

Microwave Observation of the Vibration–Rotation Spectrum of the Nonpolar C₃O₂ Molecule

The spectrum and structure of the nonpolar quasi-linear molecule carbon suboxide (C₃O₂) have been the subject of numerous recent investigations (1–8). Infrared and Raman spectra were observed and analyzed in these papers. The carbon suboxide molecule has no pure rotational spectrum in the microwave region because of nonpolarity. It has, however, the anomalously low frequency bending vibration ν_7 . The first serious attempt to determine the location of the ν_7 vibration was the investigation of C₃O₂ spectra in gaseous and solid phases in the wavenumber region above 70 cm⁻¹ by Miller and Fateley (1). They concluded on the basis of these studies that the vibrational frequency ν_7 should be lower than 70 cm⁻¹. Carreira *et al.* (2) subsequently observed the far infrared spectrum of gaseous carbon suboxide with a resolution of 0.3 cm⁻¹ in the region 20–80 cm⁻¹. They assigned a feature in their spectrum at 22 cm⁻¹ as the *Q* branch of the vibration–rotation transition ν_7 . More recent papers (5, 6) have established that the energy level of the vibration ν_7 is located 18.2–18.5 cm⁻¹ above the ground vibrational level.

The present paper reports the first direct observation of the vibration–rotation band 00000⁰0⁰1¹ ← 00000⁰0⁰0 of the carbon suboxide molecule. The C₃O₂ spectrum was studied using a submillimeter microwave spectrometer with a backward-wave oscillator and an acoustic detector (9). The carbon suboxide spectrum in the range 545–595 GHz together with assignments of the *Q*- and *R*-branch lines of the transition ν_7 is given in Fig. 1. The spectrum was recorded at room temperature and at a pressure in the absorbing cell ≈ 1 Torr.

The ground vibrational state of C₃O₂ has the symmetry Σ_g^+ , and the ν_7 vibrational state has the symmetry Π_u (2). The selection rules in a vibration–rotation band of the type $\Pi_u - \Sigma_g^+$ permit the transitions $\Delta J = 0, \pm 1$ (*Q*, *R*, and *P* branches). In molecules belonging to the *D_{∞h}* symmetry group antisymmetric rotational levels are absent because the spins of the nuclei ¹²C and ¹⁶O are both equal to zero. For the ground vibrational state this corresponds to the absence of the levels with odd *J* values and for the state $\nu_7 = 1$ to the absence of even *J*'s for the *c* component and odd *J*'s for the *d* component. In the spectrum of the transition ν_7 only lines with even values of the ground state quantum number are present. The *d*-component lines of the *P* branch of the vibration–rotation transition ($2\nu_7 - \nu_7$) (assignment is shown) are also present in the figure, the band origin of which is near the frequency 827.98 GHz. The lines 1₀₁–1₁₀ of the water H₂¹⁶O and H₂¹⁸O present in the sample as impurities (H₂¹⁸O in the natural abundance) are also observed in the spectrum. Absorption of backward-wave tube radiation power by atmospheric water (in the horn connecting the backward-wave tube with the cell) leads to attenuation of the observed C₃O₂ lines near the H₂¹⁶O line.

Line frequencies of the *Q*-branch transitions ν_7 given in Table I were measured by means of a frequency-stabilized backward-wave oscillator with a relative accuracy of $\sim 10^{-7}$. The processing of line frequencies of the *Q*-branch was performed according to the formula:

$$\begin{aligned}
 Q(J) = & \nu_0 + B'[J(J+1) - l'^2] - D'[J(J+1) - l'^2]^2 + H'[J(J+1) - l'^2]^3 \\
 & - B''J(J+1) + D''J^2(J+1)^2 - H''J^3(J+1)^3 \\
 = & \nu_0 - B' - D' - H' + (B' - B'' + 2D' + 3H')J(J+1) \\
 & - (D' - D'' + 3H')J^2(J+1)^2 + (H' - H'')J^3(J+1)^3, \quad (1)
 \end{aligned}$$

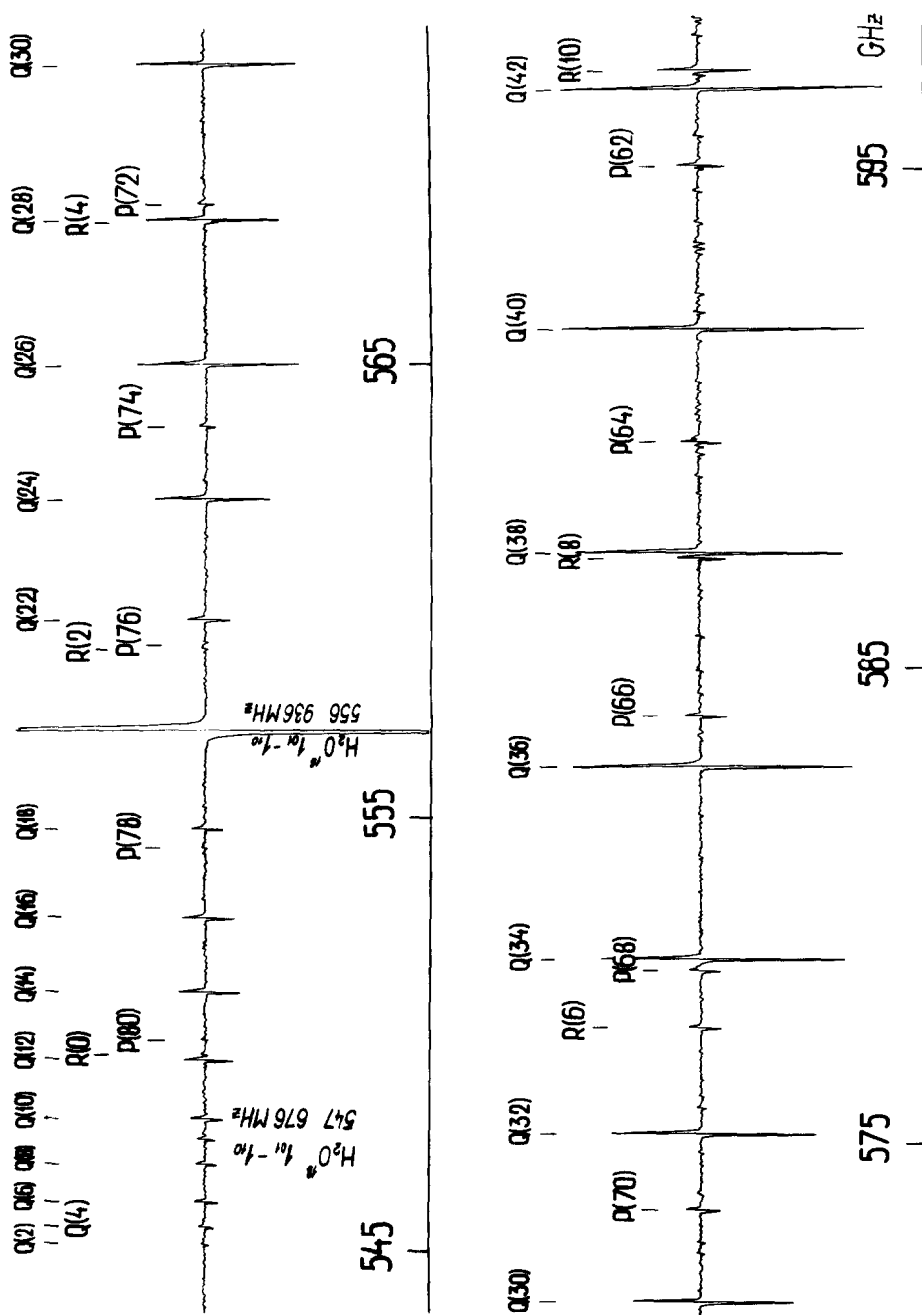


FIG. 1. The vibrational-rotational band of the $\nu_{1/2} \leftarrow 0$ transition of C_3O_2 around 570 GHz.

TABLE I
Frequencies Q Branch of the ν_7 Transition of C_3O_2

J	ν_e (MHz)	ν_c (MHz)	$\nu_e - \nu_c$ (kHz)
2	545 178.892 (100)	545 178.826 (31)	+ 66
6	546 206.509 (350)	546 206.679 (23)	-170
8	547 063.338 (100)	547 063.276 (17)	+ 62
10	548 148.339 (50)	548 148.367 (13)	- 28
12	549 461.990 (25)	549 461.995 (9)	- 5
14	551 004.203 (25)	551 004.213 (7)	- 10
16	552 775.100 (25)	552 775.076 (8)	+ 24
18	554 774.628 (30)	554 774.643 (9)	- 15
22	559 460.125 (30)	559 460.119 (11)	+ 6
24	562 146.153 (100)	562 146.138 (15)	+ 15
26	565 061.047 (70)	565 061.070 (19)	- 23
28	568 204.947 (80)	568 204.946 (21)	+ 1
30	571 577.759 (100)	571 577.783 (23)	- 24
32	575 179.589 (80)	575 179.576 (40)	+ 13

where

$\nu_0 - B' - D' - H' =$ band origin of the transition ν_7 ;

$B', D', H' =$ the rotational and centrifugal constants of the excited vibrational state;

$B'', D'', H'' =$ the rotational and centrifugal constants of the ground vibrational state;

$l' =$ the quantum number of the vibrational angular momentum.

As a result, the following values of constants were obtained:

$$\nu_0 - B' - D' - H' = 545\,007.524(32) \text{ MHz} \Rightarrow 18.1794942(11) \text{ cm}^{-1};$$

$$B' - B'' + 2D' + 3H' = 28.55016(26) \text{ MHz}; \quad D' - D'' + 3H' = -27.54(58) \text{ Hz};$$

$$H' - H'' = -0.00649(37) \text{ Hz}.$$

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