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INFRA-RED ABSORPTION SPECTRA:[1]
I. GASES.

BY W. W. COBLENTZ.

A SHORT historical review of the literature on this subject is given in a paper[2] presented to the American Physical Society April, 1903. At that time the absorption spectra of about forty organic compounds had been examined far into the infra-red. The results, as a whole, were so complicated that it became evident that in order to gain a better knowledge of infra-red absorption spectra a very extensive and systematic investigation would be necessary. This was made possible by a grant from the Carnegie Institution of Washington, which has been in force since June, 1903.

The total number of compounds now examined amounts to one hundred and thirty-five. Of this number about one hundred liquids and solids, and fourteen gases were explored to 14 μ, using a rock salt prism, while nineteen liquids were explored to 2.5 μ, using a quartz prism. In the meantime a preliminary report has appeared elsewhere[3] which gives a summary of some of the results obtained. The object of the present paper is to give some further results, as well as some details connected with the work.

The apparatus used in this work consisted of a 35 cm. focal length mirror spectrometer, a 7 cm. rock salt prism, and a Nichols radiometer. Except certain improvements, this is fully described else-

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[1] Abstract of a monograph on this subject submitted to the Carnegie Institution of Washington for publication.

[2] PHYS. REV., Vol. XVI., p. 385, 1903.

[3] Astrophysical Jour., XX., p. 207, 1904.

where[2] and need not be mentioned here. A considerable portion of the work was repeated to 7.5 μ, using mirrors of 1 m. focal length and 20 cm. aperture, mounted on a large spectrometer.

With this large apparatus the spectrometer slits were 2′ of arc, while in the smaller they were 4′ of arc on the spectrometer circle, so that for the larger apparatus the dispersion was comparable to that of fluorite. With it numerous bands from 6 to 7 μ were resolved, but only occasionally were small bands found in the transparent region, to be noticed later, from 4 to 5 μ, while the region from 3 to 3.5 μ was sometimes found complex.

For the gases a glass cell with rock salt windows on the ends was mounted in vertical ways, between the spectrometer slit and the incident energy, which was supplied by the heater of a Nernst lamp.

For the liquids different kinds of absorption cells were used. Those having boiling-points below 100° C. were placed in rock salt cells, made by bending a fine wire, 0.08 to 0.16 mm. in thickness, into a U-shape, covering it with Le Page's glue, and placing it between two plates of rock salt. After drying, the glue was not attacked by the liquids examined. The top of the cell was covered with tinfoil. The plates of rock salt were split from the natural crystal, about 2 × 3 cm. on an edge, and were more satisfactory than those polished by hand.

Liquids boiling above 100° C. could be used in thinner films, which was an advantage on account of their opacity. For these a ring of tin-foil 0.01 mm. in thickness was placed between the plates of rock salt. Around the outside edge of the plates was placed a strip of pure tin, which was 0.1 mm. thick, and hence easily bent to fit the cell, thus preventing evaporation. This form of cell is much better than that used in previous investigations, in that it can be thoroughly cleaned, while a new tin-foil ring was used for each new compound.

A block of wood having an opening cut in it, over which the rock salt cell was securely mounted, was placed in vertical ways before the spectrometer slit. The radiation from the Nernst heater passed through the opening in the block and through the rock salt cell into the spectrometer slit. A clear plate of rock salt was mounted di-

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[2] PHYS. REV., 16, 35, 1903.

rectly below this cell. In this manner no radiation except that which passed through the cell or clear piece of rock salt could enter the spectrometer.

The method of observation consisted in projecting successive portions of the spectrum upon the radiometer vane and noting its deflection when the absorption cell was before the collimator slit, and also the deflection when the clear piece of rock salt was substituted. The ratio of the deflection through the cell to that through the plate of rock salt gave the transmission through the liquid directly, and more accurately than by finding the absorption of the empty cell, and deducting it. This also meant the reduction of the work by almost one-half. After two months' use the difference in absorption of a plate of the absorption-cell and the "clear-plate" was only 3.2 per cent. beyond 3 μ, which is of no significance, since we are not concerned with the question of total absorption.

One of the chief difficulties in this work is to obtain pure chemicals, and it is of the greatest importance to prevent contamination while investigating them. Most of the compounds were imported directly from Kahlbaum, and were the purest obtainable.

Absorption Spectra of Gases.

Our knowledge of the absorption spectra of gases is confined to the work of Ångström[1] who studied CO,CO_2,CH_4,C_2H_4, and $(C_2H_5)_2O$. In fact he is the pioneer in this subject.

In studying gases the chief difficulty lies in obtaining them in a pure state. The apparatus, including generator, purifiers, and gasometers, must be air tight, so that after the air has once been removed, none can enter from outside. Fortunately we have, in liquid air, a means for obtaining small quantities of other gases in a more tangible state. By combining fractional liquefaction and fractional distillation with the usual chemical methods of purification one can obtain gases in a very high state of purity, as will be noticed in the analyses of some of the gases studied. In the present work, the gases were first purified by chemical methods. Several showed absorption bands in common, so the work was repeated,

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[1] Ångström, Öfversigt af Kon. Vetensk. Akad. Förhändligar Stockholm, Nr. 7, 1890.

using the additional method of liquefaction. The way that the general transmission has changed and the impurity bands have disappeared as a consequence will be noticed in their transmission curves.

The apparatus for generating and fractionally liquefying the gases consisted of a generating flask, a washing tube, a drying tube containing phosphorus pentoxide, two liquefaction bulbs, and a mercury gasometer (gas-pipette) of 200 cc. capacity. The drying tube was always thoroughly cleaned before making a new gas. The liquefaction bulb was made by enlarging the bottom part of a U-tube which was made from a glass tube bent narrow enough so that it could be inserted into a cylindrical liquid air container.

Petroleum thermometers were used to measure the temperature, which, of course, could be determined only approximately, but as close as one can make the fractional liquefactions. The thermometer was placed in contact with the side of the bulb, and the whole suspended over the liquid air. By raising or lowering this combination any desired temperature could be obtained. The operation consisted in fractionally liquefying the gas in the first bulb, and the part that passed from it into the second bulb was liquefied there at a lower temperature. The part that did not liquefy in the second bulb passed out into the air.

From 5 to 10 c.c. of the liquefied gas were collected in the second bulb, which was then allowed to grow warmer. After the air had been thoroughly washed out, as shown by the lighted gas, the bulb was permitted to become still warmer, and the successive fractions were distilled into the mercury gasometers where they were stored under mercury seals awaiting analysis and examination. This method of procedure, for the present work, was certainly more desirable and efficient than the usual one of joining the generator, purifiers and absorption cell with an exhaust pump. In that case, one cannot manipulate the gases after once generated. The desirability of handling the stored gases is shown in the purification of ethane (Fig. 3), which is almost impossible to obtain in a state sufficiently pure for this work. Not being satisfied with the usual washing in bromine water, and with the liquefaction method, the gasometer was placed in series with a wash-pipette of fuming sulphuric acid, and the gas was washed back and forth half an hour, after which only a suspicious trace of ethylene remained, as will be noticed at 10.5 μ in the absorption curves, Fig. 2.

The Absorption Cells. — The dimensions of the absorption cells for gases, already briefly mentioned, were: Length, 6.3 and 5.7 cm.; diameter, 2.4 and 2.2 cm.; capacity 30.8 c.c. and 21.5 c.c., respectively.

The rock salt windows were split from the natural crystal which gave smooth, plane surfaces which were not attacked by moisture, and lasted throughout the work of two months. The windows were attached with "Le Page's Glue," which became exceedingly hard on drying, and had such a low vapor pressure that no absorption bands could be detected, even after exhausting the cell to .02 mm. and permitting it to stand four days. One of the vapors to be expected from it would have been acetic acid. Before filling the cell with a new gas, it was always washed out thoroughly with air. This was done by means of a water aspirator attached to the pump, the cell being exhausted from five to seven times, each time allowing it to fill with air. The final exhaustion was carried to .02 mm. and the absorption of the cell, thus exhausted, was found each time before filling it with a new gas. Only once was an absorption found for residual gas; this was ethyl ether, at 8.7 μ, the cell having been washed but three times with air. The gases were introduced into the cells by means of a capillary tube and stop-cock, which was attached to the side of the cell.

A helix of iron wire inserted in the glass cell served as a diaphragm to prevent reflection from the walls, and seemed more serviceable than a black paint, since it also prevented occlusion of gases.

The cell was mounted in the usual manner, in a wooden carrier, which worked in vertical ways, between the source of energy and the spectrometer slit. The transmission through the exhausted cell was found each time before filling with a gas. This also served as a test for residual gas, which could have been detected if present, by setting on one of its absorption bands.

The transmission of the empty cell changed but little in two months, and as a typical example, transmitted 65 per cent. at 1.7 μ

75 per cent. at 4 μ, decreasing to 70 per cent. at 6 μ then gradually increasing to 74 per cent. at 10 μ, and to 78 per cent. at 12 μ. Except regions of selective absorption, the gases, for this length of cell, were usually perfectly transparent, so that such windows were more serviceable and cheaper than highly polished ones, which would have transmitted about 80 per cent. of the energy when new but would have soon become tarnished with moisture.

The slight variation from day to day in the transmission, through the empty cell, was attributed to reflection from the windows. Since two cells were used, on dismounting one, it was not possible to place it in the carrier exactly in the same position each time.

The cell was always securely mounted in the carrier before exhausting and no variation in its transmission could occur while filling it with gas and replacing the whole in the vertical carriers before the spectrometer slit.

Many of the gases, show but few absorption bands for the length of cell used. Whether more exist, which are very weak and can be detected only in layers of great thickness, is an unanswered question. Rubens and Aschkinass[1] using a column of CO_2 gas 65 cm. long found the same number of bands as for one 5 cm. long. On the other hand Langley's curves of the atmospheric absorption, show a great complexity.

METHANE, CH_4.

(Cell 6.3 cm., barom.[2] 750 mm., temp. 22°.)

The methane used in this work was made by heating a mixture of sodium acetate and soda lime, and washing it thoroughly in pipettes of potassium hydrate and of fuming sulphuric acid, which removes the unsaturated hydrocarbons like ethylene. The latter is also formed when methane is made by this method. Since methane boils at $-160°$ and ethylene at $-105°$ it is easy to apply the method of fractional liquefaction and fractional distillation. This was done as an additional precaution, but no change in the intensity or position of the transmission maxima, could be detected.

The spectrum of methane, Fig. 1, is distinguished by two large absorption bands at 3.31 and 7.7 μ and a smaller one at 2.35 μ.

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[1] Rubens and Aschkinass, Ann. der Phys., 64, p. 584, 1898.

[2] In filling the cell from the gasometer the pressure was made equal the barometric pressure.

Methane was investigated by Angström who found the same number of bands, but since his calibration is wrong beyond 5 μ no comparison can be made.

In discussing that compound it will be noticed that the effect produced be substituting four Cl atoms for the four H atoms of methane and thus forming carbon tetrachloride, CCl_4, is very striking. There we have an entirely different spectrum, with *no* bands in the region of 3 to 3.5 μ, characteristic to carbohydrates. In fact, carbon tetrachloride has no marked bands except at 6.5 μ and at 13 μ.

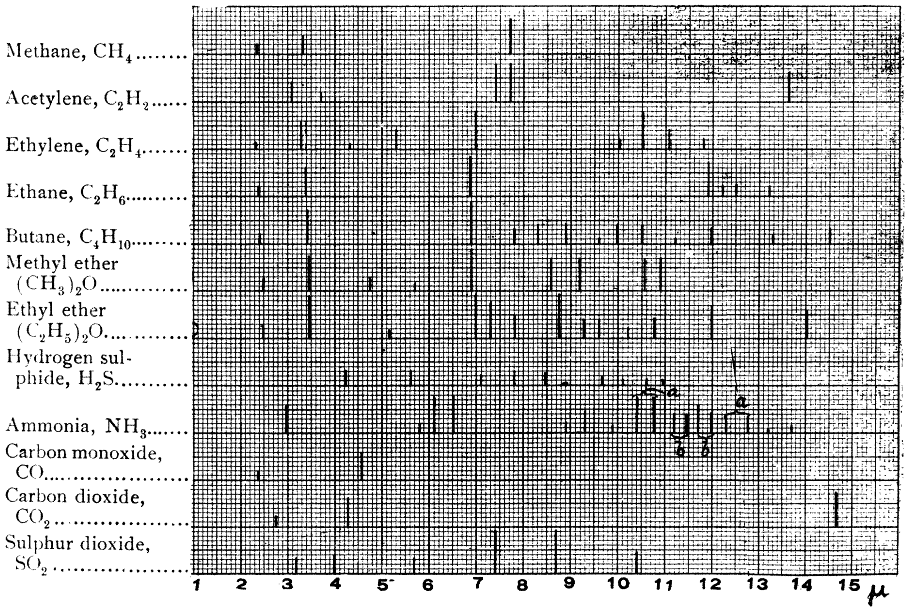

Fig. 1. Absorption Spectra of Gases. Height of Line Represents Depth of Band.

ACETYLENE, C_2H_2.

(Cell 6.3 cm.. barom. 74.5 cm., temp. 22°.5)

The acetylene used was generated from "selected calcium carbide, commercially pure for bicycle lamps."

In the preliminary examination the gas was washed in c.p. H_2SO_4 and dried in P_2O_5. For a subsequent examination the gas was washed by passing it through a solution of 20 gr. of $HCl + 10$ gr. of $HgCl_2 + 80$ gr. of H_2O to remove the phosphene, PH_3; then through a solution of KOH to remove the H_2S; then through conc. H_2SO_4 to dry it and finally through a U-tube cooled in CO_2 snow. In the latter there was a slight deposit of vapor on the side where the gas entered. This was found to be water vapor. After all this treatment, as well as an additional one to be mentioned presently, not a single band was changed appreciably in transmission, nor in the position of its transmission minima. That ordinary acetylene is quite pure has been found by Rand,[1] who found a purity of 99 per cent.

Acetylene (see Fig. 1) is distinguished by three deep narrow regions of absorption at 3.08 μ, 7.73 μ and 13.63 μ and two other bands, one at 3.7 which is harmonic with the one at 7.4 μ. In order to be able to locate the band at 13.63 μ the cell had to be exhausted to a pressure of 7 cm. Elsewere the gas is perfectly transparent. At first it seemed that the band at 3.08 μ might be due to water, but washing it thoroughly in new conc. H_2SO_4 and leaving it stand in contact with the acid for three days, in a pipette, failed to alter the intensity or position of this transmission minimum, which would indicate that this band belongs to acetylene.

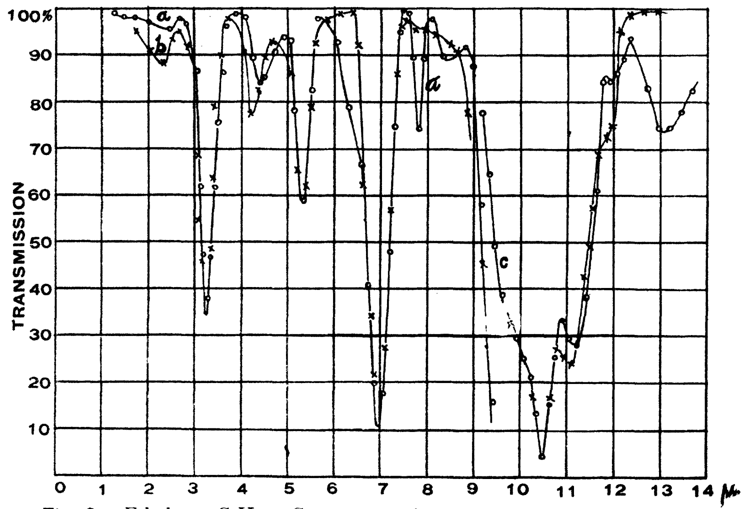

Fig. 2. Ethylene, C_2H_4. Curves : a = impure, b = pure, c = same as b, press. = 20 cm. Hg.

As a further check, a thin film of water, between fluorite plates, was examined. The first large band was found at 3.01 μ, and the second large band at 6.02 μ.

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[1] Rand, Phys. Rev., XIV.

If this band at 3.08 in acetylene were due to water, one would expect a similar one at 6.0, but in this region the gas is perfectly transparent.

ETHYLENE, C_2H_4.

(Cell 5.7 cm., barom. 73.8 cm., temp. 22°.5.)

This gas was prepared from ethylene bromide, $C_2H_4Br_2$ (from Drs. Bender and Hobein, boiling at the theoretical temperature of 131°) by using a zinc-copper couple, and was dried by passing it through a glass tube containing phosphorous pentoxide.

In the preliminary examination the gas showed ether bands. The ethylene bromide was then redistilled and a second examination was made, the gas having been passed through a tube placed in carbon dioxide snow. After the liquid air apparatus was set up, this gas was dried in P_2O_5, then fractionally liquefied in the first bulb, kept at − 97°, and the remainder in the second bulb, kept at − 120°. These were the readings of the petroleum thermometers which, although constant and in contact with the liquefaction bulbs, may not have been at the same temperature since they presented a smaller surface to the evaporating air.

In the first bulb there was a liquid having a strong odor of $C_2H_4Br_2$. In the second tube were about 5 c.c. of liquid ethylene, having a sweet odor much like that of ethylene bromide, but somewhat sharper like pure acetylene. It burned with a beautiful yellowish white flame. The second fractional distillate was used in this examination.

The transmission curves for these three samples of gas, differently prepared, showed but slight variation in the intensity and position of the minima, excepting that the ether band found at 7.8 μ, in the first sample, was absent in the others, Fig 2, curves *a* and *b*.

That the gas was very pure is shown from the analysis, by absorption, using bromine water. The quantity of unabsorbed gas was so small that it could not be measured accurately.

Amount of C_2H_4 taken	50.2 c.c.
Unabsorbed gas	0.6 c.c.
Total C_2H_4	49.6 c.c.
Purity	98.8 per cent.

A combustion analysis, made by Mr. R. C. Snowden, of the first fraction distilled, showed considerable impurity. From general experience, however, it appears that this is due to the method of analysis rather than to a real impurity.

The transmission of ethylene is entirely different from acetylene, from which it differs in composition, in having two more H-atoms. It is also different from CH_4 in which there is one less C-atom. The first large band is shifted to 3.28 μ, Fig. 1. The large transmission minima at 6.98 μ and 10.5 μ are of interest in connection with the study of CH_2-groups, and with piperidine.

For the region beyond 9 μ the pressure had to be reduced to 20 cm., curve *c*.

Ethane, C_2H_6.

(Cell 5.7 cm., barom. 74.5 cm., temp. 23°.)

This was the most difficult gas to be prepared. The chemicals used were more complex than in the case of ethylene and the reaction connot be controlled, so that ethylene, methane, etc., are formed in addition to ethane.

The ethane gas was generated according to the method first described by Frankland[1] who found a "volume purity of 97.88 per cent.," using liquefaction in addition. Equal parts of C_2H_5I (Kahlbaum) and absolute C_2H_5OH were poured over a zinc-copper couple, when the gases began to evolve immediately. No heat was

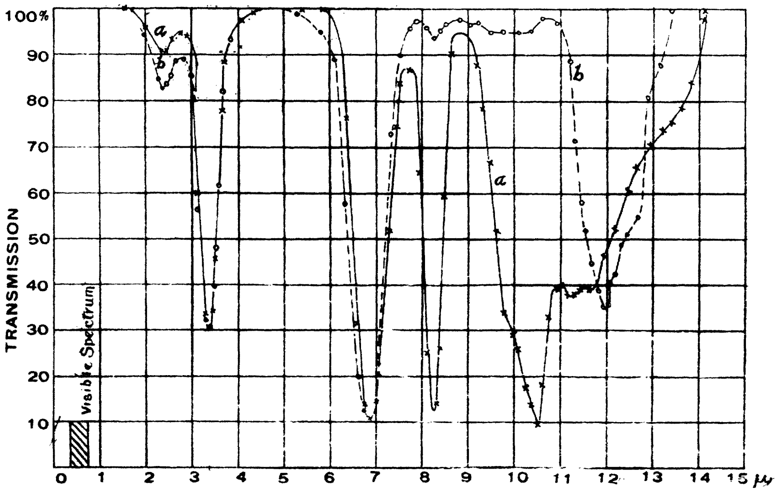

Fig. 3. Ethane, C_2H_6. *a* = purification by liquefaction, *b* = same after washing in fuming sulphuric acid.

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[1] Frankland, Jour. Chem. Soc., London, 47, p. 236, 1885.

applied since that causes greater impurity. The gas passed through bromine water in a U-tube, with liquid bromine at the bottom, to remove the ethylene, then through KOH to remove the Br, and then through a tube of P_2O_5 to remove the water. Since ethane boils at — 93° and ethylene at — 105°, fractional liquefaction and distillation is an uncertain method of purification. In this case bromine water offers the most serviceable means of separation. Methane will not liquefy till cooled to — 160°, and hence will pass through the bulb without being condensed. The same is true of the free hydrogen.

After fractional liquefaction (about 6 c.c.) and fractional distillation, the first and second fractions of the distillate were again washed in fuming sulphuric acid and KOH, and dried in P_2O_5, it being thought preferable to run the risk of letting in air in doing so, rather than be uncertain about the presence of ethylene, carbon dioxide, etc.

The analyses were not satisfactory. The second fraction was wasted in two attempts at combustion with oxygen, there being a violent explosion each time. The explosion-pipette method is less accurate on account of the small quantity (5.4 c.c.) of gas that can be used. However, three separate analyses by this method gave a fairly concordant purity of 96 per cent.

This is the first gas noticed in which the absorption bands decrease in intensity or disappear entirely, Fig. 3, which is an excellent clue to the impurities present. The change wrought in the transmission curves is most conspicuous at 10.5 μ. That band, due to ethylene, has entirely disappeared, and the bands at 12 μ, which were obscured by it, now appear in their proper intensities.

The position of the band at 3.39 μ does not vary, however. The very deep band at 8.25 μ which has almost disappeared in the curve *b* is no doubt due to C_2H_5I, used in making the gas, since that substance has a maximum at this point.

Ethane differs from ethylene in having the 2.31 and the 3.28 μ bands of the latter shifted to 2.36 μ and 3.39 μ, respectively. Some of the following gases show this same shifting for the region of 3 μ. As noted before, for rock salt dispersion all carbohydrates studied show a large absorption band, varying in position from 3.1 to 3.5 μ. The same is true for the 1.69 μ band, using quartz dispersion, but it is difficult to establish a definite shifting as is found for homologous compounds, at from 3.08 μ for acetylene, C_2H_2, to 3.39 μ for ethane, C_2H_6.

This study of gases was undertaken to learn the behavior of the CH_3-group in the molecule, as found in ethane. After studying many compounds of CH_3, simple and complex, having an absorption band at 3.43 μ which was first announced by Julius[1] to be due to CH_3, it was rather surprising to find that ethane, $HC_3—CH_3$, has its maximum at 3.39 μ.

When we compare ethane, C_2H_6, with benzene, C_6H_6, we find the latter has its transmission minimum at 3.28 μ, which again shows that structure as well as molecular weight influences the absorption.

The cell of ethane was partly exhausted, and 1 part of it was mixed with 2 parts of acetylene, and as a result, the band due to acetylene was obliterated, except a slight break at 3 μ while the band due to both was at 3.3 μ. Lack of time did not permit examination of other regions. The test was not quite a fair one, considering the one gas an impurity in the other, yet it serves to show that, for the region of 3 μ, where the dispersion of rock salt is still small, reliance upon the occurrence of an absorption band of an impurity, as a means for detecting the impurity, is not permissible. However at 4.4 μ where the dispersion is greater, one can detect the presence of CO_2 in CO, see Fig. 4.

BUTANE, C_4H_{10}.

(Cell 5.7 cm., barom. 75.4 cm., temp. 22°.)

This gas was made from ethyl iodide, C_2H_5I, by pouring it over an amalgam made of sodium and mercury.[2] The presence of the murcury retards the action of the metallic sodium upon the ethyl iodide. After drying in P_2O_5 the gas was passed through a U-tube placed in a freezing mixture of common salt and ice.

Butane liquefies at 1° while its isomer liquefies at − 17°. The attempt to liquefy it was not very successful, and the gas collected may have contained the isomer as well as other impurities.

The transmission minima of ethane C_2H_6, at 2.36 μ and 3.39 μ

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[1] Julius, Verhandl. Konikl. Akad., Amsterdam, Deel I., No. 1, 1892.

[2] Loury, Jahrsber. in Fortschritte der Chemie, p. 397, 1860.

and 6.85 μ are shifted to 2.4 μ, 3.42 μ and 6.89 μ respectively in butane, Fig. 1. Beyond 7 μ there are a number of bands which occur as impurities. The most conspicuous of these are the two at 7.8 μ and 14 μ found in ether, and the 10.5 μ band of ethylene. The bands at 8.3 and 8.9 μ (diff. = 0.60 μ) find their counterpart in methyl ether, where they are shifted to 8.58 μ and 9.16 μ (diff. = 0.58 μ) respectively, and in ethyl ether where the bands are shifted to 8.75 μ and 9.25 μ (diff. = 0.50 μ) respectively.

METHYL ETHER, $(CH_3)_2O$.

(Cell 5.7 cm., barom. 76 cm., temp. 22°.)

Prepared[1] by heating 1.3 parts of alcohol and 2 parts of sulphuric acid to 140°, and washed in KOH to absorb the SO_2 and then dried in P_2O_5.

A study of this gas is of interest in connection with ethyl alcohol, with which it is isomeric. A more striking illustration of the effect of the arrangement of the atom in the molecule upon absorption has not been found, except perhaps in the sulphocyanates and the mustard oils. From 10 to 11 μ alcohol shows transparency and beyond 13 there is complete opacity, while, for methyl ether, the very opposite effect is found. Beyond 8 μ the pressure of the ether had to be reduced to 10 cm.

The only apparent impurity band to be noticed is that of butane at 5.7 μ. The bands at 2.5 μ and 3.45 μ and 10.55 μ are shifted to longer wave-lengths, as compared with those of butane. The 6.9 band is harmonic with the one at 3.45 μ.

This compound like all the gases, is conspicuous for the great depth of its absorption bands.

ETHYL ETHER, $(C_2H_5)_2O$.

(Cell 5.7 cm., barom. 74.9 cm., temp. 24°.)

For studying this vapor, some of the anhydrous liquid was placed in the absorption cell, which evaporated, thus giving a saturated vapor. Frequent opening of the stop-cock kept it at about atmospheric pressure.

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[1] Erlenmeyer and Kriechbaumer, Berichte d. Deutsch. Chem. Gesellschaft, 7, 699, 1874.

Like methyl ether it has very deep bands, which are shifted as compared with the two preceding gases. The 4.75 μ band of methyl ether occurs at 5.15 μ in ethyl ether. The 6.9 μ band of the former is double in the latter and occurs at 7.0 and 7.3 μ. These two bands are to be noticed in this same region for ethyl alcohol, where there is but one flat band, which would no doubt be found complex, using a larger dispersion.

The 14 μ band is also to be noticed, since it occurs in compounds having CH_3- and C_2H_5-groups, while the 12 μ band is also found in many compounds.

Ethyl ether has been studied by Angström,[1] both as a liquid and as a gas. He found that the maximum at 3.45 μ did not coincide for the two states, the vapor being shifted by 4′ toward the long wave-lengths. He claims to have obtained this effect repeatedly while no shifting was observed by him for other compounds examined in the liquid and the vapor state. In the present work the region of 3.45 μ for liquid ether was explored at the same time that it was for the vapor, but no such shifting was observed.

The bands at 7.3 μ and 7.8 μ almost coincide with those of acetylene. Beyond 7 μ three sets of bands, "Triplets," have "constant differences" of their wave numbers which agree so closely as to lead to the suspicion that they belong to a spectral series.

ILLUMINATING GAS.

The sample used was taken directly from the pipes and examined. It contains bands due to CH_4, C_2H_2, C_4H_{10}, CO, CO_2, SO_2 and H_2S. Ordinary analysis shows about 60 per cent. of CH_4, 6 per cent. of CO, 2 per cent. of CO_2, and the remainder principally unsaturated carbons. The curve is of interest in showing the presence of CO and H_2S.

OXYGEN.

(Cell 5.7 cm., barom. 74.6 mm., temp. 23°.)

Made by heating $KClO_3 + MnO_2$; purified in KOH and dried by passing through a glass tube containing absorbent cotton covered with P_2O_5.

This gas is of considerable interest because it enters into so many compounds. It shows two broad shallow bands at 3.2 μ and 4.7 μ,

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[1] Angström, Öfversigt Kongl. Vet. Akad., No. 6, p. 389, 1893.

respectively. They are only 4 per cent. in depth. It appeared that this might be due to impurities, but repeated attempts to remove them failed to change the intensity. After passing the gas back and forth through a tube of P_2O_5, from one gas pipette to another, the bands still existed. The oxygen was then placed for three days in an absorption pipette containing conc. H_2SO_4, but the bands still remained, showing that their presence is not due to water vapor.

One sample was not washed in KOH, and it then showed the Cl band at 4.3 μ. Ångström[1] found this band at 4.28 μ for pure chlorine. It is interesting to note that Dewar and also Olzewski found several absorption bands of liquid oxygen in the visible spectrum.

Hydrogen.

(Generated from c. p. Zn + HCl, washed in H_2SO_4, and dried in P_2O_5.)

This gas showed no absorption bands. Paschen[2] examined hydrogen and nitrogen but, after repeated measurement, failed to find any absorption bands.

Bromine.

The vapor of bromine showed no bands. To prevent it from attacking the glue, the cell was lined with paraffine.

Carbon Monoxide, CO.

(Cell 5.7 cm., bar. 73.2 cm., temp. 23°.)

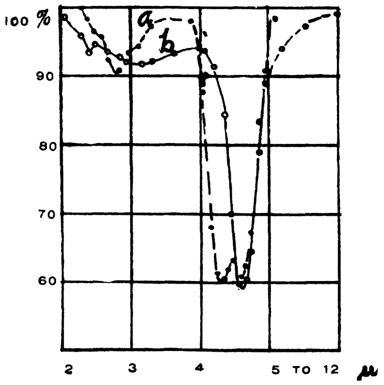

Fig. 4.

$a = CO + CO_2$, $b = CO$

Made by heating oxalic acid, $C_2H_4O_2$ and conc. H_2SO_4. This forms CO, CO_2 and H_2O. The CO_2 was absorbed by passing the gas through KOH solution after which the CO was dried in P_2O_5.

As will be noticed in curve *a*, Fig. 4, there was still some CO_2 present as shown by the maxima at 2.75 μ and 4.3 μ. After washing the gas back and forth, for half an hour, in a burette of KOH,

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[1] Ångström and Palmer, Öfversigt Kongl. Vet. Akad., No. 6, p. 389, 1893.

[2] Paschen, Ann. der Phys., Vol. 53, p. 334, 1894.

and drying in P_2O_5, the CO_2 was entirely removed as shown by curve *b*.

The maxima of CO occur at 2.4 μ and 4.6 μ. Ångström[1] found these maxima at 2.48 and 4.52 μ.

The absorption spectrum of CO was examined at 14 μ, but no maxima were found.

As shown by Ångström, the fact that the CO band occurs at 4.6 μ and the CO_2 at 4.3 μ invalidates the assumption that molecular weight has a great influence on absorption.

CARBON DIOXIDE, CO_2.

(Cell 5.7 cm., bar. 74.0 cm., temp. 23°.)

Made from $K_2CO_3 + H_2SO_4$ and dried in P_2O_5.

This gas has been examined by nearly every person who has investigated absorption spectra. It is noted for its variation in the location of its maxima in emission and absorption spectra. This is most evident at 4 μ and 14 μ.

The emission[2] band of a bunsen burner occurs at 4.4 μ, while the atmospheric absorption band occurs at 4.28 μ. Rubens and Aschkinass,[3] using a sylvite prism, studied CO_2 to 20 μ and found a large band at 14.7 μ for absorption and at 14.1 μ for emission. The column of CO_2 in the absorption work was 65 cm. in length. It will thus be noticed that at 4.28 μ the emission band shifts to the longer wave-lengths with rise of temperature, while at 14 μ the shift is towards the shorter wave-lengths.

Angström found the CO_2 bands at 2.6 μ and 4.32 μ, while in the present examination they occur at 2.75 μ and 4.29 μ. The fact that the atmospheric band of CO_2 occurs at 4.26 μ leads me to think that the present value is more nearly correct. A slight trace of CO would tend to shift it toward the band at 4.58 μ. The 14.66 μ band is in excellent agreement with the value, 14.7 μ, found by Rubens and Aschkinass,[2] when we consider that rock salt is already quite opaque in this region. As a whole, the work agrees well with that of other observers, considering how precarious a problem it is to map infra-red absorption spectra.

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[1] Ångström, loc. cit.

[2] Paschen, loc. cit., Vol. 53.

[3] Rubens and Aschkinass, loc. cit.

Carbon dioxide is the only gas studied that has *no* absorption bands between 4.5 μ and 14 μ, Fig. 1.

From the fact that gases dissociate at high temperatures, are we to conclude that as the temperature rises the CO_2 dissociates into CO, thus shifting the maximum of CO_2 at 4.26 μ toward that of CO at 4.6 μ?

SULPHUR DIOXIDE, SO_2.

(Cell 6.3 cm., bar. 74.4 cm., temp. 23°.)

Generated by adding conc. H_2SO_4 to sodium bisulphate, $NaHSO_3$, and drying in P_2O_5.

This same gas was fractionally liquefied and then fractionally distilled, but the curves coincided for the two samples, showing that nothing has been eliminated. This is a striking contrast to ethane, in which for successive purifications certain bands continued decreasing in intensity, showing that they were due to impurities.

Compared with CO_2 we have few examples which are more conspicuous in showing marked changes by substituting an S- for a C-atom.

In the region where CO_2 is transparent the SO_2 has its greatest absorption bands. The one at 10.4 μ coincides with that of ammonia.

HYDROGEN SULPHIDE, H_2S.

(Cell 5.7 cm., bar. 74.0 cm., temp. 21°.)

Generated by adding HCl to ZnS, dried in P_2O_5.

Liquefied in two fractions, one at $-15°$ the other at $-60°$. The sample liquefied at $-60°$ was distilled fractionally and several fractions examined. A sample which had been made from $ZnS + H_2SO_4$ but not liquefied, showed SO_2 bands which would naturally be expected.

The changes wrought in the absorption spectrum by substituting hydrogen for oxygen are not so marked as that from CO_2 to SO_2. For H_2S, we have a greater number of lines, especially beyond 9 μ, but there are no deep bands as in SO_2. It was noticed that the bands were not so intense after the gas had stood awhile. Whether this is due to decomposition has not been determined, on account of lack of time. Certain samples tarnished the mercury, while others did not after standing in the gasometer for some time.

AMMONIA, NH_3.

(Cell 6.3 cm., bar. 74.8 cm., temp. 22°.5.)

Made by heating NH_4Cl and solid KOH, and drying over freshly heated CaO. Upon finding several bands in common with those of certain carbohydrates, and that NH_2CH_3 or $NH_2C_2H_5$ might be present in the NH_4Cl, the latter was purified according to the method of Stas[1] by boiling with HNO_3 for half a day. The gas was liquefied in order to remove the supposed water band at 2.95 μ. A sample was placed in a combustion pipette, containing freshly-heated CaO over mercury, for five days, when the band at 2.95 μ was found to be as intense as on previous determinations. Moreover, the absorption band of water was found at the same time, at 3.0 μ, which shows that the 2.95 μ band is a characteristic band of ammonia.

It will be noticed elsewhere that this band is to be found in compounds containing amido-, NH_2, groups, as well as in certain ones containing nitrogen.

Ammonia is one of the most interesting compounds studied, because of the numerous deep narrow bands from 9 μ to 13 μ. At 5.7 μ and 7.3 μ there is evidence of existing bands, but the narrow dispersion of rock salt prevents their being resolved. This is the only compound studied having such a series of maxima, which are, in addition, so regularly distributed that it reminds one of the ammonia and the hydrogen spectrum in the optical region. Whether the "law of constant difference" of the wave numbers is true, or whether the coincidence in the values of certain wave numbers is simply accidental, is difficult to decide with the few examples at hand. We have the following examples :

I.	II.	III.
$\begin{matrix}6.1\mu\\6.5\end{matrix} > V_0 = 100$	$\begin{matrix}10.4\\10.75\end{matrix} > V_0 = 31$	$\begin{matrix}11.18\\11.43\end{matrix} > V_0 = 20$
$\begin{matrix}9\\10\end{matrix} > V_0 = 112$	$\begin{matrix}12.30\\12.78\end{matrix} > V_0 = 31$	$\begin{matrix}11.69\\11.98\end{matrix} > V_0 = 22$

It thus appears that there are three subordinate series, but how are we to establish the validity of these observations? More pairs

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[1] Stas, Fresenius Zeit. f. Anal. Chemie, 6, p. 423.

of bands are necessary, but, as we approach the visible spectrum, the pairs of maxima must lie closer together, and hence can only be resolved with a larger dispersion. In addition to this, the regions at $2\,\mu$ and $4\,\mu$ are quite transparent. This however can probably be remedied by using longer columns of the gas.