

through the energy-momentum tensor of the auxiliary field

$$M^2(\phi_\mu\phi_\nu - \frac{1}{2}\delta_{\mu\nu}\phi^2). \quad (32)$$

Its contribution to  $\tilde{T}_{\mu\nu}^{(1)}(p'$ ) is

$$\frac{-e^2M^2}{4(2\pi)^2} \int_0^1 dt \int_0^1 zdz [2m\delta_{\mu\nu} + z(i\gamma^{(\mu}P_{\nu)})] \cdot \frac{1}{C + M^2Z} \quad (33)$$

The minus sign in (33) is due to the choice of an imaginary coupling  $ie$  of this auxiliary field.

Neglecting again terms of the order  $M^{-2} \cdot \log M$ , Eq. (33) gives

$$-(e^2/2(2\pi)^2)[m\delta_{\mu\nu} + \frac{1}{4}(i\gamma^{(\mu}P_{\nu)})]. \quad (34)$$

Thus the formerly remaining stress-part (30) is now cancelled and a divergence free energy-momentum tensor is obtained. There remains, however, an infra-red term in the third line of (28). Because of the factor  $\Delta p^2$  this term plays no role in the energy-momentum four-vector  $P_\mu = \int T_{\mu 4} d^3x$ . It indicates, however, that as soon as we try to localize energy and momentum and to build up wave packets, the well-known failure of the power series approach in constructing of the physical electron becomes manifest. Expressed in terms of the operators of the present approximation, the physical

electron carries still a cloud of virtual low energy photons with itself, the effect of which is discarded on going to the one-particle, no-photon part of  $\tilde{T}_{\mu\nu}$ . Thus, to investigate the energy-momentum density distribution, the above calculation would have to be completed by a sort of Bloch-Nordsieck treatment, but which is not within the scope of the present investigation.

The discussion of the energy-momentum four vector  $P_\mu$  displays again the necessity for the inclusion of (32) into the system, in a way which, of course, is connected with the self-stress difficulty. Since the change in the physical properties of the electron due to its interaction with the radiation field vacuum consists only in a change of its mass, and since this change has already been included in the representation of the electron field,  $\tilde{T}_{\mu\nu}^P + \tilde{T}_{\mu\nu}^B$  should give no contribution at all to  $P_\mu$ . From this statement it follows that the coefficients of  $(i\gamma^{(\mu}P_{\nu)})$  and  $P_\mu P_\nu$  should vanish too for  $\Delta p^2 = 0$ . This fact is easily verified from (22), (23), (28), (29), and (34). The inclusion of the contribution  $\sim (i\gamma^{(\mu}P_{\nu)})$  in (34) is essential and exhibits again the failure of a purely formal mass regularization.

In conclusion I would like to express my gratitude to Dr. J. R. Oppenheimer for the privilege of a stay at the Institute for Advanced Study, and also for helpful criticism.

## Microwave Collision Diameters I. Experimental\*

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The diameters of fifteen polar and non-polar gases for collisions with ammonia are obtained from measurements of the pressure broadening of the ammonia 3-3 inversion line in the mixed gases at low pressures. The design of the spectroscope used and the experimental technique involved are discussed.

### I. INTRODUCTION

**P**RESSURE broadening of spectral lines has been studied for many years in the optical and infra-red regions. In 1936 a review of work done up to that time was given by Margenau and Watson.<sup>1</sup> The difficulties encountered in this region are great. A large Doppler breadth and insufficient resolution hamper measurements at low pressures while at high pressures multiple

collisions complicate the process. Because of these and other difficulties the problem suffered from neglect and never was brought to satisfactory completion.

More recently, the expansion of microwave spectroscopy has caused new interest to arise and a number of theoretical and experimental papers have appeared.<sup>2</sup> In the microwave region, resolution is high and Doppler breadth is only about 70 kc. At breadths of the order of a megacycle, the more intense lines, especially the ammonia 3-3 inversion line, may easily be displayed on an oscilloscope for observation.

In the case of collision broadening in a pure gas, the

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<sup>1</sup> H. Margenau and W. W. Watson, *Rev. Mod. Phys.* **8**, 22 (1936).

<sup>2</sup> H. Margenau, *Phys. Rev.* **76**, 121 (1949); J. H. Van Vleck and V. F. Weisskopf, *Rev. Mod. Phys.* **17**, 227 (1945); P. W. Anderson, *Phys. Rev.* **76**, 647 (1949); H. M. Foley, *Phys. Rev.* **69**, 616 (1946); B. Bleaney and R. P. Penrose, *Proc. Phys. Soc. London* **LIX**, 418 (1947); **LX**, 83 (1948).

line breadth constant  $\Delta\nu$  is given by

$$2\Delta\nu_1 = N_1\sqrt{2}\bar{V}_1b_1^2,$$

while in a mixture of two gases

$$2\Delta\nu_2 = N_1\sqrt{2}\bar{V}_1b_1^2 + N_2\bar{V}_{12}b_{12}^2,$$

where  $N_1$ ,  $\bar{V}_1$ , and  $b_1$  are the molecular density, average velocity and collision diameter, respectively, of the absorbing gas. The relative velocity  $\bar{V}_{12}$  is equal to  $(\bar{V}_1^2 + \bar{V}_2^2)^{1/2}$  and  $b_{12}$  is the collision diameter for mixed collisions. In our measurements, pressures were so adjusted that  $\Delta\nu_1 = \Delta\nu_2$  and, with the intensity ratio  $I_2/I_1 = N_1'/N_1 = I$ , the cross-section ratio becomes

$$b_{12}^2/b_1^2 = (\sqrt{2}\bar{V}_1/\bar{V}_{12})(1-I)/[(P_2/P_1) - I],$$

where pressures have been substituted for molecular densities.

The measurements needed, then, for determining the cross-section ratios are the pressure of pure ammonia, the pressure of the mixture, and the relative intensity of absorption.

## II. EXPERIMENTAL

Figure 1 is a block diagram of the spectroscopy used. The Type 2K50 klystron was chosen because of its unusually broad mode. It was found that with intensities of absorption 10 percent of that of pure ammonia no correction for curvature of the mode was necessary.

The klystron is reflector-tuned through 3 to 4 Mc to either side of the absorption line by a 60-cycle sawtooth voltage and is frequency modulated<sup>3,4</sup> by a 100-kc sinusoidal voltage of small amplitude. Upon detection, the 100-kc component is amplified and redetected by a

communications receiver tuned to 100 kc. The envelope obtained (the absolute magnitude of the first derivative of the absorption line) is displayed on an oscilloscope as in Fig. 2.

The modulated output from the klystron is fed into two X-band absorption cells (labeled "measurement cell" and "comparison cell") four meters long by a magic tee and transition sections. The measurement cell is terminated by a Type 1N26 crystal rectifier whose output is connected to the grid of a cathode follower. The load on the crystal, the grid resistor, was adjusted to give a square law response at the power level used.<sup>5</sup>

To avoid non-linearities it is desirable to have a constant signal in the signal channels of the communications receiver and oscilloscope. Accordingly, the output from the cathode follower is connected to an attenuator. In order that relative intensities might be read from the attenuator setting, it was calibrated under "use" conditions with a 100-kc signal at 0.01 volt applied to the input of the cathode follower and an oscilloscope in parallel with the input to the receiver. Signal heights as a function of attenuator setting were then photographed on a linear portion of the oscilloscope screen to give the calibration. A second-cathode follower was used to match the high output impedance of the attenuator to the low impedance input of the receiver.

The crystal calibration was obtained by introducing ammonia into the cell and tuning to the 3-3 line. Input to the crystal was then varied over a range of 14 db by means of a calibrated microwave attenuator and the output measured as the corresponding change of the 100-kc attenuator necessary to maintain the oscilloscope display at constant height.

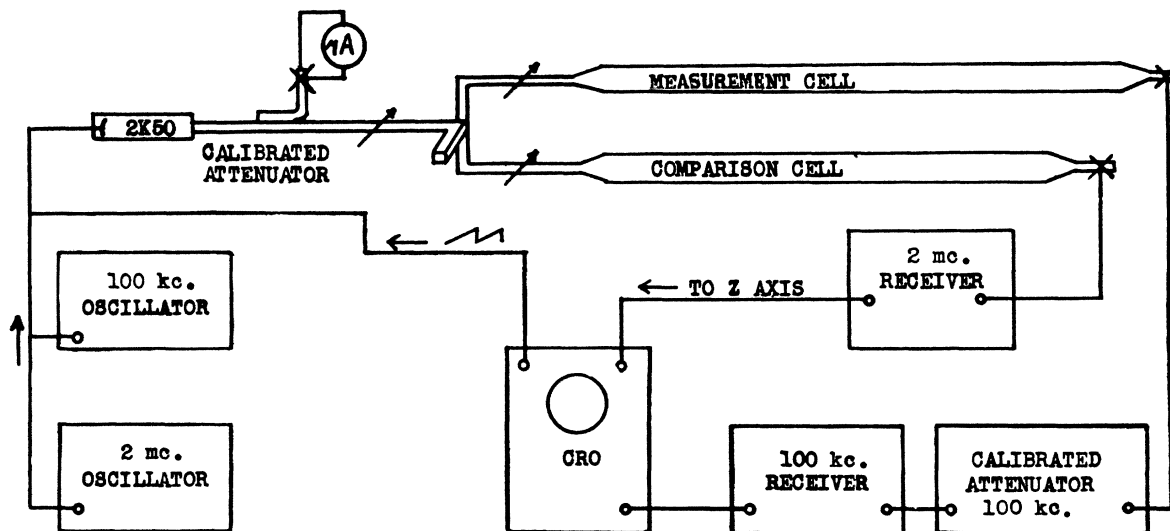


FIG. 1. Block diagram of spectroscopy.

<sup>3</sup> W. Gordy and M. Kessler, *Phys. Rev.* **72**, 664 (1947).

<sup>4</sup> Robert Karplus, *Phys. Rev.* **73**, 1027 (1948).

<sup>5</sup> H. C. Torrey and C. A. Whitmer, *Crystal Rectifiers*, M.I.T. Radiation Laboratory Series V, 15 (McGraw-Hill Book Company, Inc., New York, 1948), p. 333.

### III. CORRECTIONS AND MONITOR DEVICES

The power absorbed in the guide is given by  $P = P_0(1 - e^{-\gamma x})$ , where the absorption coefficient  $\gamma$  is given by

$$\gamma = \gamma_0(\Delta\nu)^2 / [(\nu - \nu_0)^2 + (\Delta\nu)^2].$$

Thus the line breadth, as measured between points of maximum  $dP/d\nu$ , must be corrected for the decrease of  $\gamma$  in the mixture as compared to pure ammonia. Experimental values of  $\gamma x$  were used to make the correction. This amounts to a decrease of the measured ratio  $P_2/P_1$  of 5 to 7 percent, depending on the concentration of ammonia in the mixture.

In order to insure that the frequency scale remained unchanged during the course of a measurement, the comparison cell and a third reflector modulation were introduced to give markers of known frequency spacing. The comparison cell was filled with ammonia at low pressure to give a narrow absorption line. The amplitude of the modulating signal must be kept low to avoid distorting the signal in the measurement cell. The modulation frequency, however, may be varied over a wide range and was usually set at 2 Mc. The cell is terminated by a crystal detector connected to a communications receiver and the redetected signal is applied to the intensity grid of the oscilloscope. The receiver was usually tuned to 200 kc less than the modulation frequency as the markers obtained here appear somewhat sharper than those at the oscillator frequency. Figure 2 is a photograph of the ammonia line with frequency scale markers at an ammonia concentration of about 30 percent. The unsymmetrical marker presentation is due primarily to the different response of the two detection systems involved. This is considered to be fortunate since it permits intensity measurement without the necessity of turning off the markers, as would be the case if the central marker fell on the display center. Symmetry is not necessary to the determination of a constant frequency scale or of line shifts since, in any case, the markers are of constant position.

Input power level was monitored by a crystal detector and microammeter on a directional coupler near the klystron. It was required that the power level remain constant within a few percent during the course of a run and a small correction, assuming square law



FIG. 2. Typical absorption line with frequency markers.

response of the monitor crystal, was made when necessary. The power was maintained at such a level that the small variations noted would not contribute to saturation broadening. The intensity measurement requires also that the amplitude of the 100-kc modulating signal be held constant. This was done by means of the self-contained meter in the Hewlett-Packard Type 650-A oscillator used.

### IV. GASES AND VACUUM SYSTEM

Commercial compressed gases of high purity or reagent grade chemicals were used with the following exceptions:  $\text{CH}_3\text{Cl}$  was prepared by the action of concentrated  $\text{HCl}$  and  $\text{CH}_3\text{OH}$  in the presence of  $\text{ZnCl}_2$  as a catalyst.<sup>6</sup>  $\text{ClCN}$  was prepared by chlorination of a suspension of  $\text{KCN}$  in  $\text{CCl}_4$ .<sup>7</sup>  $\text{HCN}$  was prepared by the reaction of dilute sulfuric acid and  $\text{KCN}$ .<sup>8</sup>  $\text{COS}$  was prepared by the action of dilute sulfuric acid on  $\text{NH}_4\text{CNS}$ .<sup>8</sup>

A glass reservoir of 12 liter capacity was connected to the measurement cell so that the system would "hold" to better than  $10^{-4}$  mm Hg for a 12-hour period. Pressures were measured with a McLeod gauge and the possible presence of condensable vapors was checked with a Pirani gauge. None were present.

### V. PROCEDURE

Each "run" comprises measurement of line breadth, pressure and intensity for pure ammonia and for one mixture of ammonia with a foreign gas. For the first point, ammonia is admitted into the evacuated measurement cell at a pressure of 0.02 to 0.04 mm Hg. Ammonia adsorbs very strongly onto the walls of the system. At these pressures and for this system, somewhat more than 24 hours are required to reach full equilibrium, at which time the pressure is about one-fourth of the original pressure. At about one-half hour after the gas is admitted, however, the adsorption rate has slowed to the extent that pressure and intensity measurements may be considered instantaneous, with negligible error. Because of this adsorption it is essential that both breadth and intensity of absorption be measured.

After adsorption processes have slowed sufficiently, gains are adjusted to give the oscilloscope display a fixed height and width (Fig. 2). The pressure is then measured and the 100-kc attenuator setting and the various monitor readings noted. For the mixture point measurement 70 to 90 percent of the ammonia is pumped from the system and sufficient foreign gas is admitted to return the line to its original breadth. The 100-kc attenuation is reduced to restore the display to

<sup>6</sup> James F. Norris and Hazel B. Taylor, *J. Am. Chem. Soc.* **46**, 753 (1924).

<sup>7</sup> *Inorganic Syntheses II*, W. C. Fernelius, Editor (McGraw-Hill Book Company, Inc., New York, 1946), p. 90.

<sup>8</sup> A. Farkas and H. W. Melville, *Experimental Methods in Gas Reactions* (The Macmillan Company, New York, 1939), pp. 161, 168.

its former height, and pressure and monitor readings again recorded.

Seven or more such runs were made for each of the gases reported. The time allowed for clearing the system of the foreign gas between runs varied from 2 hours for the rare gases to more than 12 hours for the adsorbing polar gases.

## VI. RESULTS

Our measured collision diameters and typical experimental values of the pressure ratio and relative intensity are given in Table I. Collision diameters as measured by Bleaney and Penrose<sup>9</sup> are given for certain of the non-polar gases. With the exception of CS<sub>2</sub> their values are higher by about 20 percent. Bleaney and Penrose deduce their diameters from intensity measurements only, assuming their gas mixtures to be known. Unknown relative adsorption of gases on the container walls or non-linearities in the detector may introduce errors in this approach. We measure two parameters, line width and intensity ratio. The accuracy of our line width measurement limits our over-all accuracy to two to three percent, as indicated by our statistical probable error. Our intensity measurements are not only carefully calibrated, but in any case enter into our results only as a correction factor of some ten to twenty percent. We should note, however, that Bleaney and Penrose's measurement of the self-broadening of ammonia does not involve these experimental difficulties, and presumably is accurate to a few percent. (Townes,<sup>10</sup> however, reports a line breadth for the 3-3 line 10 percent higher than given by Bleaney and Penrose.) Correlations of our measurements with other molecular

TABLE I. Experimental values of the collision diameters.

Mixture gas	Number of measurements	$P_2/P_1$ typical	$I$ values	$b \times 10^8$ cm (average)	Probable error (percent)	$b \times 10^8$ cm (reference 9)
NH <sub>3</sub>						13.8
He	7	19.0	0.306	2.00	2.3	2.35
A	7	13.5	0.181	3.73	1.7	4.6
H <sub>2</sub>	7	7.70	0.202	2.95	1.9	3.50
N <sub>2</sub>	11	5.74	0.190	5.54	1.4	6.4
O <sub>2</sub>	7	12.1	0.170	3.86	2.3	4.85
CO <sub>2</sub>	8	3.54	0.190	7.59	1.7	
COS	7	3.58	0.194	7.54	3.7	
CS <sub>2</sub>	7	3.55	0.163	7.72	1.9	7.5
HCN	7	1.99	0.097	9.95	2.3	
CICN	14	1.49	0.202	11.9	1.6	
CH <sub>3</sub> Cl	7	1.71	0.140	11.3	0.9	
CH <sub>2</sub> Cl <sub>2</sub>	7	2.20	0.117	10.3	1.3	
CHCl <sub>3</sub>	7	1.24	0.163	13.7	2.8	
CCl <sub>4</sub>	7	3.87	0.300	7.20	2.4	
SO <sub>2</sub>	7	2.15	0.100	10.4	1.4	

data and estimates of molecular quadrupole moments may be found in the following paper.<sup>11</sup>

No shifts of absorption line frequency were observed. Particular care was taken in the case of self-broadening of the CICN line at 23885 Mc and in the case of broadening of the NH<sub>3</sub> 3-3 line by Argon. Observations on CICN were made relative to a marker 10 Mc from the ammonia 3-3 line in the comparison cell. In these cases we estimate that the ratio of shift to line breadth was less than 0.03.

We wish to express our appreciation to Mr. Louis Moose of the Bell Telephone Laboratories for technical advice concerning operation of 2K50 klystrons and to Dr. Ralph Trambarulo for the necessary chemical preparations.

<sup>9</sup> B. Bleaney and R. P. Penrose, Proc. Phys. Soc. London LX, 540 (1948).

<sup>10</sup> C. H. Townes, Phys. Rev. 70, 665 (1946).

<sup>11</sup> William V. Smith and Raydeen R. Howard, Phys. Rev., following paper.

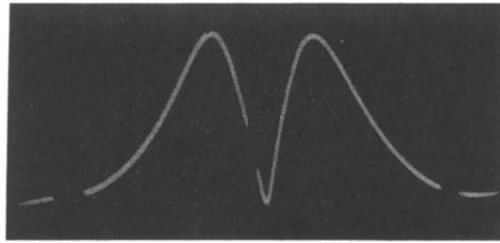


FIG. 2. Typical absorption line with frequency markers.