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The Dipole Moment of Carbon Monosulfide

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A parallel plate Stark modulated spectrometer useful in the centimeter and millimeter wave region is discussed and employed to measure the dipole moment of carbon monosulfide in the ground and first excited vibrational state. The change in the dipole moment is consistent with the possible valence bond structure.

From the Stark effect of the $J = 0 \rightarrow 1$ transition the dipole moment of carbon monosulfide has been obtained in the ground and first excited vibrational state. The CS was produced by discharging CS₂ as described by Moekler and Bird (1). In the investigation a parallel plate free-space cell was employed with conventional 100 keps Stark modulation and phase-sensitive detection. This cell has proved useful in other investigations and hence a brief discussion of the cell will be given.

The Stark cell consists of two 0.25-in. aluminum plates 3 ft long and 3 in. wide spaced 4.5 mm apart by means of Teflon spacers and enclosed in a glass tube fitted with Teflon windows. The microwave energy was fed to the cell by means of a horn with a Teflon lens at its mouth. The cell is very similar to the precision Stark cell described previously for use in the millimeter wave region (2). However, at the lower frequencies employed in this investigation it is more difficult to focus the microwave energy between the Stark plates when the plate separation is kept small. It has been found that the transmission qualities of the cell could be substantially improved, while keeping the plate separation small, by flaring the ends of the Stark electrodes as indicated in Fig. 1. The field inhomogeneities produced by this modification were found to be negligible. This cell has been operated between 20,000 Mcps and 300,000 Mcps.

A 6-ft cell has also been tested and found to function satisfactorily with the power attenuation being within the desired limits. The attenuation, however, in a 12-ft cell was found to be prohibitive. Insulated metal strips down the side of the cell did help to prevent some power loss out the side of the cell, although the improvement was not substantial. It is believed that the use of Teflon lenses judiciously placed along the cell could ameliorate the transmission properties of such a long cell.

One great advantage of such parallel plate Stark cells is the ease of construction as compared to the ordinary waveguide type. Furthermore, the rigidity of the Stark electrodes reduces the possibility of mechanical modulation by the varying electric field. Also, since the electrodes are easily accessible they may be readily coated (e.g., with Teflon, etc.) to improve the lifetime of reactive species. The present cell when coated with "Plasti-Kote, no. T-5" allowed the observation of the extremely reactive molecule H₂S₂; the lifetime being somewhat better than 4 min. In an ordinary metal waveguide cell the lifetime was too short to be observed even under flow conditions (3). Although the absorption lines of CS were found to persist for more than 1 min, it was more convenient to continuously pump CS through the cell. Another advantage offered by this cell is the ability of employing Stark modulation in the millimeter region, which is often crucial in the assignment of absorption lines. For a conventional Stark cell, the losses incurred in the millimeter wave region are too high to be applicable.

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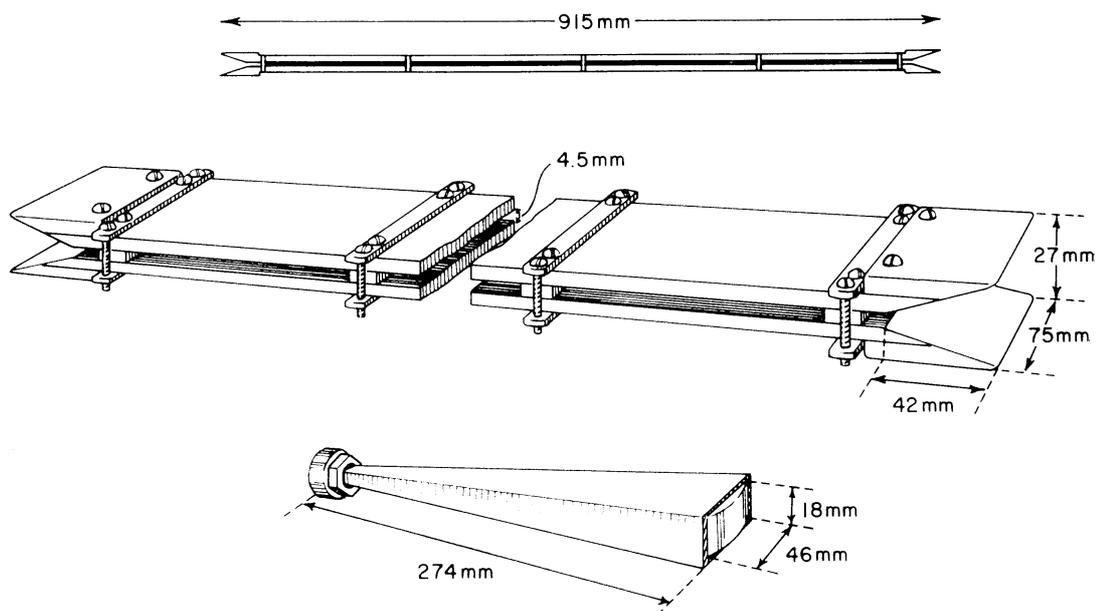


FIG. 1. Parallel plate cell and transmitting horn. The parallel plates are held together by means of nylon bolts and the metal brackets are insulated by use of Teflon strips. The transmitting horn pictured above has a K -band input. The mouth of the detecting horn (not shown) was somewhat bigger than that of the transmitting horn.

TABLE I
DIPOLE MOMENT OF CS

Transition	$(\Delta\nu/F^2)^a$	μ (D)
$J = 0 \rightarrow 1, r = 0$	1.058×10^{-5}	1.958 ± 0.005
$J = 0 \rightarrow 1, r = 1$	1.042×10^{-5}	1.936 ± 0.010

^a In units of (Meps) $(V/cm)^{-2}$. Stark conversion factor 0.50348 (Meps) (debye V/cm)⁻¹.

The dipole moments of carbon monosulfide for the ground and first excited state determined by the method of least-squares are given in Table I.² The Stark cell was calibrated with the $J = 1 \rightarrow 2$ transition of OCS (4). The decrease in the dipole moment in going to the excited vibrational state is qualitatively explicable in terms of the possible valence-bond structures:



The dipole moment in the ground state has been interpreted as arising from contributions of I and III neglecting possible atomic dipoles due to hybridization in II (5). The electric quadrupole moment, on the other hand, has been accounted for in terms of II and III with

² The dipole moment for the ground state has been given in Ref. (1) to be 1.97 ± 0.02 D.

50% s-hybridization (I). In either case, structure III contributes about 40%. Therefore, regardless whether II is considered to contribute to the dipole moment, since the largest contribution arises from the polar structure III, the decrease in the moment is consistent with favoring the structure with the longer bond, that is, I or II.

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