Electromagnetic Waves of 1.1 cm Wave-Length and the Absorption Spectrum of Ammonia

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A spectrometer, with a grating of the echelette type, was used in mapping the absorption spectrum of ammonia gas in the region from 1 to 4 cm wave-length. To accomplish this, it became necessary to produce electromagnetic waves of shorter wave-length than had been produced before by vacuum tubes. Oscillators of the magnetron type were used as the source of the continuous short wave radiation. The center of the absorption band had been predicted to be at 1.5 cm wave-length. The maximum absorption was found to occur at 1.25 cm. This shift is explained by the unsymmetrical nature of the line. The constants in a theoretical formula for the absorption coefficient have been determined. These constants involve an effective collision diameter of the molecule, and lead to the value $\sigma=8.8\times10^{-8}$ cm. The total intensity of the line was found to be 10×10^{7} cm^{-1} sec.$^{-1}$.

INTRODUCTION

THE ammonia molecule has the form of a regular pyramid with the nitrogen atom at the apex. The problem of the vibrational energy levels of the molecule has been discussed by Dennison and Hardy[1] and by Dennison and Uhlenbeck.[2] It has been shown that the energy levels are split into pairs because there exist two equivalent positions of equilibrium for the nitrogen atom. The energy difference between the two lowest levels gives rise to a doubling of the far infrared absorption lines of ammonia, which has been observed by Wright and Randall.[3] From their measurements this energy difference was found to be 0.67 cm^{-1}. The theory also predicts that ammonia gas should strongly absorb radiation of the frequency, $\nu=0.67$ cm^{-1}, corresponding to a wave-length of 1.5 cm. It is the experimental measurement of this absorption that is reported in this paper.

EXPERIMENTAL

The radiation used consisted of short electric waves produced by a magnetostatic oscillator. The wave-length was measured by a spectrometer with two brass mirrors three feet in diameter and an echelette grating of corresponding size. The ammonia gas was contained in a rubberized cloth cell at about atmospheric pressure.

The term magnetostatic oscillator was coined at the laboratory of the Westinghouse Electric and Manufacturing Company and is applied to electronic oscillators using a vacuum tube having a hot cathode and one or more anodes in combination with a constant magnetic field. The frequency depends primarily upon the time of flight of the electrons between the cathode and the anode. Zacek[4] first discovered this type of electronic oscillations. The reference given below is to some comments which he made on the subject some time after his original paper was published. Later Yagi[5] and Okabe[6, 7] built tubes which produced stable oscillations whose wave-lengths were, in the extreme case, as short as 3.16 cm. They obtained much greater output by splitting the anode into semi-cylinders, and connecting the two halves to form an oscillatory circuit. Kilgore[8] discovered the importance of inclining the magnetic field with respect to the cathode, in order to obtain maximum output. He also gave a thorough discussion of the characteristics of a tube operating at a wave-length of about 42 cm. As a result of the improvements in design made by Kilgore, tubes were built at the Westinghouse laboratories capable of giving considerable power at a wave-length of 9 cm. The

[1] Dennison and Hardy, Phys. Rev. **39**, 938 (1932).
[2] Dennison and Uhlenbeck, Phys. Rev. **41**, 313 (1932).
[3] Wright and Randall, Phys. Rev. **44**, 391 (1933).
[4] Zacek, Zeits. f. Hochfrequenztechnik **32**, 172 (1928).
[5] Yagi, Proc. I. R. E. **16**, 715 (1928).
[6] Okabe, Proc. I. R. E. **17**, 652 (1929).
[7] Okabe, Proc. I. R. E. **18**, 1748 (1930).
[8] Kilgore, Proc. I. R. E. **20**, 1741 (1932).

success of these tubes encouraged the authors to attempt to reduce the wave-length sufficiently to study the absorption by ammonia gas at 1.5 cm. The shorter waves were obtained by building tubes of very small dimensions, following the design of some of the 9 cm tubes kindly loaned to us by the Westinghouse laboratories. The anodes were of graphite, and the Lecher system connected between the anode segments was contained within the tube envelope, a type of construction which Kilgore had demonstrated to be possible. As the dimensions of the tube were decreased the applied magnetic field was increased according to the approximate relation, $\lambda H = 13{,}000$, given by Okabe,[6] in which λ is the wave-length in cm and H is the field intensity in gauss.

One of the smaller tubes, which had an anode radius of 0.027 cm and a Lecher system about 4 mm long, produced waves 1.13 cm long, with 870 volts on the anode and in a magnetic field of 11,000 gauss. The energy at this wave-length was sufficient to produce a full scale deflection of the receiving galvanometer. The characteristics of these tubes were similar to those which produced the longer wave-lengths. Each tube could be made to operate at any frequency within a small range covering about 30 percent of the mean frequency. The tuning was accomplished by varying the magnetic field and by adjusting the plate voltage, the filament current, and the angle between the filament and the field. Four tubes were used in making absorption measurements between wave-lengths of 1.06 cm and 3.8 cm.

The arrangement of the spectrometer[9] is shown in Fig. 1. The oscillator tube was placed between the pole pieces, PP, of a strong electromagnet, and at the focus of the parabolic mirror M_1. A parallel beam of the short wave radiation fell upon the grating G, which has 18 elements and a constant of 7.49 cm. The diffracted beam was focussed on a rather large slit in the metal shield S, by a second parabolic mirror M_2. An iron pyrite-phosphor-bronze crystal detector was placed inside the shield just behind the opening and was connected to a Leeds and Northrup galvanometer. A metal reflector behind the detector could be adjusted along the axis of the mirror for greater sensitivity. This arrangement served as a suitable receiver for the radiation. The elements of the grating were automatically adjusted to remain perpendicular to the bisector of the angle θ as the grating was turned, thereby giving maximum energy at any position of the grating. The reflectors R were arranged to prevent the radiation reflected from the walls of the room from reaching the detector. When they were properly placed, no radiation fell upon the detector except that which came directly from the grating. The alignment of the spectrometer was accomplished by focussing the image of the filament of the oscillator tube upon the slit in the receiver shield.

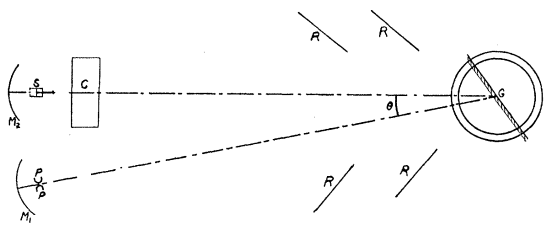

FIG. 1. Diagram of the spectrometer designed for wave-lengths below 10 cm.

[9] Cleeton and Williams, Phys. Rev. **44**, 421 (1933).

The cell C was placed in front of the receiving mirror. The cell was made of rubberized cloth cemented at the seams and supported on two wooden frames, which allowed it to collapse so that the air could be removed and pure ammonia introduced into the cell. The cross section of the cell was 36×45 inches and the length 16 inches. There seemed to be a slight diffusion of the ammonia through the rubberized cloth. To insure that there was the same amount of ammonia in the cell at all times, it was operated at a pressure of about 3 mm of oil. That the air did not diffuse into the cell was indicated by the fact that the cell would hold air at a slight pressure for hours, whereas, when the ammonia diffused outward, the cell would collapse. That the absorption readings could be repeated after the lapse of considerable time was also taken as evidence that the gas remained pure.

The procedure involved in obtaining the absorption curve was as follows. The adjustments were made on the tube such that small variations in plate current, caused by line voltage fluctuations, produced the least effect upon the intensity. The wave-length was determined in

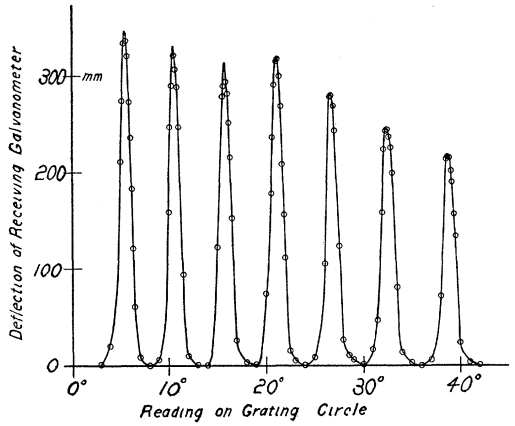

FIG. 2. Seven orders at λ1.33 cm as given by the echelette grating.

three orders by setting the grating at about six positions near the place of maximum energy and finding the peaks of the curve of the intensity plotted against the grating angle. Fig. 2 shows the complete curve for seven orders at a wave-length of 1.33 cm. The inaccuracy of the wave-length as measured by this method is less than one percent. The orders to be used were selected as high as possible, with these two limitations: that the angle between the grating and the axis of the mirror be sufficiently large to permit the full utilization of the beam, and that good definition be maintained. The absorption was determined for the average of five or more pairs of readings, taken with the cell in the path of the beam and then out of the path. After the absorption readings had been taken the ammonia was pumped out, the cell washed several times with air, then filled with air, and the same procedure followed for the same range of wave-lengths. The ammonia absorption data were then corrected for the absorption of the cell.

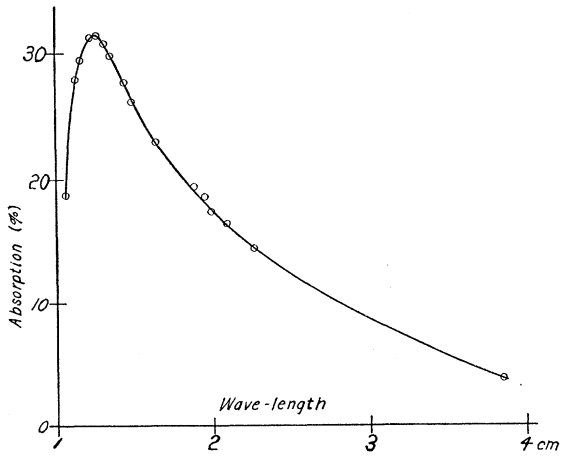

FIG. 3. The absorption band of NH_3 plotted on a wave-length scale.

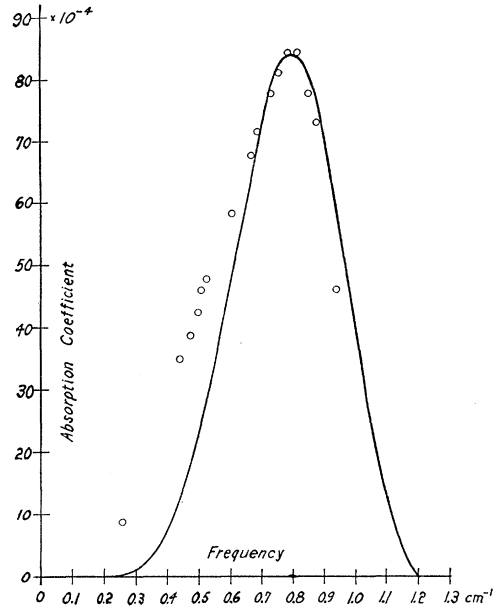

FIG. 4. The theoretical absorption curve for NH_3 and the observed experimental points plotted on a frequency scale.

RESULTS

The experimental absorption curve of the ammonia line after corrections have been made for the absorption of the cell is shown in Fig. 3. The maximum absorption of 31.5 percent occurs at a wave-length of 1.25 cm ($\nu = 0.8$ cm^{-1}).

Dennison[10] has shown that the shape of an infrared absorption line depends mainly on the limitation of the length of the wave trains which may be absorbed by the molecules. This leads to the approximate theoretical formula for the absorption coefficient at any frequency

$$\alpha_\nu = K\nu^2\left[\frac{\sin(\nu_0-\nu)\pi t}{\nu_0-\nu}+\frac{\sin(\nu_0+\nu)\pi t}{\nu_0+\nu}\right]^2$$

where ν_0 is the proper frequency of the molecule, t the time between collisions, and K a constant. This equation assumes that the time during which

[10] Dennison, Phys. Rev. **31**, 503 (1928).

a collision takes place is very short compared with the time t between collisions. We will take t to be the mean time between collisions. This assumption involves an approximation which may well explain the divergence between the experimental points and the theoretical curve. A more nearly exact theoretical relation might be obtained by using a statistical average over the time between collisions. Fig. 4 shows this theoretical curve, where K and t were adjusted to give the best appearing fit to the experimental points, and the value of ν_0 was taken as 0.67 cm^{-1} from the results of Wright and Randall at 100μ. The absorption coefficient α_ν, plotted as ordinate, is related to the percentage absorption under the special conditions by the equation

$$\text{percent absorption} = 1 - e^{-\alpha_\nu l}$$

in which l is the path length under the conditions of pressure and temperature at which the measurements were made. The kinetic theory of gases furnishes the relation among t, n, the number of molecules per unit volume, $\bar{c}$ the mean value of the velocity of each molecule and σ the effective diameter of the molecule,

$$\bar{t} = 1/(1.41\pi\sigma^2 n\bar{c}).$$

The value of t selected for the theoretical curve was 0.57×10^{-10} sec. This gives a value of 8.8×10^{-8} cm for σ, the effective diameter for this kind of process. This is of the right order of magnitude. It need not agree with the gas kinetic cross section since our σ is the minimum distance to which a molecule may approach another molecule without interrupting its wave train. The total intensity of absorption is defined by $\alpha = \int \alpha_\nu d\nu$. The value of α as determined from the experimental curve is 10×10^7 $sec.^{-1}$ cm^{-1}.

We wish to thank Dr. I. E. Mouromseff, Head of the Physics Division of the Westinghouse laboratories for loaning us some 9-cm tubes, and Dr. H. N. Kozanowski of the same laboratory for information concerning the technique of building the tubes. Also we are grateful to Professor D. M. Dennison for his advice and assistance in preparing the theoretical part of this paper.