550. *Excited States of Acetylene. Part II.*† *Experimental Methods of Recording the Near-ultra-violet Absorption Spectra of Acetylenes.*

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The ultra-violet absorption spectra of acetylene and dideuteroacetylene between 2500 and 2100 Å have been studied, attention being paid, not only to the coarse structures of the spectra, and the fine structures of the bands of the acetylene spectrum, but also to the Boltzmann variation, and to the Franck–Condon distribution of band intensity. The methods used are outlined.

Two isotopic modifications of acetylene, C_2H_2 and C_2D_2, have been studied. The C_2H_2, drawn from a cylinder or made from calcium carbide, was purified by means of reagents, condensed, and sublimed. The C_2D_2, made by interaction of D_2O with calcium carbide of special quality, kindly supplied by British Industrial Solvents, Limited, through the courtesy of Mr. W. P. Phillips, was condensed and purified by fractional sublimation. Its degree of isotopic purity was checked by spectroscopic and by mass-spectrographic analysis.

The spectra of these acetylenes were recorded in absorption between 2500 and 2100 Å, and it was necessary to obtain as much resolving power as possible from the available

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[*] Equality of angles follows from the highly plausible assumption that, in any π excited state, the two CH groups remain equivalent.

[†] Part I, preceding paper.

quartz-prism equipment. As heretofore, the microphotometer was used as an aid to frequency measurements. Temperatures from −80° to +200° C were used, absorption paths from 0·03 to 20 metre-atmospheres, and exposures from a few minutes to several days. The intensities of the more important bands were measured. All these branches of the observational work proved important for the eventual analysis of the spectra.

EXPERIMENTAL

Preparative Methods.—(a) *Acetylene*. The gas from a cylinder, after being passed through traps cooled in solid carbon dioxide, was condensed in a receiver cooled in liquid nitrogen, and resublimed through a CO_2-cooled trap. Alternatively, acetylene, generated from calcium carbide, was passed through a purifying train, and condensed and resublimed as before. The spectrally pure gas from either source was stored in large glass bulbs, and when required was frozen out, and subsequently distilled into the evacuated absorption cell.

(b) *Dideuteroacetylene*. The special carbide (*ca*. 10 g.) was baked out with continuous pumping at 400° for 2 hr. in the all-glass generating apparatus, and, after admission of dry nitrogen, 99·6% deuterium oxide (2—3 g.) was allowed slowly to drip on to the carbide, which was meanwhile cooled with an external bath of solid carbon dioxide and alcohol, or was allowed to warm slightly, as needed to regulate the reaction. The generated gas passed through a CO_2-cooled trap and was condensed in a receiver cooled in liquid nitrogen. After evacuation of the receiver, the heavy acetylene was resublimed several times through CO_2-cooled traps into N_2-cooled receivers with rejection of head and tail fractions.

(c) *Isotopic analysis*. Preparations of heavy acetylene were at first qualitatively checked for isotopic composition by two spectral methods. A discharge at 1000 v and 50 cycles was passed through the gas at 5 mm. in a small discharge tube; no trace of the bands of the CH molecule at 4315 and 3872 Å could be found, although the band of CD at 4307 Å was easily observed. The infra-red spectrum of the gas at 70 cm. pressure in a 4-cm. cell was recorded in the region 2—4μ: the band of C_2H_2 at 3282 cm.$^{-1}$ did not appear, but the band of C_2HD at 3335 cm. was present, though it was very weak compared with the band of C_2D_2 near 2439 cm.$^{-1}$.

A quantitative analysis was made, with Dr. C. A. Bunton's kind co-operation, by means of the mass-spectrometer. The heavy acetylene itself could not be introduced into the ion-source, because it attacked the hot filament. It was therefore decomposed to carbon and heavy hydrogen, and the latter was fed into the instrument. A coil of fine iron wire was first heated electrically in air so that it became oxidised on the surface, and was then heated in hydrogen until it was reduced. Its container was then exhausted, and subsequently filled with the heavy acetylene, and the wire was heated until just visible in the dark. Polymerisation of the acetylene did not occur, but long strands of carbon were formed on the wire, and after a short time the change of pressure on freezing out of the residual acetylene showed that most of it had decomposed to give heavy hydrogen. Analysis of this in the mass spectrometer showed the presence of 2·5% of protium. We could not find any bands of acetylene in the ultra-violet spectrum of the dideuteroacetylene, but some of the weak unidentified bands in that spectrum may have belonged to the monodeuterated compound.

Spectrographic Methods.—(a) *The optical system*. The spectrograph was Hilger's automatically focusing, quartz-prism instrument E492 of Littrow pattern, with aperture *f*/30, and dispersion at the plate 42 cm.$^{-1}$/mm. at 2500 Å and 27 cm.$^{-1}$/mm. at 2000 Å. The slit was used with width 0·02 mm. Reduction below this figure did not increase the resolving power, which was about 40,000.

The other parts of the system were mounted, if possible, on the optical bench belonging to the spectrograph. Three absorption cells were used. Most of the stronger bands were photographed with a fused-quartz cell 55 cm. long, containing the gas at pressures from 5 cm. up to more than 1 atm. Light from the source passed through a quartz lens, which focused it through the cell directly on to the slit, the lens and cell windows subtending angles greater than the aperture *f*/30. For weaker bands, a cell 225 cm. long and of 2 cm. internal diameter was used, in conjunction with a mirror, so that its length was employed twice. In this way, with gas pressures up to 1·5 atm. absorption paths of up to 7 metre-atmospheres could be obtained. In order to fill the aperture of the spectrograph from such a long and narrow cell, it was necessary to bring the light to a focus within it at each transit. With this object the light source was placed near the slit, but to one side, and the light was reflected by a prism away from the spectrograph, through a quartz lens, and then through its first focus within the cell, and, beyond the other end, to a concave aluminised mirror, of 160 cm. radius, which returned it, through its second focus within the cell, to the same quartz lens, which brought it to its third focus on the slit. For still weaker bands, a multiple reflexion cell of White's design (*J. Opt. Soc. Amer.*, 1942, **32**, 285) was employed, which had been built in accordance with Bernstein and Herzberg's description (*J. Chem. Phys.*, 1948, **16**, 30), by Dr. W. C. Price, who very kindly lent it to us. The light emerging from this cell converged over a sufficient angle to fill the aperture of the spectrograph. With gas at just above atmospheric pressure, this cell gave an absorption path of 20 metre-atmospheres.

With continued use, the 55- and 225-cm. cells became opaque to light of shorter wave-length than about 2300 Å: the transparency of the windows was periodically restored by heating them to about 600°. The multiple reflexion cell was not transparent to wave-lengths shorter than 2300 Å; but we wanted it only for the long-wave end, which is the weak end, of the acetylene spectrum. Whilst all three cells were used for ordinary acetylene, only the 55- and the 225-cm. cell were employed for dideuteroacetylene, because it required 30 l. of gas to fill the multiple reflexion cell, and our stock was not sufficient for the purpose.

In order to permit study of the effect of temperature on band intensities, arrangements were made to cool and to heat the 55- and the 225-cm. cell. The temperatures used ranged from $-78°$ to $+200°$. When the effect of reduced temperatures on the intensities of the strongest bands was studied, with use, necessarily, of low gas-pressures, and of the short cell with cooled sides and windows warmed to stop frosting, results were at first obtained which indicated that the gas was not coming even approximately into thermal equilibrium with the cooled cell-walls. This difficulty was overcome by making up the total pressure to 1 atm. with added hydrogen. It was shown that the addition of hydrogen did not alter band intensities when the walls, windows, and surrondings of the cell were at a uniform raised temperature.

The light source was a small hydrogen discharge lamp in a quartz envelope. Calibration spectra from a Pfund-type iron arc were placed immediately above and below the absorption spectrum.

(b) *Photography*. The spectral region 2400—2100 Å was photographed on Ilford Q 1 plates, which have the optical characteristics of Schumann plates, though their sensitive films are much more robust: they have very little gelatin, the photographic salts being in and on its surface. The plates are fine grained, and were found not to reduce the obtainable resolving power. However, they show but little contrast; and so, in order to obtain satisfactory records of, for example, the head and tail of a band, it was often necessary to make several exposures with different gas pressures. The region 2500—2400 Å was photographed on Kodak L15 plates, which have a normal type of bromide emulsion.

With absorption paths ranging from 0·03 up to 20 metre-atmospheres, exposure times ranged from some minutes to several days, and control of temperatures was therefore necessary. All the apparatus so far mentioned was contained in a room which had thermostatic regulation, and was kept throughout this work at 20·0° ± 0·1°.

(c) *Microphotometry*. Final measurements of frequency, and measurements of intensity, were made from records obtained from the spectrograms with the aid of a Zeiss recording microphotometer. The width of its monitoring slit was adjusted to give the best resolution consistent with a minimum of background due to graininess. The optimal width was that which selected 0·03 mm. of the spectrogram, a spectral interval of about 1 cm.$^{-1}$. The ratio arm of the microphotometer was so adjusted that the dispersion on the record was about 2 cm.$^{-1}$/mm.

After a section of the acetylene spectrum had been recorded, then, without any settings being altered except that of a diaphragm adjacent to the slit, and, of course, without plate or record holder being touched, the monitoring light was made to traverse, in the same direction, the corresponding section of the iron-arc calibration spectrum, the traces of the two spectra being thus imprinted on the same record.

(d) *Measurement of frequency*. Each microphotometer record was measured on a two-way travelling microscope accurate to 0·01 mm.

The measured maxima consisted of all the acetylene peaks, together with many iron-arc lines for calibration, chosen with preference for those whose wave-lengths have been determined interferometrically by Meggers. The wave-lengths were taken from Harrison's list "M.I.T. Wave-length Tables," and converted to frequencies in vacuum with the aid of Kayser's "Tabelle der Schwingungszahlen."

The interpolated acetylene frequencies, each based on records obtained from three independent primary spectrograms, were computed to 0·01 cm.$^{-1}$, and recorded as means rounded to 0·1 cm.$^{-1}$, the general consistency being about 0·2—0·3 cm.$^{-1}$. Lines separated by less than about 1·2 cm.$^{-1}$ appeared as a single diffuse line; but its diffuseness, disclosing a composite nature, could be seen; and this was still true for separations down to 0·5 cm.$^{-1}$, as subsequently determined by calculation, after the spectrum had been analysed. Much of the fine structure of the acetylene spectrum was resolved, but not much of that of the dideuteroacetylene spectrum, where there is more overlapping of bands, and the rotational structure is more closely spaced.

(e) *Measurement of intensity.* Intensities were measured of a number of bands of the strongest progression in the spectrum of acetylene. The essential measurement is that of the optical density, D_L, as a function of the frequency ν over the frequency range covered by the band. The optical density is defined by $D_L = \log_{10} (I_0/I_L)$, where I_0 and I_L are light intensities at a definite frequency, through the cell empty, and filled to a pressure expressed by the absorption path L. From the measurements of D_L, it is necessary to obtain by quadrature, the quantity $\int D_L d\nu$ over the band, ν being expressed in cm.$^{-1}$.

A disc sector with variable aperture, calibrated in terms of optical density, and put immediately in front of the light source, was run at 3000 interruptions per minute. The slit width was kept as usual at 0·02 mm. Preliminary experiments in which the speed was varied by factors of two gave unaltered values of D_L, and others with the slit opened to 0·08 mm. gave unchanged values of $\int D_L d\nu$. Exposure times were standardised to 15 min. Extremes of image density were avoided.

Ilford Q1 plates were employed. The absorption tube being evacuated, the plate was first calibrated for optical density by making adjacent exposures with the sector aperture at $D = 0{\cdot}0, 0{\cdot}1, 0{\cdot}2, \ldots 1{\cdot}2$. The aperture was then opened to $D = 0{\cdot}0$, and a number of exposures were made with acetylene in the cell at various known pressures.

Microphotometer records were then made as follows. First, one of the acetylene bands was traced. Then, over the diagram of this trace, each calibration spectrum was traced. The effect of this was to divide the area under the contour of the band into a series of nearly horizontal slices of thickness equivalent to an optical density of 0·1. Also, the current to the lamp which illuminated the recording fibre of the microphotometer was momentarily interrupted by a cam-switch at regular intervals, to produce a series of vertical white lines 1 mm. apart on the record, which was thus divided into small rectangles. The band has a certain finite background density, which is taken as given by the lowest level densities flanking the band. The area, as found by counting rectangles, between the contour of the band and the background level, when multiplied by the dispersion, as obtained from the distances between acetylene maxima of known frequency, gives the quantity $\int D_L d\nu$.

The actual intensity of the band is, of course, independent of the absorption path L, and may be expressed by $\int \alpha d\nu$, where α is the absorption coefficient. In order to obtain the intensity thus expressed, the density integral $\int D_L d\nu$ had to be multiplied by $2{\cdot}303/L$, the absorption path L being given by $273L_0p/T$, where L_0 is the length of the cell in cm., p is the pressure of the gas in atmospheres, and T is the absolute temperature. Values of $\int \alpha d\nu$ thus derived for the same band from several different spectrograms, for which p, and therefore L, had different values, were usually consistent to about $\pm$ 15%. The units of $\int \alpha d\nu$ are cm.$^{-2}$, and the mean values obtained for the bands measured are re-expressed in Part IV in dimensionless form as oscillator strengths. This involves multiplying $\int \alpha d\nu$ by a composite constant, which, as is shown in Part III, has in our cases the value $4{\cdot}78 \times 10^{-8}$ cm.^{2}.

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