and that for lower atomic numbers they may even increase. The break in the curve occurs just when the width becomes of the same order of magnitude as the ionization potential. This would be expected as an absorption limit could not have a width less than the ionization potential if it represents a removal of the K electron to the outside of the atom. Since the wave-length position of the absorption edges varies as $1/Z^2$ (Moseley law), it follows from the Z^4 law for the volt width of the absorption edges that the wave-length width is constant and independent of Z. This becomes obvious when it is noted that the "seconds" widths of the elements of Table IV are very nearly constant. It would appear then that the diffuseness of the K level is due to something like a classical damping which for lines gives a constant value for $\Delta\lambda$.

In conclusion, the author wishes to express his thanks to Professor Bergen Davis for suggesting this investigation and for his interest and advice throughout the course of the experiment.

OCTOBER 15, 1934 PHYSICAL REVIEW VOLUME 46

On the Near Infrared Absorption Spectrum of Mono-Deutero-Acetylene

ANDREW McKELLAR* AND CHARLES A. BRADLEY, JR.,* *George Eastman Laboratory of Physics, Massachusetts Institute of Technology*

(Received July 30, 1934)

The absorption spectrum of mono-deutero-acetylene has been photographed over the region 6000–10,500A in the first order of a 21-foot grating using absorbing columns up to 20 feet in length at atmospheric pressure. One band was found with origin at 10,302A. It is attributed to the molecule C_2HD. From the rotational constants of the band and similar data from the C_2H_2 bands, the interatomic distances in acetylene are computed as $r_{CC}=(1.247\pm0.008)\times10^{-8}$ cm and $r_{CH}=r_{CD}=(0.940\pm0.036)\times10^{-8}$ cm.

FROM a study of the bands of the "heavy" acetylenes considerable interesting information concerning physical properties of the acetylene molecule can be obtained. This possibility was mentioned by Randall and Barker[1] in their preliminary report of experimental results obtained on the far infrared bands of C_2D_2 and C_2HD. From the expected intensity alternation ratio in the C_2D_2 bands a check can be obtained on the nuclear mechanical moment of the deuterium atom and from the moments of inertia of any two of the acetylene molecules C_2H_2, C_2HD or C_2D_2, the internuclear distances can be directly calculated.

Consideration of previous work[2–9] on the infrared absorption spectrum of acetylene indicates that two of the valence vibrational frequencies of C_2D_2 associated with the C–D motions should have magnitudes of about 2400 and 2500 cm^{-1}. Employing the notation of Sutherland[9] these are the vibrations ν_3 and ν_2, respectively. Therefore the band of C_2D_2 corresponding to the strong λ7887 band of C_2H_2 should lie at about 10,300A. The λ7887 band, from which Childs and Mecke determined the nuclear spin of the proton, is believed assignable to the combination $\nu_3+3\nu_2$. While the present paper was being written there appeared a *Letter to the Editor of Nature* by Herzberg, Patat and Spinks[10] on the near infrared bands of "heavy" acetylene. Reference will be made to this later.

In our work the "heavy" acetylene was prepared by allowing water consisting of certainly more than 95 percent D_2O (sp. gr. 1.1054, indicating >99 percent D_2O) to drop slowly on finely ground calcium carbide. The gas generated

---

* National Research Fellow.

[1] Randall and Barker, Phys. Rev. **45**, 124 (1934).

[2] Levin and Meyer, J.O.S.A. **16**, 137 (1928).

[3] Hedfeld and Mecke, Zeits. f. Physik **64**, 151 (1930).

[4] Childs and Mecke, Zeits. f. Physik **64**, 162 (1930).

[5] Mecke, Zeits. f. Physik **64**, 173 (1930).

[6] Hedfeld and Lueg, Zeits. f. Physik **77**, 446 (1932).

[7] Lochte-Holtgreven and Eastwood, Zeits. f. Physik **79**, 450 (1932).

[8] Mecke, Zeits. f. physik. Chemie **B17**, 1 (1932).

[9] Sutherland, Phys. Rev. **43**, 883 (1933).

[10] Herzberg, Patat and Spinks, Nature **133**, 951 (1934).

passed through tubes filled with ground CaC_2 and through a trap cooled with solid CO_2 into the absorption cell. As explained below, the spectrum points to the presence of much more than the expected amount of C_2HD, and thus of protium. In photographing the λ10,370 and λ10,166 bands of C_2H_2 we found no evidence of any absorption by possible contaminating substances when the C_2H_2 was made from commercial calcium carbide and distilled water. Thus it was felt unnecessary to make special efforts to purify the acetylene made from D_2O except evacuating and flaming thoroughly the generating apparatus and absorption cell. Apparently the protium must have come from the generating materials. Very recently, Jungers and Taylor[11] in preparing the deutero-ammonias from the reaction of D_2O on magnesium nitride, found that when the magnesium nitride was not strongly heated, 100 percent D_2O produced deutero-ammonia containing only 68 percent deuterium. This they attribute to protium bound in the magnesium nitride as amido- or imido-groups. From very carefully prepared magnesium nitride they were able to obtain ammonia containing 99 percent of the hydrogen in the form of the D isotope. Thus we infer that considerable protium was probably present in our calcium carbide despite the fact that it was subjected to evacuation before being used. An obvious test of the presence of protium in the calcium carbide would be the use of calcium carbide prepared from thoroughly degassed pure carbon and pure CaO.

The absorption chamber consisted of four cells, each five feet long, three of which were arranged in the form of an N. They were filled with "heavy" acetylene to a pressure of 80 cm of mercury. The positive pole of a carbon arc served as a source of light and the spectrum was photographed in the first order of a 21 foot concave grating, higher orders being eliminated by means of a suitable filter. Eastman 1Q plates supersensitized with ammonia were used and third order iron arc lines served as standards.

Under the above conditions in the region 6000–10,500A only one absorption band was observed (except the atmospheric oxygen and water vapor bands). Its origin lies at λ10,302. It has a single *R* and *P* branch; the same structure as the ordinary acetylene bands. Its *P* branch appeared to exhibit alternating intensities though not as pronounced as in the C_2H_2 bands. Despite the evidence of the varying intensities and the fact that this band falls very close to the predicted position for a C_2D_2 band and although, as stated above, we find the presence of enough protium to form sufficient C_2HD surprising, we attribute the band to the latter molecule. The purely chance coincidence of members of the *R* branch of the extremely strong λ10,370 band of C_2H_2 with lines of the *P* branch of the present band accounts for the apparent alternation of intensities. In our most intense exposure the *P* branch of the C_2H_2 band was seen very faintly. To obtain a confirmation of the superposition mentioned here, both the C_2H_2 and the C_2HD bands were photographed side by side on one plate and each more intense line in the *P* branch of the C_2HD band was seen to occur at a wave-length corresponding to that of one of the stronger lines in the *R* branch of the C_2H_2 band. This latter band exhibits alternating intensities, the intensity ratio being 3 : 1.

Twenty-two lines in the *P* branch and twenty-six lines in the *R* branch of the band have been measured on each of three plates. The wave numbers of the lines, considered accurate to within one-tenth of a wave number, are given

TABLE I. *C_2HD band at λ10,302.*

J	$R(J)$	$P(J)$	$\Delta_2F(J)$ upper state $=R(J)-P(J)$	$\Delta_2F(J)$ normal state $=R(J-1)-P(J+1)$
1		9702.32 cm^{-1}		
2	9710.08 cm^{-1}	00.31	9.77	
3	12.17	9698.32	13.85	13.98
4	14.01	96.10	17.91	18.22
5	15.77	93.95	21.82	22.06
6	17.62	91.95	25.67	26.08
7	19.36	89.69	29.67	30.24
8	21.21	87.38	33.83	34.28
9	22.80	85.08	37.72	38.26
10	24.51	82.95	41.56	42.16
11	26.36	80.64	45.72	46.25
12	27.88	78.26	49.62	50.59
13	29.43	75.77	53.66	54.35
14	31.03	73.53	57.50	58.25
15	32.57	71.17	61.40	62.49
16	34.21	68.54	65.67	66.82
17	35.61	65.75	69.86	71.02
18	37.13	63.19	73.94	74.84
19	38.45	60.77	77.68	78.77
20	39.89	58.36	81.53	82.71
21	41.18	55.74	85.44	86.71
22	42.48	53.18	89.30	
23	43.80			
24	45.06			
25	46.16			
26	47.60			
27	48.69			

$B=0.99398\pm0.00039$
$I=(27.828\pm0.042)\times10^{-40}$ g cm²
$B_0=1.00905\pm0.00048$
$I_0=(27.412\pm0.043)\times10^{-40}$ g cm²

---

[11] Jungers and Taylor, J. Chem. Phys. 2, 373 (1934).

in Table I. Here also are given the corresponding term differences from which, by the method of least squares, were calculated the rotational constants B for the upper and lower states involved. The relations applicable here are the well-known term difference formulae, $R(J)-P(J)=4B(J+\frac{1}{2})$ and $R(J-1)-P(J+1)=4B_0(J+\frac{1}{2})$ for the upper and lower states, respectively. For the two states the moments of inertia of the C_2HD molecule were obtained directly from the B values, and are also given in the table. The probable errors of the various quantities have been computed on the basis of the internal consistency of the data with the usual expressions derived from the theory of least squares.

Previous calculations of the internuclear distances of the atoms composing the linear acetylene molecule have of necessity been based on the assumption that either r_{CH} or r_{CC} is the same as in some other molecule containing these atoms. To obtain their values $r_{\mathrm{CH}}=1.08\times10^{-8}$ cm and $r_{\mathrm{CC}}=1.19\times10^{-8}$ cm, Hedfeld and Mecke accepted for acetylene the value of r_{CH} computed for methane from the Raman data on CH_4 obtained by Dickinson, Dillon and Rasetti.[12] These data taken in conjunction with the moment of inertia of C_2H_2 enabled the computation of r_{CC}. Now, however, having available the moments of inertia of both C_2H_2 and C_2HD in their normal states, the internuclear distances can be directly calculated. The only postulate involved is that the distances r_{CH} and r_{CD} in the acetylenes are equal. This is certainly so to a high order of accuracy. From the moments of inertia $I_0=(23.509\pm0.040)\times10^{-40}$ g cm^2 for C_2H_2 and $I_0=(27.412\pm0.043)\times10^{-40}$ g cm^2 for C_2HD, we calculate the internuclear distances to be $r_{\mathrm{CC}}=(1.247\pm0.008)\times10^{-8}$ cm and $r_{\mathrm{CH}}=r_{\mathrm{CD}}=(0.940\pm0.036)\times10^{-8}$ cm. This is seen to be in good agreement with the value $r_{\mathrm{CC}}=(1.22\pm0.08)\times10^{-8}$ cm obtained by Wierl[13] from electron diffraction in acetylene.

In the previously mentioned letter by Herzberg, Patat and Spinks[10] four bands were photographed. Despite the fact that they used 93 percent pure D_2O only bands due to C_2HD were found. One of these corresponds to our λ10,302 band and the other three are beyond the region of sensitivity of the Eastman 1Q plates. They obtain for the internuclear distances $r_{\mathrm{CC}}=1.205\times10^{-8}$ cm and $r_{\mathrm{CH}}=1.062\times10^{-8}$ cm which differ from those given here by several times more than the probable error of the determinations. Herzberg and his collaborators assign their four bands to certain vibrational transitions and take as a basis for their assignments those of Lochte-Holtgreven and Eastwood[7] for C_2H_2. The latter have been shown by Sutherland[9] to lead to flagrant discrepancies. He also has shown that the anharmonic terms for C_2H_2 amount to as much as 150 cm^{-1} in some cases. It would thus seem an almost certainly fruitless task to attempt the assignment of vibrational transitions to the C_2HD bands until all the five fundamental frequencies are found in the far infrared and enough additional bands are located to permit the evaluation of the anharmonic terms. At present only the frequencies ν_4 and ν_5 are known.[1]

---

[12] Dickinson, Dillon and Rasetti, Phys. Rev. **34**, 582 (1929).

[13] Wierl, Ann. d. Physik **13**, 453 (1932).