Pressure Broadening in the Microwave Spectrum of Ammonia

C. A. POTTER,* A. V. BUSHKOVITCH, AND A. G. ROUSE
St. Louis University, St. Louis, Missouri

(Received May 14, 1951)

Half-widths of five pressure-broadened lines of the ammonia inversion spectrum have been measured as a function of total pressure. The perturbing gases were oxygen, helium, and nitrous oxide in various mix ratios. The results indicate a decrease in the collision diameters with increasing mix ratio of perturber to absorber. In the case of the nonpolar helium and oxygen the observed variation of collision diameter with quantum numbers of the lines can be compared with the predictions of the theory of collision broadening developed by P. W. Anderson. The general trend of the variation agrees with the theory, but its observed magnitude is considerably greater than predicted.

INTRODUCTION

PRESSURE broadening of the absorption spectrum lines of ammonia gas has been the subject of several experimental and theoretical investigations. Self-broadening has been observed by Bleaney and Penrose[1] for 17 lines in the inversion spectrum of ammonia. Broadening due to foreign perturbers was also investigated by Bleaney and Penrose and by Smith and Howard.[2] A rigorous quantum-mechanical theory has been developed by Anderson.[3]

This paper describes the results of measurements of microwave collision diameters correlated with quantum numbers, perturbing gas, and ratio of the number of perturbing molecules to the number of ammonia molecules at a constant total pressure. Five lines of the ammonia inversion spectrum were studied in the pressure range from 0.8 to 5×10^{-2} mm of Hg. The perturbing gases were oxygen and helium (nonpolar) and nitrous oxide (dipole, linear, nonsymmetric) in each case, each gas being used in at least two mix ratios. No ternary mixtures were used. In the case of oxygen, four mix ratios were used for the 3, 3 line.

The relations between half-width and collision diameter are[2]

$$\Delta\nu=n_1v_1b_1^2/\sqrt{2} \quad (1)$$

for self-broadening, where $\Delta\nu$ is half-width in Mc-sec^{-1}, n_1 is number of ammonia molecules per unit volume, v_1 is mean velocity, and b_1 is collision diameter.

For broadening by a foreign gas, we have

$$2\Delta\nu=\sqrt{2}n_1v_1b_1^2+n_2v_{12}(b_{12})^2, \quad (2)$$

where n_2 is the number of perturber molecules per unit volume, v_{12} is root-mean-square velocity of perturbing molecules with respect to ammonia molecules, and b_{12} is collision diameter of perturbing gas.

The half-widths at a pressure of 0.5 mm of Hg were used to calculate collision diameters.

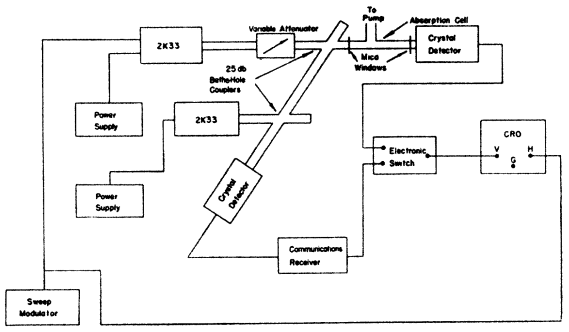

FIG. 1. Block diagram of microwave system.

EXPERIMENTAL

The spectrograph used in this investigation is a relatively low sensitivity unbalanced type, shown in Fig. 1. The data was permanently recorded as a photograph of the oscilloscope trace. For a given absorption line, the desired mix ratio was prepared and let into the absorption cell. It was then pumped out rapidly by a high speed forepump. The pressure was continuously monitored by a modified Pirani gauge. At convenient pressure intervals the pump was stopped and photographs taken. Usually twelve pressures were used, three photographs being taken at each pressure. The film strips were projected and measurements of half-width made directly. Marker pips provided the scale factor. Approximately 1500 exposures were used.

The apparatus which was used to make gas mixtures of known ratio is shown in Fig. 2. The calibrated burettes were filled with ammonia and perturber, respectively. The pressure of the gases in each tube

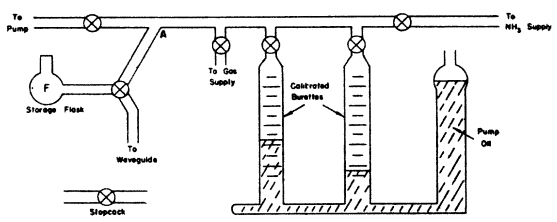

FIG. 2. Gas mixing apparatus.

* The material in this paper is a part of the author's thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Saint Louis University.

[1] B. Bleaney and R. P. Penrose, Proc. Phys. Soc. (London) **60**, 540 (1948).

[2] W. V. Smith and R. Howard, Phys. Rev. **79**, 132 (1950); R. Howard and W. V. Smith, Phys. Rev. **79**, 128 (1950).

[3] P. W. Anderson, Phys. Rev. **76**, 647 (1949).

TABLE I. Collision diameters for ammonia inversion lines at 0.5-mm Hg pressure ($\times 10^8$ cm).

J	K	Bleaney and Penrose	This paper
2	1	10.5	10.3
8	7	13.2	13.2
3	3	13.8	13.9
4	4	13.8	13.9
6	6	14.1	14.0

was very close to atmospheric, differing from it negligibly because of unequal heights of liquid in each tube. The space A above the burettes and the storage flask F were evacuated. Then a measured amount of gas was let into space A, and allowed to diffuse into flask F. The region A was again evacuated and the procedure repeated with the ammonia. The ratio of volumes of A to F is known and appears as a correction factor to the mix ratio, which is otherwise determined by the changes in height of the oil columns in the burettes. To check the reliability of the gas mixer, a sample of each gas mix was withdrawn from the wave guide and the percentage of ammonia checked, using volumetric absorption by water of NH_3 gas. The mixes checked within a few percent in all cases.

The vacuum gauge which was used to record pressure was a modified Pirani, using a very small filament as the active element in a standard bridge circuit. The gauge was calibrated *in situ* for each gas involved, using a McLeod gauge as standard. Curves for each pure gas were plotted. The indication with a known mix ratio was taken to be linearly related to the reciprocal of the sum of the partial pressures. The variation between gases was somewhat less than might be expected from a true Pirani gauge because of the small size of the filament, so that it was not possible to calculate the response of the gauge using kinetic gas theory. The advantages of such a gauge are a comparatively fast response to pressure changes and a somewhat more linear calibration curve than with a true Pirani gauge.

TABLE II. Collision diameters of ammonia inversion lines with foreign perturbers ($\times 10^8$ cm). Mix A = 45 percent perturbing gas by volume. Mix B = 70 percent perturbing gas by volume.

J	K	Gas	Mix A	Mix B	Smith and Howard	Bleaney and Penrose
2	1	O_2	3.14	2.48		
8	7		4.05	3.78		
3	3		4.31	4.02	3.86	4.85
4	4		4.52	4.28		
6	6		5.05	4.71		
2	1	He	1.88	1.52		
8	7		2.62	2.28		
3	3		2.81	2.42	2.00	2.35
4	4		2.94	2.50		
6	6		3.14	2.73		
2	1	N_2O	9.51	8.85		
8	7		10.8	10.4		
3	3		11.2	10.7		
4	4		11.4	11.1		
6	6		12.5	12.0		

TABLE III. Collision diameter of ammonia 3, 3 line in oxygen.

Percent O_2	40	45	54	70
$b_{12}\times 10^8$ cm	4.38	4.31	4.22	4.02

The half-width was determined by measurement of an absorption line which was superimposed on the mode of the klystron tube used. Because of mode curvature, half-widths greater than approximately twelve Mc-sec^{-1} were not used. The low pressure limit was determined by the gas mixture, as the pump began to pump out the gases selectively at about one-tenth of a millimeter so that the mix ratio was no longer constant. In the case of self-broadening this limitation, of course, did not appear.

Since the measurements of the trace depend on faithful reproduction of line shape, the crystal detector which was used was calibrated. Actually, it was always operated in the region where the departure from square-law characteristic was negligible.

This spectrograph is capable of producing measurements at a relatively rapid rate. All that need be recorded for a given line, perturber, and mix is the pressure-gauge reading and the marker pip setting for each photograph. A mix can be prepared and observed in less than an hour, data being taken at as many pressures as desired.

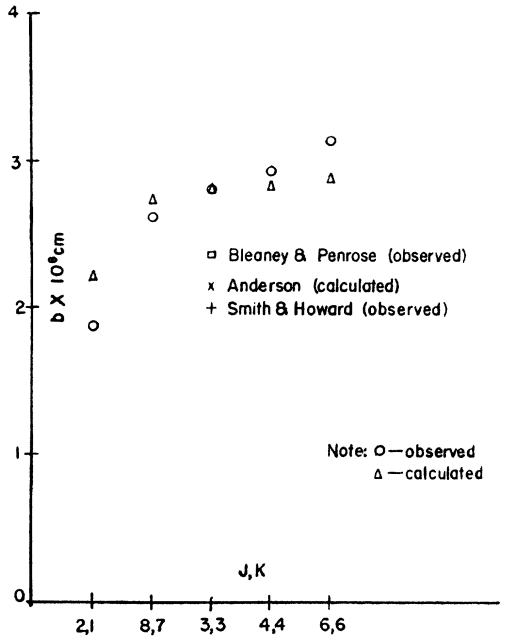

FIG. 3. Variation of collision diameter with quantum numbers of lines.

RESULTS

A. Variation of Collision Cross Sections with Mix

In all cases, the collision cross sections b_{12} decrease with increasing admixture of perturber, although Eq. (2) used for computing b_{12} should yield a constant value of b_{12}, the effect of mixture having already been allowed for. This result is disturbing, and its cause is, for the present, obscure. Experiments are under way to study this effect further. In the meantime, it seems best to take as the best value of b_{12} the result of extrapolating to 100 percent of perturber.

B. Effect of Pressure and Accuracy of Results

For any mixture, the half-width is directly proportional to total pressure in the pressure range from 0.1 to 0.6 mm of Hg. The accuracy which is claimed for our measurements is not better than about five percent in the case of broadening by foreign gases. The self-broadening collision diameters of ammonia are within one percent.

C. Self-Broadening of Ammonia

Table I gives our collision cross sections for self-broadening of ammonia, as well as those obtained by Bleaney and Penrose. Agreement is good.

D. Broadening by Foreign Perturbers

Table II gives the collision diameters as a function of mix ratio and absorbing line, for the three perturbers used: O_2 and He (nonpolar), and N_2O (dipole, linear, nonsymmetric). Values for the 3, 3 line obtained by Bleaney and Penrose and by Smith and Howard are also given; agreement with these is only fair. Table III gives the collision diameter of ammonia 3, 3 line in oxygen for several mixes, exhibiting most clearly the variation of cross-section diameter with mix, discussed under A.

E. Variation of Collision Diameter with Quantum Numbers of Lines

In the case of self-broadening of ammonia, our values agree closely with those of Bleaney and Penrose, and, therefore, in the main with Anderson's theory. In the case of nonpolar He and O_2, Anderson[4] has recently given a formula based on the interaction of the induced dipole with the quadrupole moment of the ammonia molecule which makes it possible to compute the collision cross sections as a function of quantum numbers. The results of this computation for the 3, 3 line perturbed by He and O_2 are in good agreement with the observed values obtained by Smith and Howard and are, therefore, a good deal smaller than our observed values (see Table III and Fig. 3). The variation with quantum number as given by Anderson's formulas is also a good deal smaller than observed by us, but the general type of variation is correctly given. This is exhibited in Table IV and Fig. 3. In both of these, the values for the 3, 3 line are our observed values, and the values for the other lines are computed (for He, mix A; the other cases are similar) from this using Anderson's factor depending on the quantum numbers [Eq. (14) of reference 5].

Broadening of ammonia lines by N_2O is markedly less than by the nonpolar O_2 and He. Unfortunately, an explicit formula based on Anderson's theory is not at present available for this case.

We are very grateful to Dr. P. W. Anderson for interesting and helpful discussions and correspondence and for the loan of his thesis. We would like also to thank Drs. W. V. Smith and R. Howard for sending us their results prior to publication. Our thanks are also due to J. V. Bonet, S.J., for assistance with some of the numerical computations.

TABLE IV. Comparison with Anderson's theory. Agreement is assumed for the 3, 3 line; and the values for the other lines represent, therefore, variation from the 3, 3 line.

J	K	b, observed	b, calculated	b, Anderson
		Mix A, 45 percent of perturber, by volume		
		He		
3	3	2.81	(2.81)	2.15
2	1	1.88	2.21	
8	7	2.62	2.77	
4	4	2.94	2.85	
6	6	3.14	2.89	
		O_2		
3	3	4.31	(4.31)	3.35
2	1	3.14	3.39	
8	7	4.05	4.25	
4	4	4.52	4.37	
6	6	5.05	4.44	
		Mix B, 70 percent of perturber		
		He		
3	3	2.42	(2.42)	2.15
2	1	1.52	1.91	
8	7	2.28	2.38	
4	4	2.50	2.45	
6	6	2.73	2.49	
		O_2		
3	3	4.02	(4.02)	3.35
2	1	2.48	3.16	
8	7	3.78	3.96	
4	4	4.28	4.08	
6	6	4.71	4.14	

[4] P. W. Anderson, Phys. Rev. **80**, 511 (1950).