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The Ammonia Spectrum and Line Shapes Near 1.25-cm Wave-Length

CHARLES HARD TOWNES
Bell Telephone Laboratories, Murray Hill, New Jersey

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The ammonia "inversion" lines near 1.25-cm wave-length are resolved, their widths being decreased at low pressures to 200 kilocycles. Line shapes, intensities, and frequencies are measured and correlated with theory. Calculated intensities and Lorentz-type broadening theory fit experimental results if frequency of collision is fifteen times greater than that measured by viscosity methods. Splitting due to rotation is in fair agreement with a recalculation of theoretical values. A saturation effect is observed with increase of power absorbed per molecule and an interpretation made.

SINCE the measurements of Cleeton and Williams[1] on ammonia absorption in the 1-centimeter region techniques for producing and measuring 1-centimeter radiation have improved markedly. The fine structure of this line can now be resolved and line frequencies and shapes measured with exactness. This affords a more accurate check on pressure broadening theory than can be obtained in the infra-red region, as well as additional information about the ammonia molecule. There are some small differences between the results presented here and those of Bleaney and Penrose[2] and of Good[3] which were published after the present work was largely complete, and their work is extended in certain respects.

GENERAL THEORY

The ammonia absorption at approximately 1.25-cm wave-length is caused by the ability of the ammonia molecule to "turn inside out," the nitrogen atom going through the plane of the hydrogens. Various functions[4] for the potential of the nitrogen atom as it goes through the plane of the hydrogens have been found which satisfactorily fit the frequency of this inversion line as well as the frequency of the similar line for the first excited vibration state. Sheng, Barker, and Dennison[4] calculated the additional splitting of the first vibrational state due to the fact that the molecules may be in different rotational states each of which has a slightly different inversion frequency and found agreement with experimental determinations. They also calculated the splitting of the inversion line in the ground state which is the line discussed here, but had no experimental data accurate enough for a comparison. Their formula for frequency is given by

$$\nu/hc=(W_0{}^a-W_0{}^s)/hc \\ +(A_0{}^a-A_0{}^s)(J^2+J-K^2)+(C_0{}^a-C_0{}^s)K^2, \quad (1)$$

where J and K are the usual angular momentum quantum numbers. A definition of the other quantities and their calculated values may be found in their paper. Substituting these values,

$$\nu/hc=0.66-0.0011(J^2+J-K^2) \\ +0.0005K^2\ \mathrm{cm}^{-1}. \quad (2)$$

It may be seen from this formula that an angular momentum about the symmetry axis (K) tends to force the hydrogens apart and allow the nitrogen to pass through their plane more freely, thus increasing ν, whereas an angular momentum perpendicular to the symmetry axis $(J^2+J-K^2)^{\frac{1}{2}}$ creates a centrifugal force which retards this motion and decreases ν. Cleeton and Williams[1] observed the combined effects of all of these lines since their measurements were at atmospheric pressure where the lines were very broad and superimposed.

The intensity and shape of each of these lines assuming collisions are the main cause of line broadening is predicted theoretically by Van Vleck and Weisskopf[5] to be

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[1] Cleeton and Williams, Phys. Rev. **46**, 235 (1934).

[2] Bleaney and Penrose, Nature **157**, 339 (1946).

[3] Good, Phys. Rev. **69**, 539 (1946).

[4] Sheng, Barker, and Dennison, Phys. Rev. **60**, 786 (1941); Dennison and Uhlenbeck, Phys. Rev. **41**, 313 (1932).

[5] Van Vleck and Weisskopf, Rev. Mod. Phys. **17**, 227 (1945).

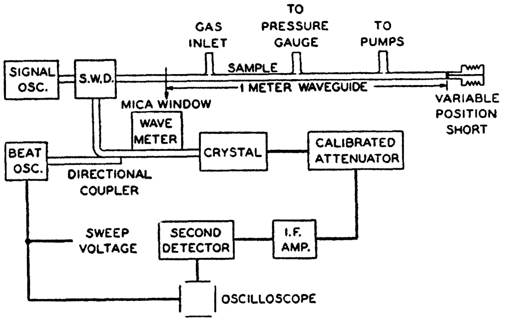

FIG. 1. Schematic diagram of apparatus used for ammonia pressures $\geqq 0.27$ mm Hg.

$$\gamma=\frac{2\pi^2Nf}{3ckT}|\mu_{ij}|^2\nu^2\left[\frac{1/2\pi\tau}{(\nu-\nu_0)^2+(1/2\pi\tau)^2}+\frac{1/2\pi\tau}{(\nu+\nu_0)^2+(1/2\pi\tau)^2}\right], \quad (3)$$

where

γ = the absorption in nepers/cm
N = the density of molecules
f = the fraction of molecules in the rotational state considered
μ_{ij} = the matrix element of dipole moment
ν = the frequency
ν_0 = the resonant frequency and $h\nu_0 \ll kT$
τ = the time between collisions which produce a large change of phase of the oscillation
c, k, T = velocity of light, Boltzman constant, and absolute temperature, respectively.

As long as the second term is small, this formula predicts that the half-width of the line is directly proportional to pressure and that the intensity at resonance ($\nu=\nu_0$) is constant independent of pressure. Thus within the approximations of the formula, that is neglecting the natural width of the line, the Doppler effect, collisions of molecules with the walls of the container, and saturation effects which will be discussed below, the lines are expected to become narrower with decreasing pressure but to stay constant in intensity at the resonant frequency. This conclusion is in contrast, however, with some measurements[6] in the infra-red region which indicate that the intensity at the resonant frequency is proportional approximately to the square root of the pressure.

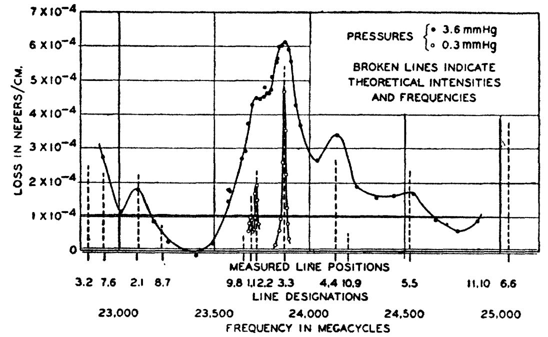

FIG. 2. Envelope of the NH_3 absorption spectrum at 3.6 mm Hg.

LINE SHAPES AND INTENSITY—APPARATUS AND RESULTS

To resolve the ammonia lines and measure their shapes and intensities the apparatus shown schematically in Fig. 1 was used. The ammonia was contained in a one-meter wave guide with small pinhole outlets so that the gas pressure could be measured and changed but the radiation could not leak out. One-mil mica windows inserted in the wave guide isolated the ammonia from atmospheric pressure. The signal and beat oscillators used were type 2K33, the beat oscillator being swept over approximately 10 megacycles by applying a sine wave to its reflector. The standing wave detector (S.W.D.) is a probe which may be moved several wave-lengths along the wave guide and thus pick up the maxima and minima of the standing wave. The intensity of the detected signal was adjusted by means of the calibrated attenuator so that it gave a standard deflection on the oscilloscope. The difference in attenuator settings with the standing wave de-

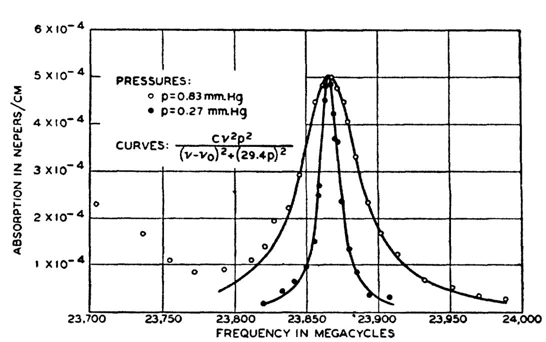

FIG. 3. The NH_3 (3.3) absorption line. The absorption in wave guide is shown here and in Fig. 1. Absorption in free space may be obtained by multiplying by 0.8.

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[6] For a summary see W. M. Elsasser, Harvard Meteorological Studies No. 6 (1942), pp. 45–48.

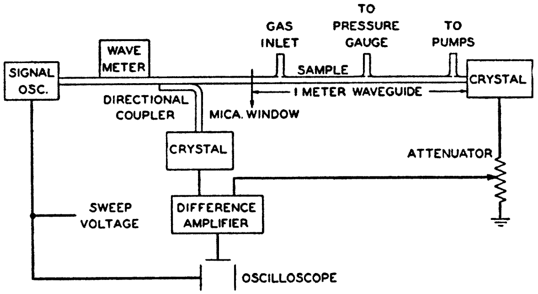

FIG. 4. Schematic diagram of apparatus used for ammonia pressures less than 0.27 mm Hg.

tector at maxima and minima allows a determination of the attenuation undergone by the radiation which travels down the wave guide to the variable position short and back again. Measurements were made with two settings of the variable position short one-quarter wavelength apart. An average of these two measurements cancels out certain types of errors such as that due to a small reflection at the mica window. The evacuated wave guide showed an attenuation of approximately 6×10^{-4} neper per cm. This was of the same order as the absorption due to ammonia and was subtracted from the total measured attenuation after the ammonia gas was let in. The wave meter is a tunable resonant cavity with small coupling to the wave guide. It was calibrated from 23,500 megacycles to 24,500 megacycles against a second wave-meter which had been calibrated in the same region by comparison with multiples of a standard 100-kilocycle frequency. Frequencies outside this range were determined by a semi-theoretical extrapolation of this calibration. Attenuation measured in this way is thought to be accurate in absolute value to approximately 2×10^{-5} neper per cm and reproducible to half of this. The wave-meter calibration is thought to have a probable error of 2 megacycles in the range directly calibrated and 5 megacycles in the extrapolated range.

An envelope of the ammonia absorption at 3.6 millimeters of mercury pressure is shown in Fig. 2 as well as measurements of 3 lines at 0.3 millimeter pressure. The most intense single line later identified as $J=3$ and $K=3$ was examined in some detail at 0.83- and 0.27-mm Hg as shown in Fig. 3. The formula given above for the line shape was fitted to the points obtained and as may be seen from this figure agrees within experimental error. The intensity at resonance does indeed stay constant. The second term of this formula was negligible at the pressures used. On the low frequency side of the 3, 3 line another interfering line may be seen at 0.83-mm pressure.

The half-width obtained by fitting the theoretical formula (3) to these curves shows that the time between collisions τ equals $6.7\times10^{-9}p$, where p is the pressure in mm Hg. Thus collisions affecting this oscillation are fifteen times more frequent than the collisions found by ordinary kinetic measurements. As pointed out by Bleaney and Penrose,[2] the long range dipole-dipole forces may effect this transition although they are ineffective in transferring linear momentum which is essential for most kinetic processes. Using the experimentally determined half-width of the 3, 3 line, and a value 0.0637 calculated for f, the fraction of molecules in the $J=3$, $K=3$ state at 25°C, the peak intensity of this line may be calculated from the expression (3). If the dipole moment $|\mu_{ij}|$ is 1.45×10^{-18} e.s.u., the peak intensity should be 4.9×10^{-4} neper/cm. The experimental value is 5.0×10^{-4} neper/cm in wave guide, or 4.0×10^{-4} neper/cm for a plane wave.[7] This value is considerably higher than the 0.18 db/meter or 2.1×10^{-4} neper/cm given by Good.[3] The probable error of the measurement is thought to be $\pm0.2\times10^{-4}$ neper/cm. The calculated value 4.9×10^{-4} has a probable error of about five percent due to an uncertainty in the pressure at which the line breadth was measured and in addition a few percent error due to uncertainties in the value of $|\mu_{ij}|$. The discrepancy of 20 percent between measured and calculated attenuations thus is slightly larger than expected from the estimated errors.*

As a check on the nature of the forces producing such a large half-width, argon was mixed with ammonia to determine the consequent line broadening. The resulting line when 0.5 millimeter of ammonia and 9.5 millimeters of argon were mixed was symmetrical and its peak frequency unchanged. Its half-width was only twice as great as that for 0.5-millimeter ammonia alone. This indicates the frequency of collision between ammonia and argon is approximately the same as

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[7] W. D. Hershberger, J. App. Phys. **17**, 495 (1946).

* In computing the theoretical intensities, $|\mu_{ij}|^2$ was erroneously taken equal to the square at the dipole moment μ rather than to $K^2\mu^2/J(J+1)$ [see D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931)]. The corrected theoretical intensity for the $J=3$, $K=3$ line is 3.7×10^{-4} neper/cm which is in good agreement with the experimental value.

TABLE I. Absorption lines of NH_3 in frequency range 22,800 to 25,100 megacycles.

Line designation		Calculated intensity nepers $\times 10^{-4}$/cm	Frequency in megacycles		
J	K		Experiment	From formula (4)	Difference
1	1	1.65	23,693	23,699	+6
2	2	2.41	23,722	23,725	+3
3	3	5.50	23,870	23,869	−1
4	4	2.74	24,137	23,134	−3
5	5	2.42	24,529	24,522	−7
6	6	3.86	25,046	25,039	−7
2	1	2.28	23,097	23,108	+11
3	2	2.53	22,840	22,843	+3
7	6	2.32	22,927	22,920	−7
8	7	0.77	23,231	23,224	−7
9	8	0.47	23,656	23,650	−6
10	9	0.54	24,202	24,202	0
11	10	0.14	24,877	24,890	+13

obtained by kinetic measurements and that the large number of collisions between ammonia molecules is probably caused by dipole-dipole forces.

LINE FREQUENCIES—APPARATUS, RESULTS, AND RECALCULATION OF THEORY

The technique described above and shown schematically in Fig. 1 could not be used at pressures much lower than 0.3 mm Hg because the signal oscillator was not stabilized in frequency and would drift an appreciable distance on the curve during a single measurement. For these lower pressures a second technique was used as shown in Fig. 4. A single oscillator was swept over approximately 10 megacycles and its output sampled by one crystal before entering the wave guide containing ammonia and by a second crystal after traversing the ammonia. The difference between the signals from these two crystals was amplified and put on the vertical plates of an oscilloscope whose horizontal sweep is synchronized with the oscillator sweep. If the oscillator frequency is centered near an ammonia absorption line, a pip corresponding to the line then appears on the oscilloscope. As the pressure is decreased the line becomes narrower but remains of constant peak intensity as predicted until it reaches a width of approximately 500 kilocycles when it begins to fade out. Causes for decrease in intensity at this point will be discussed below. The narrow and weak lines may be detected by this method more easily than by the first, and frequencies can be more accurately measured. The frequency of the line is measured by tuning the wave-meter until it produces a pip on the oscilloscope. Its pip may be superimposed on that due to an ammonia line to an accuracy of a fraction of a megacycle.

Thirteen lines were detected in the frequency range 22,800 to 25,100 megacycles, their identification and frequencies being given in Table I. The "hyperfine structure" reported by Good[3] was not observed. The frequencies may be fitted to a formula of the same form as (2) but having somewhat different constants. Such a formula is

$$\nu = 0.79356_6 - 5.015_8\times 10^{-3}(J^2+J-K^2) + 1.964_6\times 10^{-3}K^2 + 6.3\times 10^{-7} \times[-5.02(J^2+J-K^2)+1.96K^2]^2\ \mathrm{cm}^{-1} \quad (4)$$

or

$$\nu = 23{,}790.5 - 150.34_1(J^2+J-K^2) + 58.87_8K^2 + 2.1\times 10^{-5}[-150(J^2+J-K^2) + 59K^2]^2\ \text{megacycles.}$$

Here a higher order term is included which is not given by Sheng, Barker, and Dennison,[4] but whose form and magnitude is obtained immediately from their theory as a term in an exponential expansion. It will be noted from Table I and from Fig. 2 that the frequencies given by this formula and the theoretical intensities fit well with experimental observations, but also show some systematic deviations. This formula is to be compared with the results of Bleaney and Penrose[2]

$$\nu = 0.7940 - 0.0050(J^2+J-K^2) + 0.0020K^2 + 0.63[-0.005(J^2+J-K^2)+0.002K^2]^2\ \mathrm{cm}^{-1}$$

and of Good[3]*

$$\nu = 0.7932 - 4.8\times 10^{-3}(J^2+J-K^2) + 2.0\times 10^{-3}K^2\ \mathrm{cm}^{-1}.$$

Bleaney and Penrose also find the higher order term useful in fitting the experimental data. Another higher order term of the same magnitude should be included, however, if theory is to be considered this accurate. It is $-(\Delta/h)[2\mu|\delta V-\delta E|]^{\frac{1}{2}}\delta y_1$ in the notation of Sheng, Barker, and Dennison. This term is calculated to be $-0.590|J^2+J-1.56K^2|^{\frac{1}{2}}(J^2+J$

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* Good has informed me privately that his more recent results are in good agreement with formula (4).

$-1.56K^2$) megacycles. Its inclusion results, however, in a definitely worse fit than if it is omitted. Since both this term and the higher order term included in (4) are only a few percent as large as the main term, it is hardly to be expected that the approximate theory which has been used will predict them correctly.

The line shapes, intensities, and spacing ratios therefore agree reasonably well with theoretical expectations, the main discrepency being in the magnitude of the line spacing. It appeared possible that a numerical error had been made in calculating the line splitting in the ground vibration state so a recalculation was made with the same theory and potential function used by Sheng, Barker, and Dennison.[4]

The quantities desired are given within sufficient approximation by

$$A_0-A_s(\mathrm{cm}^{-1})=-\frac{\Delta_0}{2\pi}\left(\frac{\mu h}{2c}\right)^{\frac{1}{2}}$$

$$\times\int_0^{y_1}\frac{\dfrac{1}{\mu r^2\sin^2\alpha+3/2mr^2\cos^2\alpha}-\dfrac{1}{\mu r_0{}^2\sin^2\alpha_0+3/2mr_0{}^2\cos^2\alpha_0}}{\left[66{,}551\,\mathrm{sech}^4\left(\dfrac{y}{0.09586(\hbar/c\mu)^{\frac{1}{2}}}\right)-109{,}519\,\mathrm{sech}^2\left(\dfrac{y}{0.09586(\hbar/c\mu)^{\frac{1}{2}}}\right)+44{,}642\right]^{\frac{1}{2}}}dy,$$

$$C_0-C_s(\mathrm{cm}^{-1})=-\frac{\Delta_0}{2\pi}\left(\frac{\mu h}{2c}\right)^{\frac{1}{2}}$$

$$\times\int_0^{y_1}\frac{\dfrac{1}{3mr^2\cos^2\alpha}-\dfrac{1}{3mr_0{}^2\cos^2\alpha_0}}{\left[66{,}551\,\mathrm{sech}^4\left(\dfrac{y}{0.09586(\hbar/c\mu)^{\frac{1}{2}}}\right)-109{,}619\,\mathrm{sech}^2\left(\dfrac{y}{0.09586(\hbar/c\mu)^{\frac{1}{2}}}\right)+44{,}642\right]^{\frac{1}{2}}}dy,$$

where

$$\alpha=\alpha_0 y/y_0$$

and

$$r=r_0[1-0.05\alpha_0+0.05\alpha_0(y/y_0)^2].$$

The basis for these expressions and definitions of quantities involved may be found in the abovementioned article. The expressions were evaluated both for the first excited state and the ground state and although results for the excited state are in essential agreement with those previously found, there is a significant difference for the ground state as shown by Table II. The recalculated quantities agree much more closely with experiment. The remaining discrepancy between experiment and theory can probably be eliminated by using a somewhat modified potential function which will still be consistent with other observed data.

SATURATION EFFECTS

Calculation shows that the Doppler effect and collisions between molecules and the wave-guide walls should make the formula (3) above for the line shape begin to break down at about 150 kilocycles total width at half-maximum, and should prevent the low pressure width of the lines from decreasing below about 75 kilocycles. However, on first examination the lines began to decrease in peak intensity when they were still wider than 1000 kilocycles, and would not become narrower than about 500 kilocycles. A closer investigation showed that the fraction of power absorbed and the apparent width of the absorption line depends on the amount of power sent through the absorbing tube. Thus under certain conditions an increase of power through the

TABLE II. Recalculated values of the ground state and first excited vibrational state of NH$_3$.

	Calculated value Sheng, Barker, and Dennison[a]		Experimental value		Recalculated value	
	A^a-A^s	C^a-C^s	A^a-A^s	C^a-C^s	A^a-A^s	C^a-C^s
Ground state	−0.0011	0.0005	−0.005015	0.001964	−0.00330	0.00175
First excited vibrational state	−0.162	0.06	−0.17	0.06	−0.156	0.066

[a] See reference 4 in text.

absorbing tube by a factor of ten increases the power absorbed at the resonance frequency by only a factor of two or three, and broadens the apparent width of the line by about the same amount. At somewhat higher pressures and the same amounts of power this phenomenon does not occur. By decreasing the power level, lines of total width at half-maximum of 200 kilocycles were obtained. A further reduction of power to obtain still narrower lines was not practical with the experimental setup used.

Three possible causes for this dependence of absorption coefficient on power presented themselves.

1. A simple increase in temperature of the gas due to the power absorbed.
2. A disturbance of the distribution of molecules between the ground and excited states by their absorbing quanta faster than they can dispose of the energy, depleting the supply of molecules capable of absorbing.
3. A decrease in the lifetime of both upper and lower states of the molecule due to very rapid induced transitions. This broadens the line and decreases the absorption at resonance.

The first effect can be shown to be negligible, since for the powers used (~1 mw) the increase in temperature is of the order of 1 degree. The results of the second and third effect are derived below and their magnitudes agree with the somewhat rough observations made.

The expression for the absorption coefficient, neglecting the non-resonant term, may be written using (3) above

$$\gamma=\frac{4\pi^2}{3}\frac{(n_0-n_1)}{hc}|\mu_{ij}|^2\frac{\omega^2}{\omega_0}\times\left[\frac{\frac{1}{\tau}+\frac{1}{2\tau_0'}+\frac{1}{2\tau_e'}}{(\omega-\omega_0)^2+\left(\frac{1}{\tau}+\frac{1}{2\tau_0'}+\frac{1}{2\tau_e'}\right)^2}\right]. \quad (5)$$

Here $\omega=2\pi\nu$ and $\omega_0=2\pi\nu$. $1/2\tau_0'$ and $1/2\tau_e'$ have been added to allow for the frequency of disturbance of the ground and excited states respectively by processes other than collisions. n_0-n_1 is the difference between the number of molecules in the lower and the upper states of the particular transition in question. If n_q represents the rate at which each of these molecules makes transitions due to the radiation present, then

$$n_0-n_1=\frac{Nfh\nu_0/2kT}{1+n_qt},$$

where N and f are defined in formula (3), and t is the relaxation time of the molecule, or the average time required to get rid of one absorbed quantum independently of the radiation field. n_q may be shown to be

$$\frac{I\gamma}{Nh\nu f/2kT-I\gamma t}$$

if I is the intensity of incident radiation in quanta per second per square centimeter. Since $1/\tau_0'=1/\tau_e'=n_q$, formula (5) becomes

$$\gamma=\frac{\pi}{3}\frac{Nf}{ckT}|\mu_{ij}|^2\omega^2\left[1-\frac{I\gamma t}{Nh\nu f/2kT}\right]\times\left[\frac{\frac{1}{\tau}+\frac{I\gamma}{Nh\nu f/2kT-I\gamma t}}{(\omega-\omega_0)^2+\left(\frac{1}{\tau}+\frac{I\gamma}{Nh\nu f/2kT-I\gamma t}\right)^2}\right]. \quad (6)$$

Thus saturation effects set in when either

$$\frac{I\gamma t}{(Nh\nu f/2kT)} \text{ approaches } 1$$

or

$$\frac{I\gamma}{[(Nh\nu f/2kT)-I\gamma t]} \text{ approaches } 1/\tau.$$

For $I\rightarrow\infty$, $I\gamma\rightarrow Nh\nu f/2kTt$. Observations show that saturation sets in when $I\gamma/(Nh\nu f/2kT)$, the rate of transition per molecule assuming the distribution is undisturbed is approximately equal to the rate of collision. Thus for 1.8 milliwatts into the absorption tube (cross section 10.7 mm×4.3 mm) at a pressure of 4×10^{-2} mm Hq, the effect just becomes noticeable. For this condition $I\gamma/(Nh\nu f/2kT)\approx3\times10^6$ and $1/\tau\approx6.4\times10^6$. This indicates also that $t\approx\tau$, or that molecules lose their excitation on almost every collision, otherwise saturation effects would show up at somewhat smaller power values. Observation is in agreement with the above theory that the power at which saturation effects occur decreases as the square of the pressure.

ACKNOWLEDGMENT

This work has benefited from the contributions of many members of the Bell Laboratories. Mention should be made especially of the aid and encouragement of Dr. S. O. Morgan, of the considerable laboratory help of Messrs. W. H. Hewitt and F. R. Merritt, and of the work of the computing staff which obtained the values given in Table II and assisted in other calculations.

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Helium Molecular Energy States as Detected by Collisions of the Second Kind in Helium

ROLAND MEYEROTT
Sloane Physics Laboratory, Yale University New Haven, Connecticut

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From a survey of the literature on spectra enhanced by collisions of the second kind, which take place in helium, evidence is presented for the existence in measurable concentrations of both the helium molecule-ion and the helium metastable molecule. From the intensity distribution of the enhanced spectra, the repulsive energy between two helium atoms at separations of 1.052A and 1.090A is derived to be 6.8 volts and 5.8 volts, respectively. The rates of formation of the molecular states are discussed in the special case of a steady-state discharge and the molecular states are shown to be very probable at high pressures. From this it is shown that the ion whose mobility is found to be 21.4 cm^2/sec. volt is probably that of He_2^+ in helium and, hence, the discrepancy between the theoretical and experimental values of the mobilities can be removed by such an interpretation. The existence of neon molecules is also suggested.

INTRODUCTION

DIFFICULTY in interpreting certain types of experiments in electrical discharges in gases has led to the conclusion that processes which take place under such conditions are exceedingly complex and that little can be gained by their study. In helium, the simplest of all gases, we find numerous examples. The experimental value for the mobility of He^+ in He, 21.4 cm^2/volt sec., as measured by Tyndall and Powell,[1] is almost double the theoretical value, 12 cm^2/volt sec., calculated by Massey and Mohr.[2] The rate of decay of metastable helium atoms in pure helium is much larger than can be accounted for by the theory, or by comparison with the other noble gases.[3] Selective excitation of impurities in helium discharges is in disagreement with theory. Duffendack and Smith,[4] Takahashi,[5] and others[6] have had difficulty in accounting for the enhanced spectra produced in helium. They assume the helium metastable atoms in the $1s2s^1S$ and $1s2s^3S$ states, and the helium ion, He^+, to be the carriers of the excitation energy. This requires in some cases an assumption of changes in kinetic energy in collisions of the second kind of 3 to 5 ev, which theory hardly permits. Experiments by Richardson[7] and others on the effect of helium on the hydrogen molecular spectra has led to the belief that, in the H_2 triplet spectrum, helium merely enhances the o,o bands with little or no effect on the states of higher vibrational energy. These results have led Smith[8]

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[1] A. M. Tyndall and C. F. Powell, Proc. Roy. Soc. **A134**, 125 (1931).

[2] Massey and Mohr, Proc. Roy. Soc. **A144**, 188 (1934).

[3] See Mitchell and Zemansky, *Resonance Radiation and Excited Atoms* (The Macmillan Company, New York, 1934), pp. 236–250.

[4] O. S. Duffendack and H. L. Smith, Phys. Rev. **34**, 68 (1929).

[5] Y. Takahashi, Ann. d. Physik **3**, 49 (1929).

[6] For complete list consult Bibliography in references 4 and 5. See also L. S. Headrick and O. S. Duffendack, Phys. Rev. **37**, 736 (1931).

[7] For summary, see Richardson, *Molecular Hydrogen and its Spectrum* (Yale University Press, New Haven, Connecticut, 1934), pp. 194–218.

[8] N. D. Smith, Phys. Rev. **49**, 345 (1936).