(1)=1$	10520.73	21040.89	31561.0
$v_A(2)=1$		21025.73	31536.8

Experimental errors for the frequencies of the ground state and $v_E(1)=1$ state are 0.1 Mc./sec. For the weaker transitions except l-type doublets, the experimental errors are 0.6 Mc./sec. For the l-type doublets the experimental errors are larger. It is possible that experimental errors are as large as 2 Mc./sec.

* l-Type doublets

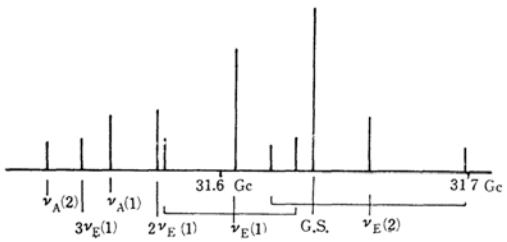

Fig. 2. $J=3\leftarrow2$ transition of *s*-trioxane.

small, the excited states up to $v_E(1)=3$ have been clearly observed. Up to $v_E(1)=3$, there is no indication of the inversion of the ring and the spacings between the satellites are normal.

The other two satellites must be assigned to the totally symmetric A_1 species, since no more low frequency degenerate vibration is expected. One of them, named $\nu_A(1)$, is fairly strong; it is evident that it corresponds to the totally symmetric vibration with the lowest frequency. The other one is rather weak and appears far from the ground state line. It is probable that the line corresponds to another totally symmetric vibration, but we cannot disregard the possibility that this might be due to the $\nu_A(1)+\nu_E(1)$ state. The values of α and q_l for the various vibration are listed in Table V.

TABLE V. MOLECULAR CONSTANTS FOR THE EXCITED STATES (IN Mc./sec.)

Vibrational state	B_v	α_s	q_l
$v_E(2)=1$	5276.95	− 3.72	7.50
$v_E(1)=1$	5268.16	4.95	12.60
$v_E(1)=2$	5263.23		
$v_E(1)=3$	5258.45		
$v_A(1)=1$	5260.25	12.98	
$v_A(2)=1$	5256.28	16.95	

Statistical Spin Weights of the Rotation-vibrational States

The statistical spin weights of the rotational state of symmetric top molecules in the ground vibrational state has been worked out by Wilson.[11] In order to ascertain the statistical spin weights of the rotation-vibrational states of symmetric top molecules, it is necessary to extend his theory.

The rotational subgroup for the molecule with C_{3v} symmetry is C_3, the character table of which is shown in Table VI. Since ^{12}C and ^{16}O are Bose particles with spin zero, the symmetry of the spin-wave function of *s*-trioxane is determined solely from the hydrogen atoms. It can be shown, by directly applying Wilson's method,[11] that the wave function of *s*-trioxane has the symmetry of $24A+20(E_1+E_2)$. The symmetry of the rotational wave function is classified by the value of K as:[11]

TABLE VI. CHARACTER TABLE FOR C_3 SYMMETRY

C_3	E	C_3	C_3^2
A	1	1	1
E_1	1	$e^{2\pi i/3}$	$e^{4\pi i/3}$
E_2	1	$e^{4\pi i/3}$	$e^{2\pi i/3}$

$$K=0 \qquad (2J+1)A$$
$$K=3p\,(p\neq0) \qquad 2(2J+1)A$$
$$K=3p+1 \qquad (2J+1)E_1$$
$$K=3p-1 \qquad (2J+1)E_2$$

In discussing the symmetry of rotation-vibrational states, K is the quantum number for the total angular momentum along the symmetry axis, including the vibrational angular momentum. The symmetry of the vibrational part of the wave function which is multiplied to the rotational wave function can be specified by l, the quantum number of the vibrational angular momentum along the symmetry axis, as follows:[12,13]

$$l=0 \qquad A$$
$$l=3p\,(p\neq0) \qquad 2A$$

11) E. B. Wilson, Jr., *J. Chem. Phys.*, 3, 276 (1935).
12) L. D. Landau and E. M. Lifshitz. "Quantum Mechanics Non-Relativistic Theory," Addison-Wesley Publishing Company, Reading, Massachusetts.
13) J. T. Hougen, *J. Chem. Phys.*, 37, 1433 (1962).

$$1=3p+1 \qquad E_2$$
$$1=3p-1 \qquad E_1$$

The symmetry of the total rotation-vibrational wave function, including spin, can be obtained by taking a direct product of these three parts.

Any operation in the C_3 point group applied to the trioxane molecule corresponds to an even exchange of the nuclei, so the total wave function must be totally symmetric. Thus, the spin weights of the states are derived as shown in Table VII.

TABLE VII. SPIN WEIGHT FOR THE ROTATION-VIBRATIONAL STATES OF *s*-TRIOXANE

	$K=0$	$K=3p$	$K=3p+1$	$K=3p-1$
$l=0$	24	48*	20	20
$l=3p$	48*	96*	40	40
$l=3p+1$	20	40	24*	20
$l=3p-1$	20	40	25	24*

* These states may show doubling if some terms in the vibration rotation Hamiltonian are large.

Low Frequency Vibrations in *s*-Trioxane

Since the spin weight of each quantum state has been obtained, it is possible to estimate the frequencies of the low frequency vibrations *s*-trioxane from the observed relative intensities of the vibrational satellites. The relative intensities were measured for the three transitions, $J=1\leftarrow0$, $2\leftarrow1$ and $3\leftarrow2$, but the data from $J=1\leftarrow0$ gives the most reliable value because of the simple Stark effect. The frequencies thus obtained are listed in Table VIII, together with the infrared results. Because of the rather large experimental errors in the intensity measurement, the uncertain in the vibrational frequencies are large. However, the assignment is in agreement with the infrared results for the lowest three frequencies. The frequency of $\nu_A(2)$ has not yet been definitely determined.

TABLE VIII. LOW FREQUENCY VIBRATIONS OF *s*-TRIOXANE (IN cm^{-1})

	Present work	Stair and Nielsen
$\nu_E(1)$	290 ± 40	307
$\nu_E(2)$	490 ± 30	472
$\nu_A(1)$	470 ± 30	524
$\nu_A(2)$	650 ± 100	748

Thermal Decomposition

In order to test the thermal stability of *s*-trioxane, the absorption cell was heated to about 250°C, but no trace of a formaldehyde line was observed. The observation was accomplished by using the $32_{5,27}\leftarrow32_{5,26}$ transition line of formaldehyde, which comes close to the $J=1\leftarrow0$ line of *s*-trioxane.[1] It can be said, therefore, that *s*-trioxane is stable up to this temperature.

Dipole Moment

The dipole moment of *s*-trioxane has been determined from the second order Stark shift of the $J=3\leftarrow2$ line. This absorption line splits into a triplet when a strong electric field (~1000 V./cm.) is applied. From the spacings of the triplet, the dipole moment has been determined to be 2.07 ± 0.04 Debye. If tetrahedral angles are assumed between the bonds in *s*-trioxane, the dipole moment of this molecule can be experessed by the bond moment along the C–O axis and that along the C–H axis as

$$\mu = 2(\mu_{CO} + \mu_{CH})$$

The experimental value gives $\mu_{CO}+\mu_{CH}=1.04$ Debye. This value should be compared with that of methanol for which $\mu_{CO}+\mu_{CH}=0.88$ Debye.

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