

On the Absorption of Acetylene and Di-Deutero-Acetylene in the Photographic Infrared

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Using an absorbing column 9 meters long of over 90 percent pure C_2D_2 at a pressure of 85 cm, we observed no absorption bands in the region 7000 to 11,500Å. This lack of absorption is discussed. A new absorption band of C_2H_2 is found with origin at 7859Å when an absorbing column 7.5 meters long at 90 cm pressure is used. The possible vibrational transitions giving rise to this band are discussed.

ALTHOUGH the absorption spectrum of acetylene¹ in the photographic infrared has been studied extensively, its interpretation is still in doubt. A careful study of the absorption spectrum of the "heavy" acetylenes, C_2HD and C_2D_2 , in conjunction with the results for C_2H_2 should result in the correct interpretation of the spectra and also yield unique values for C—C and C—H and C—D distances.

The absorption of "heavy" acetylene has been examined by Randall and Barker² in the far infrared and by Herzberg, Patat and Spinks³ and by the authors⁴ in the photographic infrared. In the two latter cases only bands due to the mono-deutero-acetylene, C_2HD , were observed.⁵ Since no quantitative analyses of the relative abundance of C_2HD and C_2D_2 were made in these cases, the effective lengths of the absorbing columns of the gases are not accurately known.

On the basis of the dependence of vibrational frequency upon mass as enunciated in the theory of the effect of isotopy on the structure of band

spectra, the vibrational frequencies for C_2D_2 were calculated. The expressions derived by Mecke¹ and Olson and Kramers⁶ were used in the computation. From the frequencies so obtained, it was found that the bands $\nu_3+2\nu_2+\nu_1$, $3\nu_3+\nu_1$ and $\nu_3+3\nu_2$ using the notation and assignments given by Sutherland¹ (we obtain sensibly the same results from the assignments of Herzberg and Spinks) should occur at the wavelengths 11,100, 11,200 and 10,250Å, respectively. In these calculations the anharmonic terms were considered equal to those found for C_2H_2 . In all likelihood these terms are smaller in absolute value for the heavier molecule. Therefore since for C_2H_2 the anharmonic constants are negative, the above given wavelengths are to be considered as the longest at which the respective bands would be expected to occur. These calculations are in close agreement with the recent work of Colby⁷ who has calculated the vibrational frequencies for the heavy acetylenes.

EXPERIMENTAL

Through the kindness of Professors H. C. Urey and J. E. Zanetti, of Columbia University, we were able to obtain 9 grams of 100 percent pure D_2O and some special CaC_2 for the preparation of the C_2D_2 . The CaC_2 was prepared with a slight excess of carbon to eliminate the possibility of containing free line. Extreme precautions were taken in the handling of the carbide to eliminate any contamination by reaction with atmospheric water. The carbide was received in a sealed

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¹ Levin and Meyer, *J. Opt. Soc. Am.* **16**, 137 (1928); Hedfeld and Mecke, *Zeits. f. Physik* **64**, 151 (1930); Childs and Mecke, *Zeits. f. Physik* **64**, 162 (1930); Mecke, *Zeits. f. Physik* **64**, 173 (1930); Hedfeld and Lueg, *Zeits. f. Physik* **77**, 446 (1932); Lochte-Holtgreven and Eastwood, *Zeits. f. Physik* **79**, 450 (1932); Mecke, *Zeits. f. Physik* **83**, 1 (1932); Sutherland, *Phys. Rev.* **43**, 883 (1933); Herzberg and Spinks, *Zeits. f. Physik* **91**, 386 (1934).

² Randall and Barker, *Phys. Rev.* **45**, 124 (1934).

³ Herzberg, Patat and Spinks, *Zeits. f. Physik* **92**, 87 (1934); *Nature* **133**, 951 (1934).

⁴ McKellar and Bradley, *Phys. Rev.* **46**, 236, 664 (1934).

⁵ It should be pointed out that the two bands ascribed to C_2D_2 in the recent paper *Hydrogen Isotope of Atomic Weight Two* by H. C. Urey and G. K. Teal (*Rev. Mod. Phys.* **7**, 87 (1935)) are the 10,370Å and 10,167Å bands of C_2H_2 . This error is undoubtedly due to a misinterpretation of a table in the article of Herzberg, Patat and Spinks (*Nature* **133**, 951 (1934)).

⁶ Olson and Kramers, *J. Am. Chem. Soc.* **54**, 136 (1932).

⁷ Colby, *Phys. Rev.* **47**, 388 (1935).

bottle and only exposed to the air while being transferred to the reaction flask. The D₂O was opened in vacuum and distilled into the dropping funnel of the acetylene generating apparatus. The C₂D₂ was prepared by allowing the D₂O to drop slowly upon the CaC₂. The gas was dried by passing through a trap cooled with solid CO₂; from there it passed directly into the absorption cells. Previous to the generation of the C₂D₂ the whole generating apparatus and the absorption cells were evacuated thoroughly (to a pressure of 10⁻⁴ mm) and flamed.

The absorption cells were two lengths of Pyrex tubing, one 7.5 meters long, the other 1.5 meters long, and 20 mm in diameter. The tubes were mounted in the shape of an L.

The positive crater of the carbon arc served as a light source. The beam was collimated by a quartz lens, passed through the long cell, was reflected by an aluminum mirror through the short cell and a red filter which cut off light of wavelength less than 6300Å, and was focused upon the slit of a 21-foot, 15,000 lines per inch concave grating.

First, by using a glass prism spectrograph, plates were taken from the visible region up to about 10,500Å. No absorption bands appeared on these photographs. Then through this 9-meter path of C₂D₂ exposures were taken on the grating from 8900Å to 11,500Å. No bands whatsoever were observed. The exposure times were up to 18 hours. Eastman 1P and 1Q plates and also those with the new 1Z type emulsion were used. These last-mentioned plates possess a maximum sensitivity at 10,900Å and a sensitivity range from 7500Å to 11,800Å. All the plates were supersensitized with ammonia. With only the 1.5-meter cell of C₂D₂ as the absorbing column, exposures of four hours gave good blackening up to 12,500Å. Under these conditions again no bands were observed.

Inasmuch as the absorbing column we used was more than twice as long as we considered necessary to observe the bands we have mentioned above, and in particular the C₂D₂ analog of the 7887Å band of C₂H₂, this lack of absorption was somewhat surprising. Observation of the fundamental bands in the far infrared offers a means of testing the purity of the gas, for in the region of the ν_4 fundamental band (18 μ) the

“heavy” acetylenes absorb very strongly. Accordingly a small sample of our gas was taken from the cells and sent to Professor E. F. Barker who had very kindly offered to test it for us. He has informed us that the gas was well over 90 percent C₂D₂. Besides the C₂D₂ fundamental he observed much more faintly the one due to C₂HD. Additional proof of the scarcity of C₂HD and C₂H₂ in our tube is given by our failure to detect any trace of the very strong absorption bands due to these molecules at 10,302Å and 10,370Å, respectively. Further evidence as to the purity of our gas was obtained when some of the heavy acetylene was taken from the cells and excited in a hollow cathode discharge tube at a pressure of about one millimeter. The spectrum of the discharge was photographed in the first order of the Institute’s 10-meter 30,000 lines per inch concave grating. The atomic lines of deuterium and also the bands due to the CD molecule with heads at 4307Å and 3867Å were observed without any trace whatsoever of the atomic lines of hydrogen or the CH bands at 4315Å and 3872Å. The analysis of the CD bands as well as intensity measurements in the 4315Å CH band are now in progress.

It was decided to rephotograph the bands in the absorption spectrum of C₂H₂ at 7887, 10,167 and 10,370Å in order to test our experimental arrangement. The 7.5-meter cell was filled with C₂H₂ at 90 cm pressure. The above-mentioned bands were easily observed.

This lack of absorption indicates a considerable difference in behavior between C₂D₂ compared to C₂H₂ and C₂HD. In a previous experiment⁴ we observed at 10,302Å a band due to C₂HD. It could be photographed with a 1.5-meter tube which contained also some C₂H₂ and considerable C₂D₂ so the path length required was only of the order of one meter or less of C₂HD. Herzberg, Patat and Spinks³ observed no bands due to C₂D₂ in this region of the spectrum and four due to C₂HD. It is to be noted that in the Raman spectrum⁸ of C₂D₂ while lines corresponding both to ν_1 and ν_2 have been observed, the latter one only appears on prolonged exposure.

The frequency of a band origin may be expressed to a first approximation by the formula

³ Glockler and Davis, *Phys. Rev.* **46**, 535 (1934); Glockler and Morrell, *Phys. Rev.* **47**, 569 (1935).

$$\nu = \omega_1 V_1 + X_{11} V_1^2 + \omega_2 V_2 + X_{22} V_2^2 + \omega_3 V_3 + X_{33} V_3^2 \\ + \omega_4 V_4 + X_{44} V_4^2 + \omega_5 V_5 + X_{55} V_5^2 + X_{12} V_1 V_2 \\ + X_{13} V_1 V_3 + \cdots + X_{45} V_4 V_5$$

where the ω 's are the normal frequencies of vibration, the V 's the vibrational quantum numbers, and the X 's the anharmonic constants. The interpretations of the C_2H_2 spectrum by Sutherland¹ and by Herzberg and Spinks¹ indicate that the combination bands which appear most strongly are those which involve the largest anharmonic constants. This has also been found to be the case in the interpretation of the CO_2 vibration-rotation spectrum.⁹

Let us compare the frequencies of vibration for C_2H_2 and C_2D_2 .

	C_2H_2 (obs)	C_2D_2 (Calc. by Colby)
ν_1	1974	1750
ν_2	3372	2690
ν_3	3288	2414
ν_4	730	535
ν_5	605	505

In the case of C_2H_2 the anharmonic constants (X 's) are the following (Herzberg and Spinks' values):

$$X_{22} = +13.6; X_{33} = -28.1; Y_{333} = -2.3; X_{55} = -26.3; \\ X_{12} = -4.9; X_{13} = -4.9; X_{23} = -112.1; X_{14} = -1.3; \\ X_{15} = -0.2; X_{24} = -9.3; X_{25} = -1.2; X_{45} = -18.8.$$

It has been observed¹⁰ in the case of isotopic molecules that the potential energy functions are the same to a high degree of approximation for corresponding electronic states. One can conclude therefore that for a state represented by certain vibrational quantum numbers the energy of that state will be less for C_2D_2 than for C_2H_2 and that the vibrations for C_2D_2 will be for any state more nearly harmonic than for the corresponding one of C_2H_2 . This would indicate that for C_2D_2 the anharmonic terms would be smaller than the analogous ones for C_2H_2 . Thus it might be expected that vibration-rotation bands of C_2D_2 would be less intense than the corresponding bands of C_2H_2 . It may further be pointed out that in the case of C_2H_2 the coefficient, X_{23} , coupling the two largest frequencies is larger than their difference. This will in all likelihood not be so for C_2D_2 .

⁹ Adel and Dennison, Phys. Rev. **43**, 716; **44**, 99 (1933).
¹⁰ Beutler and Mie, Naturwiss. **22**, 419 (1934); Mie, Zeits. f. Physik **91**, 475 (1934).

Both experimental and theoretical work on the intensities of vibration-rotation bands is very meager¹¹ and no work has been done on polyatomic molecules. For diatomic molecules Dunham¹¹ has shown that the electric moment, μ , can be expressed as a power series expansion in terms of ξ , where $\xi = (r - r_e)/r_e$ and the observed intensities agree fairly well with those he has calculated. Mulliken¹¹ has indicated the probable behavior of μ as function of r for the hydrogen halides and has drawn some interesting conclusions regarding the intensities of the observed bands for H_2O . He points out that while H_2O has a large permanent electric moment, i.e., $\mu_z \neq 0$, $\mu_y = 0$ for the nonvibrating molecule where z is the symmetry axis, bands associated with a varying μ_z ($\Delta V_3 = \text{even}$) are weak, while those associated with a changing μ_y ($\Delta V_3 = \text{odd}$) are strong. Thus probably μ_z is near its maximum for the nonvibrating molecule, and in the first case terms analogous to the coefficients of ξ for diatomic molecules are small, while in the latter case the terms are large.

In the comparison of C_2H_2 and C_2D_2 , the ν_4 band is probably of comparable intensity for both as it has been found to appear quite strongly. This is a \perp type band and one may suppose that while of course for the nonvibrating molecule $\mu_z = \mu_y = 0$, the terms analogous to the coefficients of ξ for diatomic molecules are large and of comparable magnitude. Since the ν_3 fundamental has not yet been observed for C_2D_2 , and the present results indicate combination bands involving ν_3 to be several times weaker for C_2D_2 than for C_2H_2 , the coefficients are probably many times smaller for C_2D_2 than for C_2H_2 .

A NEW C_2H_2 BAND AT 7859A

A very careful study of our photograph of the C_2H_2 band at 7887A taken with the 7.5 meters absorbing column at 90 cm pressure revealed the presence of a heretofore unreported band. It was made manifest by the appearance of a series of weak lines extending outwards from the end of the R branch of the 7887A band towards

¹¹ Dunham, Phys. Rev. **35**, 1347 (1930); **34**, 438 (1929); Bourgin, Phys. Rev. **29**, 794 (1927); Matheson, Phys. Rev. **40**, 813 (1932); Bartholome, Zeits. f. physik. Chemie **B23**, 131 (1933); Mulliken, J. Chem. Phys. **2**, 400, 712 (1934).

shorter wavelengths. The series obviously corresponded to the *R* branch of a new band, the *P* branch of which was obscured by the strong *R* branch of the band at 7887A. The faint *R* branch showed alternating intensities and six of the stronger lines (odd *J* values) were measured and two of the weaker ones (even *J* values). These lines are quite apparent on the reproduction given by Hedfeld and Lueg¹ of the 7887A band but are designated by them as higher members of the *R* branch of that band. That their assignment is erroneous may be seen by taking first differences in the list of frequencies for the *R* branch lines given by these authors. Upon doing so one finds that the differences decrease, reaching a minimum at *R*(26), and then *increase*.¹² The frequencies of the lines of the new band at 7859A measured with reference to the lines of the 7887A band are given, along with their assignments, in Table I. Because of the faintness

TABLE I. *Frequencies of the lines of the band at 7859A.*

<i>J</i>	0	1	2	3	5	7	9	11
<i>R</i> (<i>J</i>)	12,722.0 cm ⁻¹	24.2	26.4	28.7	32.9	36.8	40.8	44.6

of the lines, we do not consider the frequencies accurate to more than ± 0.2 cm⁻¹.

¹² Hedfeld and Mecke¹ in the original photographic work on acetylene absorption reported a band at 7956A. We used twice their path length but found no trace of this band in which the above authors measured over 30 lines. It is odd that the 7956A band is not reported by Hedfeld and Lueg¹ who used a path length of 24 meters. However, several lines designated by them as members of the *P* branch of the 7887A band coincide with lines reported by Hedfeld and Mecke as members of the *R* branch of the band at 7956A. Herzberg and Spinks¹ give two possible vibrational transitions to which this band may be ascribed but the agreement between observed and calculated frequencies is poor in both cases, observed minus calculated values being 70 cm⁻¹ and 144 cm⁻¹.

In order to determine the allotment of rotational quantum numbers to the lines of the new band, it was assumed that the structure of the band, in particular the spacing of the lines, is the same as for the strong band at 7887A. This is quite probably justifiable. We calculate that the origin of the faint band is at 12,720 cm⁻¹. This is considered accurate to ± 4 cm⁻¹ (corresponding to the numbering of the lines being correct to within $\Delta J=2$).

According to Sutherland's arrangement of the C₂H₂ bands the combination band occurring closest to our band at 12,720 cm⁻¹ would be $\nu_1+2\nu_2+\nu_3+2\nu_5$ which, with his constants, should lie at 12,766 cm⁻¹. Closer agreement is found if one uses Herzberg and Spinks' constants and assignment. With these it is found that the combination band $\nu_1+3\nu_3+2\nu_5$ should lie at 12,708 cm⁻¹. Although Herzberg and Spinks assign the band at 7956A to this combination, in view of the data concerning this band given in footnote 12, we consider the assignment of the combination $\nu_1+3\nu_2+2\nu_5$ to the new band at 12,720 cm⁻¹ more trustworthy than the former assignment of this transition. Additional weight is added by the definite alternation of intensities evident in the observed band which would classify it as a || type vibration.

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