

NEW ABSORPTION BANDS OF AMMONIA, METHYL BROMIDE,
METHYL IODIDE AND CARBON DIOXIDE IN THE
INFRARED SPECTRUMBY W. W. SLEATOR
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ABSTRACT

Work done with the recording spectrometer at the University of Michigan has shown near the wave-length 16.1μ an absorption band of ammonia not hitherto observed in detail, and bands due to methyl bromide and methyl iodide, near wave-lengths 16.4μ and 18.8μ respectively. It has also shown the strong absorption band due to carbon dioxide near 15μ to be more complex and extensive than has previously been indicated.

I. INTRODUCTION

THE cooperative work recounted here is preliminary to more precise and more extended investigations now going on, but seems of sufficient interest to merit a brief presentation. It has opened the way to observations of importance in infrared spectroscopy.

II. APPARATUS

During a spectroscopic investigation with another purpose the author used the recording prism spectrometer constructed and described by Randall and Strong.¹ Already known spectra of the substances reported upon were used to calibrate the instrument and the new absorption bands were photographed incidentally. Auxiliary equipment comprised the gauge and pumps for evacuating the case in which the path of the radiation was entirely enclosed, and a Moll thermal relay, used ordinarily to give an amplifying factor of 20 to 50. The source of radiation was a platinum strip bent to form a V, heated by a current of about 28 amperes. The spectra of ammonia and carbon dioxide were given by a 30° prism of potassium chloride silvered on the back, the other two by a prism of potassium bromide of about 60° , used with a Wadsworth and a Littrow mirror. The two slits were 0.2 mm wide. This means that in the region of 16μ the interval in the slit before the thermopile with the chloride prism was 0.045μ , or 1.7 waves per cm. For the bromide prism which has double the angle but whose material in this region has about six-tenths the dispersion, the slit corresponds to 0.038μ or 1.4 waves per cm.² Calibration was empirical. Known wave-lengths of emission and absorption lines were plotted against the position of the prism which moves uniformly with respect to the drum on which the photographic paper is carried. The

¹ H. M. Randall and John D. Strong, Rev. Sci. Inst., in press.

² Data on the dispersion of potassium bromide have recently been given by E. Grundlech, Zeits. f. Physik **66**, 775 (1930).

vertical lines appearing equally spaced in Fig. 1 and Fig. 3 have each a number representing a position of the prism and therefore a particular wave-length.

III. THE ABSORPTION BANDS

Ammonia. An actual photographic record such as the apparatus produces, was submitted for Fig. 1. At the left side of the figure appear the details at the long wave end of the great absorption band of ammonia analysed by Barker³ and given completely, from another photographic record, by Randall and Strong (reference 1). To the lines have been assigned the arbitrary

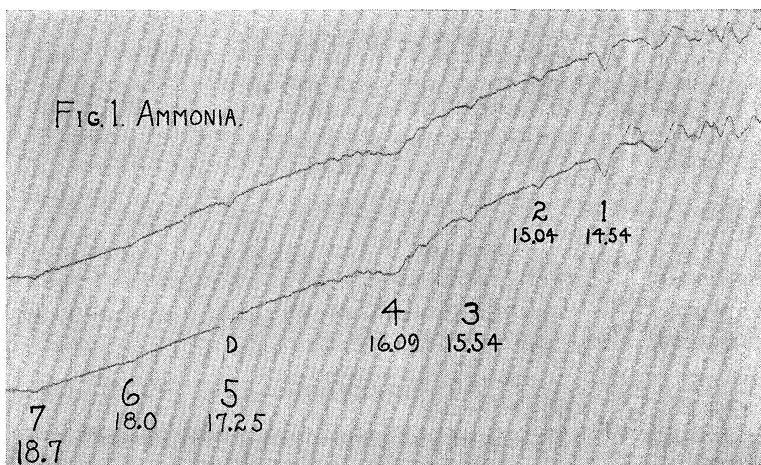


Fig. 1.

numbers 1 to 7, and wave-lengths are written on the figure. No. 4 at 16.09μ is evidently the center of a band which is in a state of resolution slightly showing the influence of rotation.⁴ The absorption is due to ammonia at 68 cm pressure in a cell 12 cm long at about 30°C . The fine vertical lines one of which is labelled *D*, below the lower trace, represent the displacement or deflection which occurred when the shutter was closed, cutting off the entering radiation. These lines enable one to estimate the extent of the absorption. The center of line 4 represents about 40 percent. The fact that the lines slope generally toward the left is due to a drift of the zero, which was troublesome when these records were made, but has since been eliminated. The fact that two independent and successive curves are so closely parallel speaks for the reality of the absorption lines which appeared unmistakably on other records as well.

³ E. F. Barker, Phys. Rev. **33**, 684 (1929).

⁴ The center of No. 4 is shown, probably, as the sharp line marked *d* in Fig. 1, by Sir Robert Robertson and J. J. Fox, Proc. Roy. Soc. **A120**, 168, 193, 197 (1928). This band is considered by Robertson and Fox to be one member of a rotation series of which the band found at 63μ by Rubens and Wartenberg is the first term. The wave-length of *d* is given as 15.91μ .

Methyl bromide and methyl iodide. So many details, involving spectra of several other substances, appear on the same photographic record, that it was necessary to make ink tracings of the original for Fig. 2. From these the minute fluctuations noticeable in Fig. 1 have disappeared, but the tracing faithfully represents the significant details of the original. It represents them at least, in so far as comparison of several records permits one to distinguish significant from insignificant variations. The upper curve shows the absorption—about 50 percent at the highest, near 16μ —due to methyl bromide at 20 cm pressure in the 12 cm cell. The lower shows that due to methyl iodide

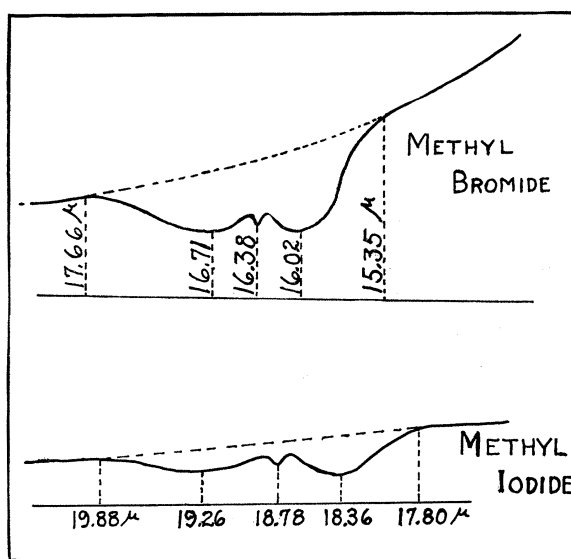


Fig. 2.

at 44 cm pressure in the same cell. The dotted vertical lines show how the deflection generally declines as wave-length increases, and the probable course of the record, had the gas been absent, is given by the dotted curve. The gases were at about 30°C . Those spectra were taken with the potassium bromide prism.

The infrared absorption spectra of the methyl halides have been investigated by Bennett and Meyer.⁵ Their observations did not extend beyond 15μ , but according to the scheme shown in Fig. 4 of their paper the two bands given here belong to the *A* series. They have the same general appearance as the methyl chloride band whose center is at 13.65μ . As is shown in the case of methyl chloride the *P* branches in the new bands are of greater extent than the *Q* branches.

By means of Raman spectra Ball⁶ has determined infrared wave-lengths for the absorption by methyl chloride, bromide and iodide. It was first

⁵ Willard H. Bennett and Charles F. Meyer, *Phys. Rev.* **32**, 888 (1928).

⁶ Gajendra Nath Ball, *Zeits. f. Physik* **66**, 257 (1930).

thought that these values could be used as points on the calibration curve of the potassium bromide prism. The wave-lengths were such, however, that either the curve had to be distorted beyond probability, or else many wave-lengths determined in this laboratory had to be discarded. Therefore these values were not relied upon. It is plain that for an infrared wave-length determined by the Raman effect the precision of measurement is less as the wave-length is greater. Recent work by Cleeton and Dufford⁷ gives certain wave number differences observed in the Raman spectra of methyl bromide and methyl iodide as 603 and 534 respectively. These numbers correspond to the wave-lengths 16.58μ and 18.73μ .⁸

Carbon dioxide Fig. 3 shows three curves from a photographic record by the sylvite prism. For curve *A* the absorption cell, which is entirely within the spectrometer case, was empty. The general slope of the curve, like that

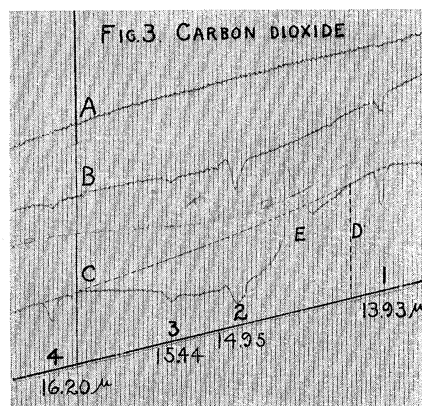


Fig. 3.

of the other two, is due to a drift of the zero. The fine fluctuations are due to Brownian motion, and perhaps in a small measure to vibrations of the building. These variations are absent when the amplifier is not used, and can be much stronger than here shown—easily of amplitude one or two centimeters—if the amplifying factor is high. The three curves appeared on the same sheet so that the vertical lines should be continuous. The paper was cut and glued for the sake of the order of the curves, and to diminish the diagram. Curve *B* shows the effect of carbon dioxide occupying the cell at 5 cm pressure. For curve *C* the pressure was 23 cm, the temperature in both cases about 30°C . It is plain that an increase in pressure tends to obscure the “zero branch,” if such it be, at 14.95μ , while it accentuates the absorption at 13.93μ and 16.20μ . The deflections for curve *C* are shown by the dotted line *D* and

⁷ C. E. Cleeton and R. T. Dufford, *Phys. Rev.* **37**, 362 (1931).

⁸ A. Dadiou and K. W. F. Kohlrausch, *J.O.S.A.*, **21**, 286, 297 (1931), give the wave numbers 594 and 522, corresponding to 16.84μ and 19.16μ , for methyl bromide and methyl iodide respectively, in the liquid state. These are wave number differences for anti-Stokes Raman lines.

the heavy base line. The dotted curve indicates as before the probable course of the record if the gas had been removed. At *E* some disturbance occurred which caused a temporary deflection; perhaps it was due to radio waves which penetrated out shielding. In the recent book by Schaefer and Matossi⁹ this absorption band of carbon dioxide is shown as a strong band with principal maxima at about 14.8μ and 15.4μ , very much as it has been known since the work of Burmeister. It was some what of a surprise to find this material absorbing radiation as is indicated in Fig. 3.

From consideration of different records for the same material, and of the definiteness with which certain lines appear at particular places on the photographic record, we may make some estimate of the precision of the wave-lengths here presented. For the center lines of methyl bromide and iodide, the lines of carbondioxide, and the lines numbered 1, 2 and 3 of ammonia, we should write the wave-lengths with the probable error $\pm 0.01\mu$. Line 4 of ammonia is naturally indefinite on account of its width and lines 5, 6 and 7 are not so precisely given.

For the long wave part of our calibration curve, on which the values of these wave-lengths depended, observations were made on the spectrum of water by L. R. Weber, using the recording spectrometer. Wave-lengths of some of these lines were measured by Norman Wright and H. M. Randall, using a large grating and residual rays from quartz. Wave-lengths of other lines were taken from observations on atmospheric absorption made with a combination spectrometer by E. K. Plyler. One of the lines of carbon dioxide and the center line of methyl bromide were measured directly with a grating by E. F. Barker and P. E. Martin. A very convenient material was acetylene, which furnished a wave-length determined by Levine and Meyer. In taking the photographic records the author has the efficient help of V. H. Fraenckel.

Note added June 29, 1931. Information now available, after the proof of this article had been read and returned, indicates that the values given for the wave-lengths in the ammonia spectrum are too great. These values are hereby withdrawn. The wave-length of the center of line No. 4, given as 16.09μ , is probably nearly 15.92μ . The values for the other materials are still believed to be correct

⁹ Cf. Schaefer and F. Matossi, *Das Ultrarote Spektrum*, Springer, Berlin, 1930, p. 225.

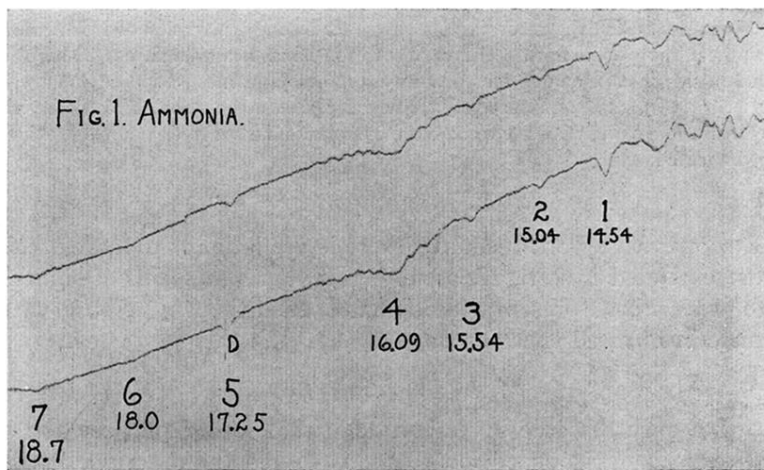


Fig. 1.

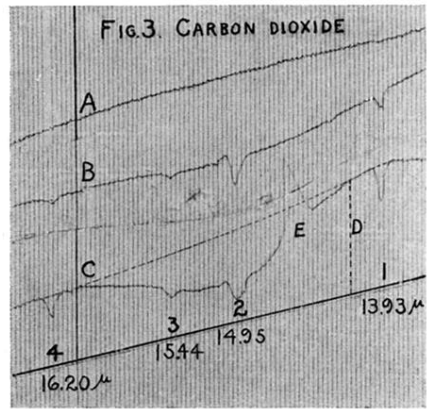


Fig. 3.