Pressure Broadening of OCS in Foreign Gas Mixtures

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(Received June 1, 1954)

Line widths of the $J=1-2$ OCS line in mixtures with foreign perturbing gases have been measured. The perturbers were N_2O, He, and O_2 in three different percentages of mix, about 20 percent, 50 percent, and 75 percent of perturber. Systematic variation of collision diameters with mix ratio, previously reported, was not observed.

INTRODUCTION

IN a previous investigation in this laboratory[1] pressure broadening of several lines of the microwave spectrum of ammonia in foreign gas mixtures was studied.[2] We have now measured line widths of the $J=1-2$ OCS line in mixtures of three different percentages with N_2O, He, and O_2 as perturbers, as well as in the case of self-broadening of this line. In this latter case the results are in good agreement with the value recently obtained by Smith,[3] our value being 9.20×10^{-8} cm as compared with the value of 9.28×10^{-8} cm given by Smith.

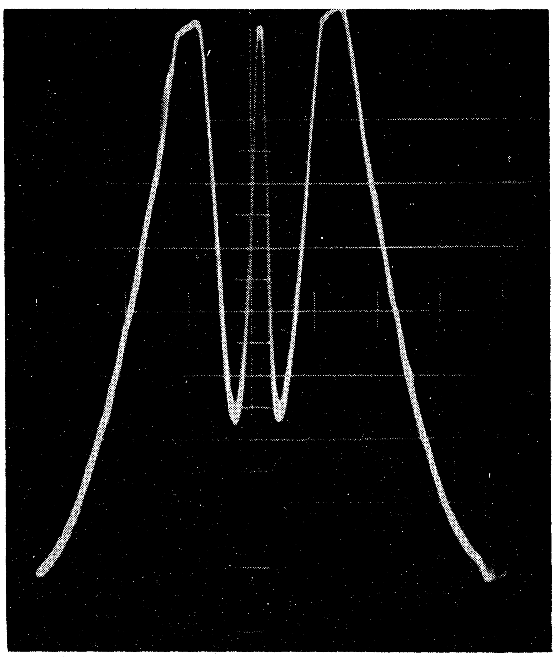

FIG. 1. Typical line; OCS at 100 microns pressure; the pattern is the absolute magnitude of the first derivative of the line contour superimposed on the U-shaped klystron mode.

OCS is a linear nonsymmetric molecule. This asymmetry gives to the molecule a dipole moment sufficient to cause relatively strong absorption lines. The line corresponding to $J=1-2$ rotational transition can be observed within the frequency limits of the 2K33 klystron. The absorption due to this transition takes place at a frequency of 24 325.92 Mc/sec[4] and has an intensity of 5.5×10^{-5} cm^{-1}. From the pressure-broadening data for this line the collision diameters have been obtained for both the mutual collisions of OCS molecules and for collisions with foreign perturbers by means of the formulas of reference 1.

EXPERIMENTAL

The spectrograph was of the unbalanced type, employing 45 feet of K-band wave guide for the absorption cell. The 2K23 klystron was swept over its mode by a saw-tooth voltage applied to its repeller grid. The same voltage was used for the horizontal sweep of the oscilloscope, so that a plot of absorption *versus* frequency was obtained. Upon this saw-tooth wave form there was superimposed a small sinusoidal voltage of 205 kc/sec, the effect of which was to sweep the klystron frequency rapidly over the region of varying absorption when it slowly passes the mode.[5] The line is then an effective frequency discriminator and can be detected by an AM reciever tuned to the same frequency. This receiver amplifies the signal from the crystal detector at radio-frequency, demodulates it, amplifies the resulting audio-frequency, and applies it to the vertical deflection plates of the oscilloscope. The amplification at the radio-frequency has the advantage of considerably improving the signal-to-noise ratio, with a good over-all sensitivity as a result. With this system the resulting pattern is the absolute magnitude of the first derivative of the line contour superimposed on the U-shaped klystron mode. The line width is the frequency difference between the two maxima multiplied by $\sqrt{3}$. Additional line broadening is introduced by the second modulation; it was corrected for by extrapolating the line widths to zero-frequency modulation. A resonant cavity wave meter was used to identify the line and to locate it on the oscilloscope.

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[1] Potter, Bushkovitch, and Rouse, Phys. Rev. **83**, 987 (1951).
[2] For a general review of the subject of pressure broadening in microwave spectroscopy, see W. V. Smith, Ann. N. Y. Acad. Sci. **55**, 891 (1952); also Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley & Sons, Inc., New York, 1953), Chap. 4.
[3] W. V. Smith, University of Delaware Research Report AF 18(600)-449 No. R-357-10-4 (unpublished). We should like to thank Dr. Smith for sending us a copy of this report.
[4] Dakin, Good, and Coles, Phys. Rev. **71**, 640 (1947).
[5] W. Gordy, Revs. Modern Phys. **20**, 668 (1948).

To provide horizontal frequency markers, a second identical klystron was coupled to the system by means of a 25-db Bethe hole coupler. The output of the two klystrons was fed into a crystal mixer, which in turn was connected to a 1-Mc/sec communications reciever. Selective tuning of this receiver provides two sharp pips on the oscilloscope, 2 Mc/sec apart.

The two signals, the line pattern and the pips, were fed into a Tektronix model 514AD oscilloscope via two separate inputs, either one of which can be selected by means of a switch. They were recorded separately on photographic film. The line widths were plotted against pressure for each mixture and the collision diameters calculated by means of the formulas of reference 1.

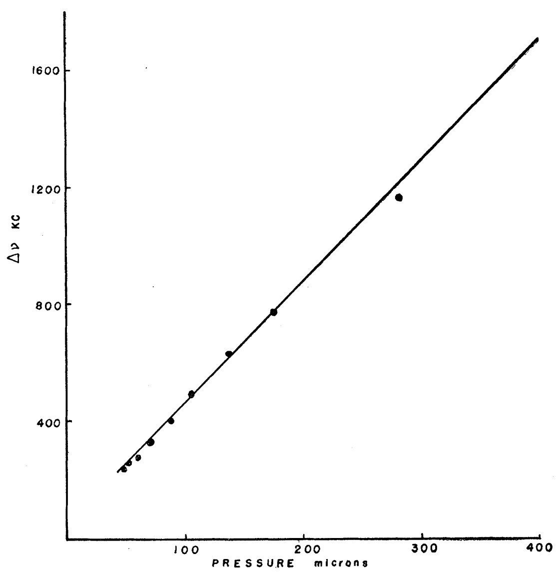


FIG. 2. Half-width *vs* pressure; OCS with 50.1 percent of O_2.

TABLE I. Collision diameters of OCS in mixtures ($\times 10^8$ cm).

OCS				Average 9.20
N_2O	22.6 percent 7.39	50.7 percent 7.49	74.4 percent 7.39	7.42
He	22.8 percent 3.13	50.4 percent 2.85	75.2 percent 3.11	3.03
O_2	20.2 percent 4.60	50.1 percent 4.95	77.5 percent 5.44	5.00

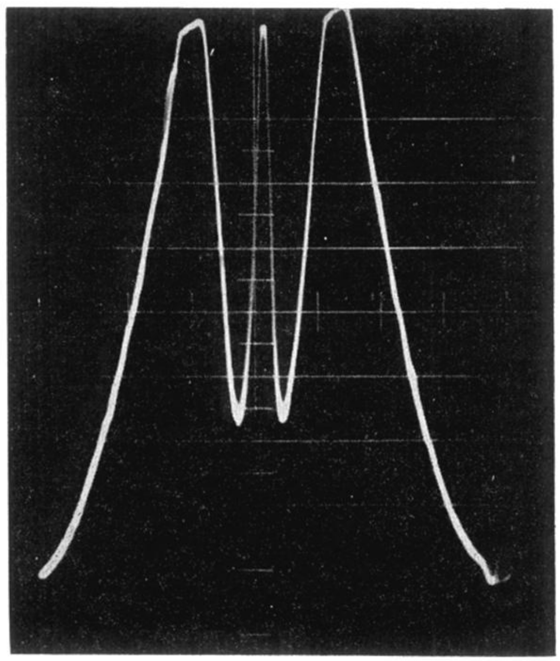
Figure 1 gives a typical line, while Fig. 2 is a typical plot of line half-width *versus* pressure.

The OCS gas was prepared in the laboratory through decomposition of ammonium thiocyanate with sulfuric acid.[6] Three different gases were used as perturbers: N_2O, He, and O_2, mixing each one of them with OCS in three different ratios. The mixing apparatus was the one described in reference 1.

RESULTS

The results are summarized in Table I. It is thought that the variations of the collision diameter with mix ratio are not significant, since the variation does not appear to follow a consistent pattern. This is contrary to reference 1 where there appeared to be a consistent decrease in collision diameter with increasing proportion of perturber. The results for self-broadening are thought to be accurate to within 1 percent; those for foreign broadening to within 10 percent. The substantially lower accuracy of foreign broadening results is thought to be due primarily to difficulties connected with the mixing process.

[6] We wish to thank Dr. Schaeffer and members of the Chemistry Department of St. Louis University for assistance in the preparation of OCS gas.



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