552. *Excited States of Acetylene. Part IV.* Description and Analysis of the Near-ultra-violet Absorption Spectra of Acetylene and Dideutero-acetylene: Nature of the Excited State.*

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From the description and analysis mentioned in the title, it is concluded that the first excited state of acetylene is a *trans*-bent state, showing a completed change of σ-bond hybridisation from linear *sp* to plane-trigonal sp^2. A three-electron bond joins the carbon atoms, which between them have three unshared electrons in two *trans*-related orbitals. The electronic motion has the symmetry of the model, except that, as in other π-electron systems, the molecular plane is a nodal plane. Bond lengths, bond angles, and the stretching, and planar-bending force constants in excited acetylene are almost as in normal benzene.

(1) The spectra

The near-ultra-violet spectrum of acetylene to be discussed is that of the band-system which we observe in absorption to commence very weakly at 2500 Å and to continue with markedly increasing strength to about 2100 Å, where the sudden rise in the number and confusion of the bands indicates overlap by a stronger band-system belonging mainly to the vacuum-ultra-violet. The near-ultra-violet spectrum of dideuteroacetylene is generally similar, though with many quantitative differences. The spectrum of acetylene has been described, and its analysis attempted a number of times, but without producing any agreed conclusion. The near-ultra-violet spectrum of dideuteroacetylene has not been previously recorded.†

(a) *Previous Investigations of the Spectrum of Acetylene.*—Henri and Landau believed that they described this spectrum, but most of their bands were due to impurities, and it is not even certain that any was due to acetylene (*Compt. rend.*, 1913, **156**, 697). The weakness of the acetylene spectrum makes the necessary standard of purity high. Hopfield briefly mentioned the band-system (*Phys. Review*, 1927, **29**, 356). Kistiakowsky measured a number of genuine acetylene bands, which he assigned to three progressions in 100 cm.$^{-1}$ with intervals of 1012 and 1032 cm.$^{-1}$ between the progressions; and he found continuous absorption from about 2300 Å (*ibid.*, 1931, **37**, 276). Herzberg observed the band-system, decided that intervals of 865 and 1365 cm.$^{-1}$ separated the main bands, and tentatively assigned the electronic transition to a spin-forbidden intercombination (*Trans. Faraday Soc.*, 1931, **27**, 379). Kato arranged his observed bands into progressions in 390, 418, 600, 630, and 1050 cm.$^{-1}$; and he reported that the bands were continuous, indicating pre-dissociation (*Bull. Inst. Phys. Chem. Res., Tokyo*, 1931, **10**, 343). Price was mainly concerned with vacuum-ultra-violet band-systems, but he mentions the long-wave system of acetylene, concluding that the reported continuum beyond 2300 Å is due to impurities, and that the bands show no signs of predissociation (*Phys. Review*, 1934, **45**, 843; 1935, **47**, 444). Jonescu arranged the acetylene bands in three progressions in about 1000 cm.$^{-1}$, with intervals of 570 and 640 cm.$^{-1}$ between the progressions; and he examined the line structures of some bands, deducing that the electronic transition is of $\Sigma - \Sigma$ type (*Compt. rend.*, 1934, **199**, 710; 1935, **200**, 817), a strange conclusion inasmuch as all the stronger bands are double-headed, indicating P, Q, and R branches. Göpfert arranged the bands in many progressions in about 1000 cm.$^{-1}$ (*Z. wiss. Phot.*, 1935, **34**, 156). Woo, Liu, Chu, and Chih concluded that the spectrum contained three progressions, called A, B, and C, each in about 1050 cm.$^{-1}$, for which intensity is not increased by a reduction of temperature;

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* Part III, preceding paper.

† Using acetylene with a path-length of 20 metre-atmospheres, we have explored the ultra-violet from 2500 Å to the beginning of the visible region in an unsuccessful search for a longer-wave, but weaker, band-system. Thus the band-system now to be discussed arises from the *lowest* electronic excitation detectable with our equipment.

however, they could make no assignment of the bands in accordance with selection rules, and concluded that the electronic transition is in some way forbidden (*J. Chem. Phys.*, 1938, **6**, 240). These authors usually recorded only the heads of bands, but their measurements agree well with ours. On the other hand, we do not fully confirm their work on the effect of temperature on band intensity.

From the variety, and also the reserve, in the above conclusions, almost the only agreed feature of which is that a frequency near 1000 cm.$^{-1}$ is important, it will be clear that there is nothing very obvious about the structure of the spectrum, or the lines along which it might be analysed.

(b) *General Description of the Spectrum of Acetylene.*—A section of the spectrum, as photographed at −78° and +20°, is reproduced in Fig. 7 at (*a*). From the point of view of analysis, the spectrum contains an embarrassingly large number of bands, with little obvious regularity. From 2500 to 2100 Å, the general order of band intensity increases by many hundred times; yet even at its strong end, the spectrum is some thousands of times weaker than is normal for an allowed electric-dipole transition. All the stronger bands are double headed, are shaded to red, and have well-defined rotational structures.

Although the spectrum is essentially a rich collection of bands, it seems to have a weak continuous background. This appearance is probably due, at least in part, to unresolved weak bands or overlapping tails of bands, because the lowest absorption coefficients that can be measured between the visible bands vary less regularly than would be expected of a real continuum :

λ (Å)	2308	2251	2232	2204	2194	2157
ε (cm.$^{-1}$)	0·06	0·02	0·01	0·04	0·02	0·05

However, the presence of a genuine continuum, having absorption coefficients of the order of 0·01 cm.$^{-1}$ or somewhat less, is not excluded.

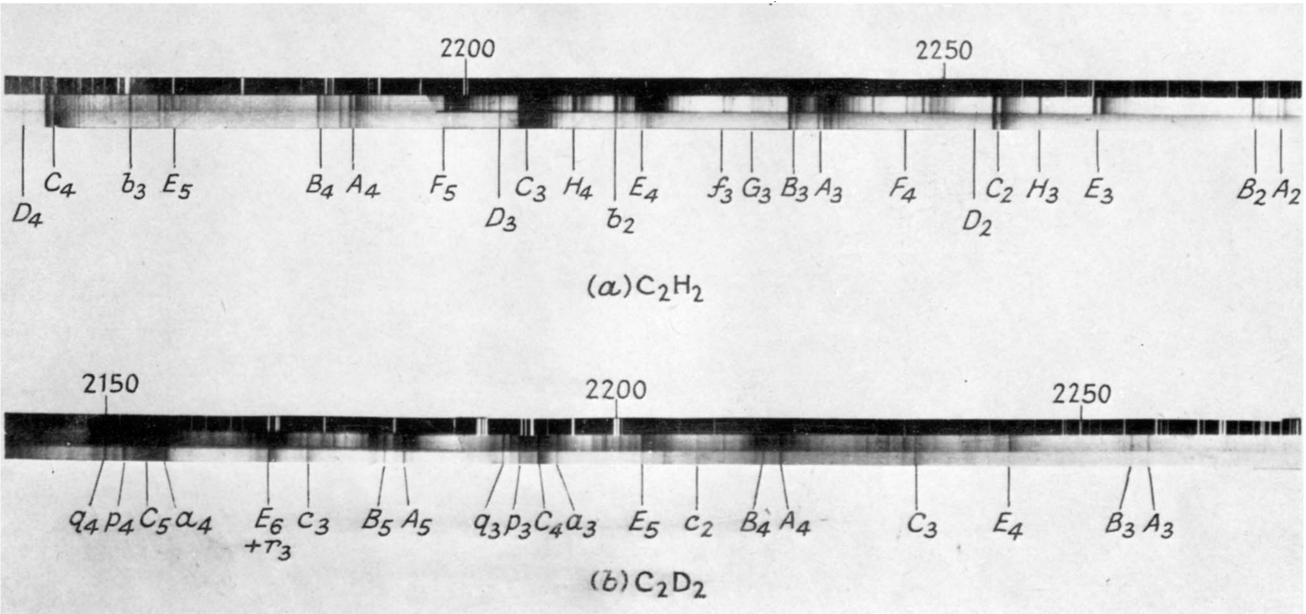
For the purpose of describing the band pattern of the spectrum, we use Woo, Liu, Chu, and Chih's labels, A, B, and C, for the three strongest progressions of bands, and supply further letter-labels for others to be described. Contrary to those authors, we find only one progression of strong bands whose intensity is not decreased by cooling the gas, namely, progression C. These bands form the main " milestones " of the spectrum, and are labelled C_0, C_1, C_2, . . . : we shall later justify the assumption that the first observed band C_0 is the theoretical origin of the progression, so that the subscripts represent the number of quanta with which the relevant upper-state vibration is excited. The interval between successive bands is about 1000 cm.$^{-1}$, but as the progression continues towards higher frequencies, the interval gradually falls. The bands have R and Q heads with a separation of about 17 cm.$^{-1}$.

Associated with each C band is a set of bands, labelled A, B, D, E, ..., with the same subscript as the C band. These bands form a pattern, which, except for band D, spread out on the low-frequency side of the C band. Such a pattern is repeated about each C band, the patterns overlapping. In Fig. 8, a typical pattern of the acetylene spectrum is shown at (*A*), the entered frequency intervals being the separations of R heads. As we shall note later, the pattern is really more extended on the low-frequency side than Fig. 8 represents. The relative frequencies and intensities, and the differences in the temperature dependence of intensity, within a pattern, are generally the same for all the patterns; but the frequency intervals differ slightly from one pattern to another. It will be clear that each of the labels A, B, D, E, . . ., designates a progression to higher frequencies in about 1000 cm.$^{-1}$, the successive intervals diminishing as in the C progression.

About 40 cm.$^{-1}$ on the high-frequency side of each C band lies the D band, which is much weaker than the C band, but, like it, is not weakened by cooling. The D bands appear to have a single head.

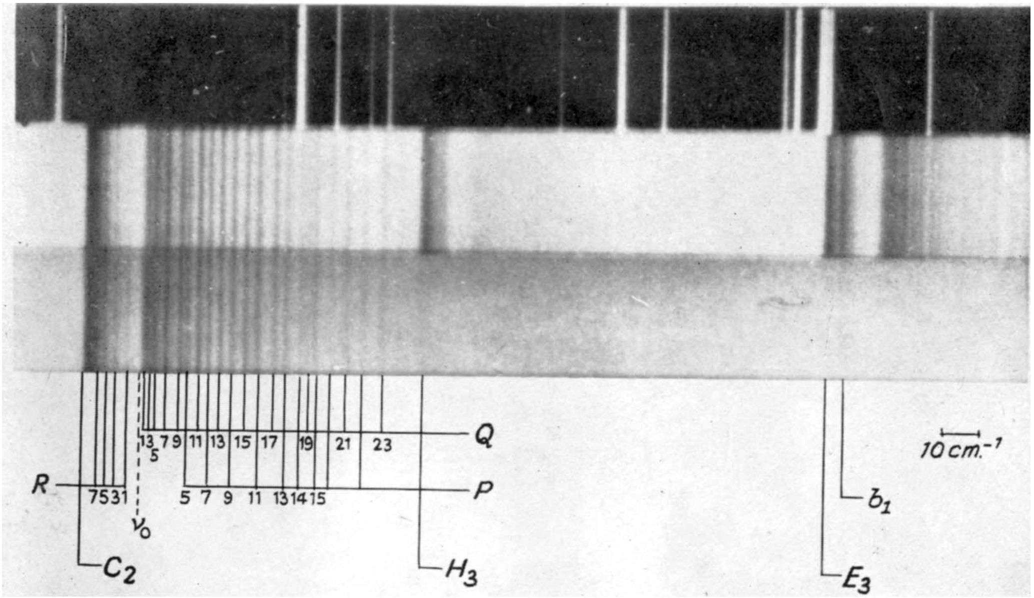
Approximately 600 cm.$^{-1}$ to the low-frequency side of the C bands are the A and the B bands, separated by about 50—60 cm.$^{-1}$ from each other, each having an intensity roughly one-third of that of the C band. The A and the B bands are double-headed. They are diminished in intensity, but not extinguished when the gas is cooled from +20° to −78°. The interval between the D and the B bands remains almost constant at 611—

FIG. 7. *Part of the absorption spectra of acetylene and dideutero-acetylene*



(Top) *Iron-arc comparison spectrum.*
(Central) *Absorption spectrum with gas at* + 20° c.
(Bottom) *Absorption spectrum with gas at* – 78° c.

FIG. 11. *Absorption spectrum of acetylene in the region 2255—2270 Å.*



(Top) *Iron-arc comparison spectrum.*
(Central) *Absorption spectrum with gas at* +20° c.
(Bottom) *Absorption spectrum with gas at* −78° c.

(*Rotation lines are labelled with the J-values of their lower-state energy levels.*)

613 cm.$^{-1}$ throughout the spectrum, but all the other intervals between the bands mentioned vary more widely from pattern to pattern.

The A and the B bands have very weak satellites in the G bands, which lie about 50 cm.$^{-1}$ on the high-frequency side of the B bands. The G bands are weakened by cooling the gas, in much the same way, as far as can be judged, as are the A and the B bands. Some at least of the G bands are double-headed, but with a head separation which is much narrower than that of other double-headed bands in this spectrum.

Approximately another 600 cm.$^{-1}$ to the low-frequency side of the A and B bands lie the E and the H bands, both of which are less intense, and show greater relative weakening when the temperature is reduced, than the A and the B bands. They are double-headed. The various intervals involving E and H bands vary appreciably from pattern to pattern. One very simple relation holds: it is that the separation between R-heads of the E and the H bands is always close to twice that of the A and the B bands, the one interval becoming exactly twice the other, if we use band origins instead of R-heads.

After yet another step of about 600 cm.$^{-1}$ to lower frequencies, we come to the J and the F bands, which are still weaker, and still more temperature-sensitive, disappearing completely from the spectrum at $-78°$. They are also double-headed. The simple and exact relation here is that their frequency separation is equal to that of the A and the B bands.

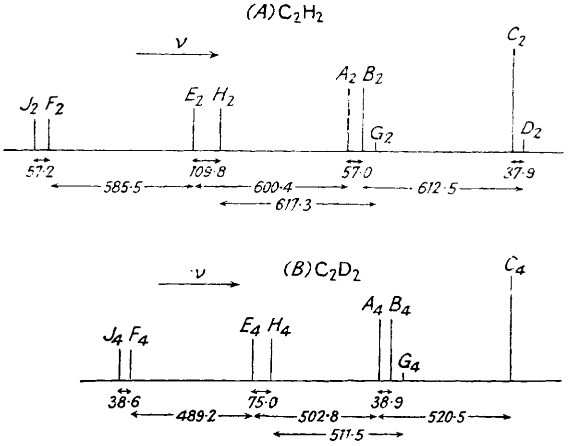


FIG. 8. *Examples of main parts of the unit-patterns, which by repetition form progressions in the absorption spectra of acetylene and dideuteroacetylene.* (*A*) *Pattern* 2 *of acetylene.* (*B*) *Pattern* 4 *of dideuteroacetylene.* (*The frequency separations are between R-heads in cm.*$^{-1}$.)

Most of the spectrum so far described is repeated, much more weakly, with a shift of 1380 cm.$^{-1}$ to higher frequencies. Corresponding to the progressions A, B, C, E, F, H, and J, we find these weakened and shifted progressions, which we label a, b, c, e, f, h, and j, respectively. Bands of the progressions a, b, c, . . ., show temperature effects on intensity analogous to those of bands of the corresponding progressions A, B, C, . . .

(c) *General Description of the Spectrum of Dideuteroacetylene.*—This spectrum, a part of which is shown in Fig. 7 at (*b*), is generally similar to the spectrum of acetylene. It lies in approximately the same spectral region, but the frequency intervals are smaller, with the result that the spectrum is more compact, and that there is more overlapping of bands. Moreover, the bands themselves have a closer rotational structure, often not resolved with our equipment. The general order of band intensity is lower, and the increase of intensity towards higher frequencies is not so steep, as in the spectrum of acetylene.

The progressions A, B, C, E, F, G, H, and J, and also a, b, c, e, f, and j, are all observed in the spectrum of dideuteroacetylene. With respect to relative intensity, and the variation of intensity with temperature, all these dideuteroacetylene bands qualitatively resemble the corresponding acetylene bands, with the exception that the progressions a, b, c, . . ., are not so weak relatively to the progressions A, B, C, . . ., in this spectrum as in the acetylene spectrum. Two weak progressions, namely D and h, of the spectrum of acetylene have not been found in that of dideuteroacetylene. They are believed to be obscured by overlapping. On the other hand, a whole new group of related weak progressions, labelled p, q, r, t, u, w, and y, have been found in the spectrum of dideuteroacetylene.

In all ascending progressions the frequency interval is about 800 cm.$^{-1}$, falling steadily towards higher frequencies. In the patterns which extend from each C band to lower frequencies, the large interval, separating the pairs or trios of more closely spaced bands, is about 500 cm.$^{-1}$, as shown in Fig. 8 at (*B*). The bands of the progressions a, b, c, e, f, and j, lie about 1300 cm.$^{-1}$ higher than corresponding bands of the progressions A, B, C, E, F, and J, respectively. The bands of the progressions, p, q, r, t, u, w, and y, lie about 2200 cm.$^{-1}$ above the correspondingly numbered bands of progressions A, B, C, E, F, H, and J, respectively.

(d) *Additional Bands appearing at Higher Temperatures.*—In photographs of the spectrum of acetylene at 200°, parts of four more weak progressions can be seen, which we label K, L, M, and N. These progressions are more temperature-sensitive than any of those considered above. In so far as these " hot " progressions are developed in the spectrum, they extend by two more intervals of about 600 cm.$^{-1}$, as shown in Fig. 9, the pattern of bands which runs from each C band towards lower frequencies. The extensions join on to the original patterns at the F and J bands. Actually only the patterns associated with the bands C_1 and C_2 were observed to be thus extended at 200°, but that is doubtless because the intensity distribution in the spectrum is more favourable for observation of extensions of these two patterns than of the others.

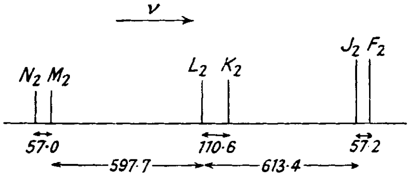


FIG. 9. *Example of the pattern of " hot " bands, an extension of the corresponding main pattern of the acetylene spectrum. (The frequency intervals are between R-heads in cm.$^{-1}$.)*

The K and L bands lie about 600 cm.$^{-1}$ on the low-frequency side of the F and J bands. Their separation from each other is exactly the same as that of the E and H bands. The M and N bands lie approximately a further 600 cm.$^{-1}$ towards low frequencies. Their separation from each other is identical with that of the F and J bands, and therefore with that of the B and A bands. Thus, except for the fact that all the periods of about 600 cm.$^{-1}$ are slightly different from each other, the extension of pattern produced by heating is an exact replica of that part of the old pattern which runs from the B and A bands to the F and J bands.

Members have been observed of very weak k and l progressions, displaced 1380 cm.$^{-1}$ above corresponding bands of the K and L progressions.

(2) DIFFICULTIES FOR THE HYPOTHESIS OF A LINEAR EXCITED STATE

The assumption that the lower excited states of acetylene are linear, like the ground state, seems so normal that strong reasons are needed for rejecting it. Classified reasons are given below: they are equally the reasons for adopting the particular non-linear model, the consequences of which we shall pursue later.

(a) *General Character of Spectrum.*—Our band-system is essentially a weak system of double-headed bands. We have seen (Fig. 3, p. 2715) that the nearest 2-quantum excited state to which transition from the ground state is allowed is the singlet Σ_u^+ state, though according to Ross's calculations, it should lie in the far ultra-violet (near 700 Å). Under the hypothesis now considered, our band-system is too weak to be credibly assigned to an allowed electronic transition. The intensity alone might be consistent with the spin-forbidden transition to the triplet Σ_u^+ state, the calculated position of which, while still in the vacuum region, is much nearer the position of the observed band-system. The difficulty is, however, that the bands are double-headed, therefore having P, Q, and R branches, so that the upper state cannot be a Σ state of any kind (eqn. 14, p. 2719).

One could assume an orbitally forbidden transition to one of the lowest singlet states, Σ_u^+ or Δ_u, supposing that some non-totally symmetrical vibration generates therefrom vibronic states, transitions to which can borrow intensity from allowed electronic transitions further out in the ultra-violet. But there are no vibrations capable of thus producing vibronic states, transitions to which could borrow intensity from the transition to the Σ_u^+ state (Table 2 and Fig. 4, pp. 2710 and 2715); and even if we could assume some more complicated perturbation so to act, the bands produced would not be double-headed (eqn. 14). The vibration Π_g (Fig. 4) would generate vibronic states, transitions to which could borrow intensity from allowed transitions to a Π_u electronic state; and the bands produced would be double-headed (eqn. 13, p. 2719). This is a possibility that we can try to entertain, even though none but high-lying Π_u electronic states are expected.

(b) *Coarse Structure of the Spectrum.*—The only upper-state vibration which appears in long progressions is that whose frequency in acetylene diminishes from 1049 to 972 cm.$^{-1}$ over the first five quanta. This must be a totally symmetrical vibration (Part III, p. 2717), and, on the hypothesis of linear states, can be nothing else than the C–C stretching vibration of the upper state. The fundamental frequency of the triple bond in the ground state of acetylene is 1974 cm.$^{-1}$ (Table 9, p. 2716). The fundamental frequency 1049 cm.$^{-1}$ of the upper state suggests a single bond. The C–C bond in the ground state has the length 1·208 Å (Table 16, p. 2720). We can roughly estimate the length of the upper-state C–C bond from the empirical relation, known to hold for different electronic states of a diatomic molecule, namely, $r^2\nu = \text{const.}$ (Herzberg, "Spectra of Diatomic Molecules," van Nostrand, New York, 1950, p. 456), if we make the approximation of regarding each CH-group as equivalent to an atom. The result is 1·65 Å.

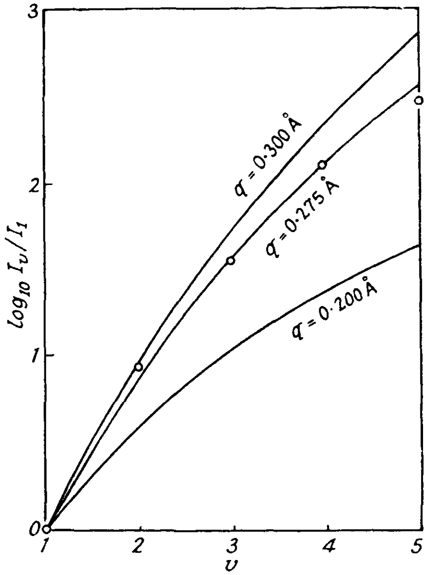


FIG. 10. *Observed intensities of C bands relatively to C_1, and calculated relative intensities based on different assumed values* q *of the separation of the origins of the co-ordinates of the vibration in the two electronic states.*

A somewhat similar result is obtained if we consider the variation of intensity along any of these upper-state progressions, for instance, the strong C progression, transitions to which start from the vibrationless ground state. From C_1 to C_5 the bands increase in intensity by some 300-fold. This gradient depends (eqns. 9 and 10, p. 2717) on the separation of the origins of co-ordinates of the vibration in the two states; and, by trial, we can find, as is illustrated in Fig. 10, that a separation $q = 0{\cdot}275$ Å reproduces the observed intensity gradient. The difference of bond-length would be $\sqrt{2}$ times this, and hence the upper-state bond has the length 1·60 Å.

On either method of estimation we have in the upper state, supposed linear, a remarkably long C–C bond. This in itself is not a *reductio ad absurdum*; but it will become one when we follow up its consequences for the rotational structure of the bands.

In the meantime, the upper-state progression presents us with another difficulty. On the hypothesis of two linear combining states, the only vibrations which can give progressions are bond-stretching vibrations. Frequencies of about 1000 cm.$^{-1}$ could arise from the stretching of certain types of C–C bond, but are much too low to involve a significant amount of C–H stretching. Since, then, there is little independent hydrogen motion, we have to expect only a small hydrogen-isotope effect on frequency. In fact we find a large hydrogen-isotope effect, the interval of the progression dropping from about 1000 cm.$^{-1}$ in acetylene to about 800 cm.$^{-1}$ in dideuteroacetylene.

A further serious difficulty, one insoluble on the basis of a linear upper state, arises concerning the lower-state progressions, those in about 600 cm.$^{-1}$ in the spectrum of acetylene, and in 500 cm.$^{-1}$ in that of dideuteroacetylene. They are shown to be ground-state progressions by their direction, and by the increasing temperature sensitivity of the successive band-groups, even though some complicating phenomenon, still to be elucidated, is making each such progression one of band-groups, rather than of single bands. The responsible vibration can only be Π_g (Table 9, p. 2716). Five successive quanta of this vibration can be seen in the spectrum taken at 200°. It is flatly against the selection rules for vibronic transitions between states of the linear model (Part III, p. 2717) that this non-totally symmetrical vibration should (*a*) appear in long progressions, and (*b*) occur, however weakly, with odd quantum numbers. This is true, even if the whole occurrence of the band-system is due to the presence throughout of one quantum of an upper-state Π_g vibration, as was tentatively assumed above: when this quantum is excluded, the total number of quanta in the lower plus upper states of this, as of any, non-totally symmetrical vibration must be even.

The coarse structure of the spectrum presents one other major difficulty for the hypothesis of a linear upper state, namely, that of explaining why most of what would have been expected to be single bands are replaced by groups of bands, groups showing certain regularities, but also differences of form.

(c) *Fine Structure of the Bands.*—Even on the shorter of our two estimates of the C–C bond-length in the linear upper state, 1·60 Å, its moment of inertia must be much larger, and its rotational constant smaller, than those of the ground state, for which the C–C length is 1·21 Å. For acetylene, the rotational constant B must drop from 1·18 cm.$^{-1}$ in the ground state to about 0·7 cm.$^{-1}$ in the excited state. Such a large difference in rotational constants involves the consequence that the R branch of any band will fold back very quickly on itself to form a head. It can be calculated (eqn. 17, p. 2720) that, with $B'' =$ 1·18 cm.$^{-1}$ and $B' =$ 0·7 cm.$^{-1}$, the separation of the R-head from the band origin, which must be very nearly the same as the separation of the R- and the Q-heads, is only 2 cm.$^{-1}$.

The structure of a C band is illustrated in Fig. 11 (facing p. 2727). Here, and throughout the C progression, the separation of the R- from the Q-heads is 17 cm.$^{-1}$. Over all the progressions of double-headed bands, the head-separations lie in the range 13—17 cm.$^{-1}$. In order to provide for such large separations, we need rotational constants of the upper state not much smaller than those of the ground state. Calculation shows (eqn. 17) that, in order to produce the head-separation observed in the C progression, the upper-state value $B' =$ 1·10 cm.$^{-1}$ is required. This in turn leads to a C–C bond-length of 1·27 Å, not much larger than in the ground state, and quite irreconcilable with the lengths deduced from the separations, and from the intensities of the C bands themselves.

The other difficulty presented by the rotational structure is just as serious. It is that the same B' value will not fit the rotational spacing of all three branches of a band. For bands of the C progression, the value $B' =$ 1·10 cm.$^{-1}$ will fit the P and R branches, but the value $B' =$ 1·05 cm.$^{-1}$ is required for the Q branch. This shows that the rotational levels of the excited state are split into doublets, and that transitions giving P and R lines end on the upper, and those giving Q lines on the lower, components of the doublets. On the hypothesis of a linear upper state, we have to interpret this as K-type doubling (Part III, p. 2724); but 5% seems an incredibly large difference for which to blame our inability to factorise out the rotational part of the wave function accurately.

Having called attention to Fig. 11, we should note here that the apparent lack of the expected alternation of intensity (Part III, p. 2724) among some of the P and Q lines is not a difficulty. Among P lines the alternation can be clearly seen only above $J'' = 13$, and among Q lines above $J'' = 18$, although alternation is visible in the R branch up to the unresolved head. The reason, as calculation of the line structure shows, is that, throughout the lower values of J'', the strong (J'' odd) P lines almost coincide with the weak (J'' even) Q lines, and the weak P lines with the strong Q lines, though the two series gradually separate until, for higher J'' values, they are fully resolved.

(3) ANALYSIS ON THE BASIS OF A *trans*-BENT EXCITED STATE

(a) *General Picture of the Lower-state Progressions.*—All the difficulties discussed in preceding Sections are removed if we assume a planar *trans*-bent excited state. We choose the *trans*-bent, rather than the *cis*-bent planar state for continued consideration, because the former offers an obvious hope, which the latter does not, of accounting for the progressions towards decreasing frequencies in intervals of about 600 cm.$^{-1}$ in acetylene and 500 cm.$^{-1}$ in dideuteroacetylene. It is included in this hope that we can supply adequate interpretations of the rather complicated variations in the precise intervals, and of the appearance at each step of band-groups instead of single bands; but we leave aside these points for the moment. Naturally, a correct analysis will give a good account also of the upper-state progressions, and of the peculiar fine-structures of the bands.

The only vibration of normal acetylene, whose frequencies are even roughly of such magnitude that it might conceivably be made responsible for the observed lower-state progressions, is the *trans*-bending vibration Π_g, the fundamental frequencies of which are 613 cm.$^{-1}$ in acetylene and 511 cm.$^{-1}$ in dideuteroacetylene. The only kind of acetylene model with respect to which this vibration is totally symmetrical is the *trans*-bent model (C_{2h}). The first essential condition for a vibration to produce progressions is that it should be totally symmetrical with respect to the *common* symmetry of the combining models; and the common symmetry of the straight and bent models is the same as the symmetry of the bent model. The two Σ_g^+ stretching vibrations and the Π_g bending vibration of the linear model correlate with the three totally symmetrical vibrations of the *trans*-bent model, and thus all three vibrations of either state are qualified by their symmetry to appear without restriction as to quantum number (Fig. 4, p. 2715).

But if the transition is from a lower linear to an upper *trans*-bent state, then on the general grounds of the Franck–Condon principle, we should expect the Π_g vibration to generate the really important lower-state progressions. For this, more than any other, is the vibration which, before excitation, can deform the molecule towards the shape in which it has to live after excitation. Up to a point, each previously present quantum of this vibration must increase the transition probability. And so we can understand why, in spite of most forbidding Boltzmann factors, up to five quanta can be seen, a most unusual occurrence for lower-state progressions in absorption spectra. Thus, from any C band, the first lower-state quantum leads to the A and B bands, which at 20° are each about one-third of the strength of the C band, although if the transition probability did not alter, their Boltzmann factors would make each one-twentieth of the strength of the C band. The effect of the moderated intensity ratio on the observable length of the progression is evident.

The two Σ_g^+ vibrations have fundamental frequencies so much larger than that of the Π_g vibration (Table 9, p. 2716), and therefore Boltzmann factors so much smaller (10^{-4} to 10^{-7} at 20°), that we should not expect them to generate observable lower-state progressions, especially as they cannot produce counteracting increases of transition probability comparable to those given by the Π_g vibration.

(b) *General Picture of Upper-state Progressions.*—Under the hypothesis of a *trans*-bent excited state, symmetry laws will allow upper-state progressions to be generated by any of the totally symmetrical vibrations of the upper state, that is, any from among the two stretching vibrations, A_g(C) and A_g(H), and the bending vibration, $A_g(\alpha)$, which correlate respectively with the stretching vibrations Σ_g^+(C) and Σ_g^+(H), and the bending vibration Π_g, of the linear state (Fig. 4, p. 2715). However, on the basis of the Franck–Condon principle, we expect the long and dominant progressions, those about 1000 cm.$^{-1}$ in acetylene, and about 800 cm.$^{-1}$ in dideuteroacetylene, to be generated by the bending vibration $A_g(\alpha)$. This is the vibration which, more than any other, must be produced up to large classical amplitudes in consequence of excitation from a linear ground state to a *trans*-bent excited state. As Boltzmann factors do not enter into intensity relations in an upper-state progression, we can understand why successive bands in these progressions get continually and markedly stronger towards higher frequencies. The large increase in C–C length, which on the hypothesis of a linear upper state was required to explain this strengthening along upper-state progressions, is here replaced by the large change in the CCH angles.

We have no difficulty now in reconciling the magnitude of the frequencies of the upper-state vibration with their isotopic separation. For 1000 cm.$^{-1}$ is an entirely normal value for a CCH bending frequency, and, since most of the motion is in the hydrogen atoms, a large hydrogen-isotope shift is to be expected.

On this basis we can understand the greater weakness of the progressions of dideuteroacetylene at the low-frequency end of the spectrum, and also their smaller increase in intensity along the spectrum, towards higher frequencies, as compared with the progressions of acetylene. The CCD bending vibration will have a smaller classical amplitude than the CCH vibration : quantally, the oscillator wave-function of the former will be the more compact. It follows that upper- and lower-state vibronic wave functions will overlap less at low quantum numbers, and that the increase in overlap with increasing quantum number will be less, for C_2D_2 than for C_2H_2. This, according to the Franck–Condon principle, will produce just those intensity relations which have been described.

Since Boltzmann factors do not inhibit the appearance of upper-state frequencies, one might expect to find those of the totally symmetrical stretching vibrations A_g(C) and A_g(H), though only in relatively weak and short progressions, because these vibrations are much less important for the mutual accommodation of the combining models. The interpretation which we shall offer of the many weak series of bands, those labelled with lower-case letters, is that they represent the first steps of progressions in these upper-state stretching vibrations.

(c) *Development of Band Groups in Lower-state Progressions.*—A simplified statement can be made about the observed structure of lower-state progressions, if at first we neglect the weak bands D and G, which will be considered separately later. Then, each progression originates with a single band, C, but continues with band pairs : B, A; H, E; F, J; K, L; M, N. The separations between the bands of the pairs are alternately narrow and wide, the two spacings, one just half the other, being precisely repeated along any one lower-state progression. The intervals between the pairs are near 600 cm.$^{-1}$ in the acetylene spectrum, and the spacings are near 60 and 120 cm.$^{-1}$, but increase somewhat as we pass from one lower-state progression to the successive replicas of it which are encountered on ascending upper-state progressions. In the spectrum of dideuteroacetylene the gaps between the pairs are about 500 cm.$^{-1}$, and the two pair-spacings are about 40 cm.$^{-1}$ and 80 cm.$^{-1}$.

The hypothesis of the bent upper state explains all this. The bent state is an asymmetric top with three different rotational constants A, B, and C. Without troubling yet about precise figures, let us consider their orders of magnitude. Supposing that the bending is moderate, say 30° or 60°, then, because of the mass ratio of carbon and hydrogen, A will be one order of magnitude larger than B and C, which will both be comparable to the B of normal acetylene, and thus of the order of 1 cm.$^{-1}$ (Table 16, p. 2720). Hence A must be of the order of 10 cm.$^{-1}$. Furthermore, because of the relation between moments of inertia in a planar molecule, the reciprocals of B and C will differ approximately by the reciprocal of A, so that B and C should show a difference of the order of 0·1 cm.$^{-1}$. It is the magnitude of A which will concern us first.

Since the bent upper state is a near-symmetric top, its rotational energy will approximately obey eqn. 18 (p. 2720). It follows that the manifold of energy levels will contain a system of large spacings dependent upon K : as K takes on the values 0, 1, 2, 3, . . ., so the energy is increased by 0, 1, 4, 9, . . ., units $\{A - \frac{1}{2}(B + C)\}$, each unit of the order of 10 cm.$^{-1}$. Therefore, when, as in the upper part of Fig. 12, we sort out the energy levels into a series of gyrovibronic stacks, distinguished with respect to K, the stacks will start successively higher by 1, 4, 9, . . ., units $\{A - \frac{1}{2}(B + C)\}$ above the starting point of the lowest stack.

As eqn. 15 shows (p. 2719), there are two possible selection rules for K, depending on the direction of the oscillating transition moment, which in turn depends on the symmetry, still to be discussed, of electronic orbital motion in the excited state: if the oscillating moment is parallel to a, then $\Delta K = 0$; but if perpendicular, then $\Delta K = \pm 1$. The second of these rules is required to explain our band pattern.

When transitions start from the vibrationless ground state, a Σ_g^+ vibronic state for which $K'' = 0$, then they have to end in the upper gyrovibronic state for which $K' = 1$; and thus we obtain the single band C, which heads the progression.

When transitions start from the next higher vibronic state, the Π_g state, which has one quantum of the Π_g vibration, with its unit of angular momentum, so that $K'' = 1$, they may end either in the upper gyrovibronic state for which $K' = 0$, or in that for which $K' = 2$. The former alternative gives band A, whose separation from band C is equal to the lower-state vibration quantum plus one of the upper-state gyrovibronic spacing units: $\Pi_g(1) + \{A - \frac{1}{2}(B + C)\}$. The latter alternative leads to band B, whose separation from C is the vibration quantum less three of these spacing units: $\Pi_g(1) - 3\{A - \frac{1}{2}(B + C)\}$. Thus the B — A spacing is $4\{A - \frac{1}{2}(B + C)\}$—roughly 60 cm.$^{-1}$ in acetylene, or 40 cm.$^{-1}$ in dideuteroacetylene, according to observation.

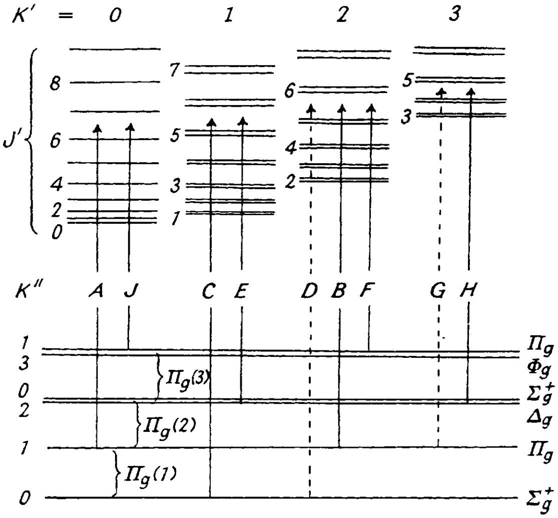


FIG. 12. *Gyrovibronic transitions obeying the rule* $\Delta K = \pm 1$ *(full-line arrows) to* trans-*bent upper state: explanation of band groups in the lower-state progressions. The long horizontal lines each mean one vibronic state, but the whole of the upper part of the diagram represents a single vibronic state dissected into its gyrovibronic states, and their levels and sub-levels. (Two forbidden transitions are marked by broken-line arrows.)*

With two Π_g vibration quanta initially present, the vibronic Δ_g state, for which $K'' = 2$, can combine with upper gyrovibronic states for which $K' = 1$ and 3. The former transitions produce band E, separated from C by the two Π_g quanta only: $\Pi_g(1) + \Pi_g(2)$. The latter transitions give band H, separated from C by the two vibration quanta less eight gyrovibronic spacing units: $\Pi_g(1) + \Pi_g(2) - 8\{A - \frac{1}{2}(B + C)\}$. Thus the H — E spacing is $8\{A - \frac{1}{2}(B + C)\}$—about 120 cm. in acetylene and 80 cm.$^{-1}$ in dideuteroacetylene, that is, twice the B — A spacing.

The whole of this can be followed from Fig. 12, the upper part of which represents the detail of one upper vibronic state, and is on a much more open scale than the lower part, which comprises, but without detail, a series of lower vibronic states. When the lower electronic state is furnished with successive Π_g quanta, each of which may either add its unit of angular momentum to, or subtract it from, the total of the units already present, groups of vibronic states arise which alternately contain all even and all odd numbers of units of angular momentum. Thus in the successive groups of lower vibronic states, K'' takes on the following values: 0; 1; 0, 2; 1, 3; 0, 2, 4; 1, 3, 5; . . . The states of a given group are separated in energy on account only of the anharmonicity of the Π_g vibration. According as K'' is 0, or 1, or 2, we get respectively, the single band, such as C, the closer type of band pair, such as B, A, and F, J, and M, N, or the doubly spaced type of band pair, such as H, E, and K, L.

A number of bands are allowed by the K selection rule which are not observed, namely, those of the initial vibronic states for which $K'' = 0$ in the two- and four-quantum groups, and those of initial vibronic states for which $K'' = 3$ or more. The missing bands of the states having $K'' = 0$ should be nearly coincident with, and may possibly be obscured under, bands E and L. Bands involving high K's should be well separated from other bands in some cases; but they are expected to be weak, and presumably are too weak to be observed.

(d) *Symmetry of the Upper Electronic State.*—We have mentioned three features of the spectrum, which provide more than enough evidence to determine the symmetry of orbital motion in the excited electronic state. By dealing with this point now, we can shorten the more quantitative discussions of band forms given later.

First, it was noted (Section I, p. 2726) that nearly all the bands, in fact all that can be clearly observed except the D bands, are double-headed. It follows by relations (13), (14), and (8) (pp. 2719 and 2716) that the electronic oscillations of the transition are perpendicular to axis a. It then follows from Table 8 (p. 2712) and Fig. 3 (p. 2715) that the oscillations of the transitions are almost certainly parallel to axis c, since if they were perpendicular to c we should find strong bands indicating electronic oscillations both parallel and perpendicular to a. The conclusion is that the upper state has A_u symmetry, that is, that it has the two-fold c axis of the bent model, but changes sign on reflexion through the plane of the atoms.

Secondly, we have found (Section 3c) that the selection rule $\Delta K = \pm 1$ is required to explain the characteristic band pattern of the spectrum. This leads directly to relations (8), and thus to the chain of conclusions stated in the last paragraph.

Thirdly, we have the approximate analysis of C bands already described. As the experiments on the temperature dependence of band intensity show, the transitions giving C bands start from the vibrationless ground state; and, by the selection rule $\Delta K = \pm 1$, they must end in the upper gyrovibronic states for which $K' = 1$. As Fig. 12 shows, each J' value here, as in all upper gyrovibronic states for which $K' > 0$, is theoretically to be represented by a doublet, because the excited molecule is only a near-symmetric top, so that B and C are slightly different, the difference being of the order of 0·1 cm.$^{-1}$, as we have seen. We noted in Section 2c (p. 2730), that the rotational structure of C bands makes it empirically clear, not only that the upper rotational levels are in fact double, with a difference of rotational constant of this order of magnitude, but also that the principle of construction of the band branches is that Q-branch transitions end on the lower, while P- and R-branch transitions end on the upper sub-levels of the doublets. If now we recall the overall selection rules (20) and (21) (pp. 2722, 2723), and consult Fig. 5 (p. 2721), we see that the only upper gyrovibronic state having $K' = 1$, with which the lower vibronic state Σ_g^+ (col. 1) could combine to give bands formed according to this principle, is the gyrovibronic state A_u (col. 8). As the only vibrations which may be present are totally symmetrical, this means that the electronic state has A_u symmetry.

(e) *Rotational Structure of C Bands.*—Our next task is to deal with the structure of the C bands quantitatively, and thus to determine the three rotational constants A, B, and C of the excited molecule. The broad relation between the structure and the constants is that the doublet splitting depends on the difference between B and C, and, because of the approximate reciprocal relation already mentioned, on A, while the J spacings depend essentially on the magnitudes of B and C themselves. The displacement of the whole gyrovibronic band from the vibronic origin depends mainly, as we have noted, on A, and thus indirectly on the difference between B and C.

By using the exact equation for the energy of an asymmetric top (eqn. 19, p. 2720), and the associated tables of King, Hainar, and Cross, it is possible, by trial and error, to find values of the three rotational constants of the excited acetylene molecule, which give calculated positions for the rotational lines in good agreement with the measured positions. These calculations have been carried through for the four bands C_0—C_3, and, for illustration, the results of one such calculation, and their comparison with the observational data are given in Part V (following paper). Here we direct attention to the rotational constants thus derived, which are assembled in Table 17. The quantities $\{A - \frac{1}{2}(B + C)\}$

are also listed for comparison with values obtained from the separations of band pairs, and recorded below.

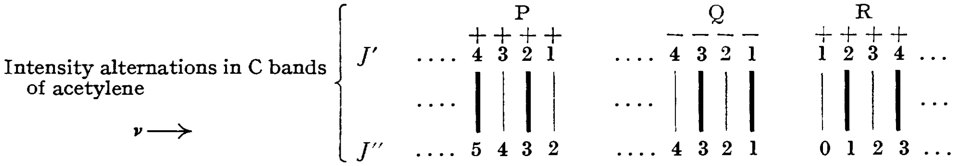
TABLE 17. *Rotational constants* (*cm.*$^{-1}$) *of the* trans-*bent state of acetylene from the analysis of C bands* (C_v).

v	A	B	C	$A - \frac{1}{2}(B + C)$
0	12·50	1·125	1·032	11·42
1	13·80	1·126	1·030	12·72
2	15·10	1·123	1·025	14·03
3	16·36	1·123	1·025	15·29

In Table 17, v represents the number of quanta of the $A_g(\alpha)$ vibration (Fig. 4, p. 2715) in the upper vibronic state. That A increases markedly with the energy of this vibration is consistent with our picture of the geometry of the excited molecule and of this vibration. Without troubling about a mathematical proof, one can see this intuitively by thinking of a classical $A_g(\alpha)$ vibration of such large amplitude that the separation of the mass-points from axis a alternately becomes double the equilibrium separation, and zero : then the instantaneous A will vary between a quarter of its equilibrium value and infinity, so that its average value is infinite.

These calculations confirm such assignments of J values to observed lines as are illustrated in Fig. 11 (facing p. 2727) : the assignments are uniquely determined by the necessity of obtaining the correct doublet splitting simultaneously with the correct J spacing. The calculations and assignments confirm the assumption of coincidences, too close for resolution with our equipment, between odd-numbered P lines and even-numbered Q lines, and between even-numbered P lines and odd-numbered Q lines, over the first 12 lines of the P branch, an assumption that we have to make for the independent reason that only thus can we account for the apparent absence of intensity alternations in this range, despite its evident presence elsewhere in the bands.

The assignments also bring about agreement between observation and theory as to the precise pattern of the alternations in the C bands. The theory can be deduced from Fig. 5 (p. 2721), remembering that the *a* levels have the higher statistical weight in acetylene. The pattern is shown in the following diagram, in which upper and lower members of doublet levels in the electronic upper state are distinguished by + and − signs, respectively. Lower-state J'' values being used, as always, to number the lines, the rule for C bands is simply that odd-*numbered* lines are the stronger in all three branches :



Intensity alternations in C bands of acetylene

(f) *Rotational Structures of the Stronger Temperature-sensitive Bands*.—The bands A and B have a common vibronic origin which lies lower than that of the bands C by the fundamental vibration Π_g of the electronic ground state. The distinction between the bands A and B, both as to position and structure, is gyrovibronic. The A-band transitions end in the upper gyrovibronic state for which $K' = 0$. Hence the gyrovibronic origins of bands A are identical with their vibronic origins; and hence also all the upper-state energy levels are single. The B-band transitions end in the upper gyrovibronic state for which $K' = 2$. Therefore the gyrovibronic origin of bands B will lie higher; and also all the upper-state levels will be double. However, since the transitions start from degenerate Π_g levels, transitions from each such level will end on both members of the upper-state doublets involved; and hence all lines of all branches of bands B will be double.

Having deduced our rotational constants from the C bands, we can use them to calculate, again using eqn. 19 and the tables of King, Hainar, and Cross, the positions relatively to their vibronic origin, of the gyrovibronic origins, and of the individual lines, of the A and B bands. These calculations have been made for the bands A_1, A_2, A_3, B_1, B_2, and B_3, of acetylene, and the detailed results for the lines of one A band and one B band are reported in Part V, where they are compared with the experimental measurements.

As can be followed with the aid of Fig. 5 (p. 2721), intensity alternations should theoretically appear in the A bands; and they can be seen, except when masked by lack of resolution near band heads, or by overlap of lines of the P and Q branches. The pattern of the alternations is slightly different from that of C bands: for acetylene it is that odd-numbered lines of Q branches, and even-numbered lines of P and R branches, are stronger than the intervening lines. Theoretically, the doublets of the B bands should have a strong and a weak component, which change sides as we pass from one doublet to the next along a branch. Experimentally, the lines of the B bands appear somewhat diffuse and without alternation of intensity: the reason is that our photographs do not resolve the doublets, though we do see the shelving intensity due to their weaker components.

The bands E and H have a common vibronic origin, lying below that of the bands A and B by another quantum of the Π_g vibration. The transitions giving the bands E and H end in the upper gyrovibronic states for which $K' = 1$ and 3, respectively. The positions of the gyrovibronic origins, and of the individual lines, relatively to the vibronic origin, have been calculated for some of the bands. The results of such calculations are indicated by some line assignments given in Part V.

Theoretically, the lines of E and H bands are doublets, each with a strong and a weak component, just like the lines of the B bands. Experimentally, we observe with E and H bands, as with B bands, a series of somewhat diffuse lines, representing unresolved doublets, and showing no alternation of intensity. This is how we know that the transitions giving the E bands start from the vibronic state Δ_g, and not from the neighbouring 2-quantum state Σ_g^+: if they started from the Σ_g^+ state, the E bands would show intensity alternations like C bands.

The bands J and F have another common vibronic origin displaced by a further Π_g quantum below that of the E and H bands. In separation and structure, these bands are simply weaker replicas of the A and B bands, respectively. This shows that the transitions giving the bands end in upper gyrovibronic states for which $K' = 0$ and 2 respectively, and therefore must commence in the 3-quantum vibronic state Π_g for which $K'' = 1$. Some assignments based on calculated line positions are given in Part V.

The " hot " bands were observed too weakly to permit an extensive examination of their rotational structures. However, the separation of the K and L bands, identical with that of the H and E bands, makes it almost certain that the transitions start in the 4-quantum vibronic state Δ_g, and end in upper gyrovibronic states for which $K' = 3$ and 1, respectively. Again, the separation of the M and N bands, identical with that of the B and A bands, and the F and J bands, makes it highly probable that the transitions start in the 5-quantum vibronic state Π_g and end in upper gyrovibronic states for which $K' =$ 2 and 0, respectively. Some calculated line assignments are given in Part V.

Comment is necessary concerning the accuracy of the calculations of line positions. King, Hainar, and Cross give tables of $E(\kappa)$ for κ values spaced 0·1 apart; they also give methods of interpolation for intermediate values of κ. Our κ's lie about 0·014—0·017 within one end of the range of κ, and we obtained the corresponding $E(\kappa)$'s by three-point graphical interpolation. This method of calculation is not as accurate as some of the experimental measurements would warrant. The alternative would have been to use the above-named authors' methods of numerical interpolation. However they are so difficult in this particular application that the labour seemed unjustified. With the rapid methods used, we could deduce the rotational constants, and, for C bands, calculate the positions of the lines to about the accuracy of measurement. For other bands, we could compute the gyrovibronic-origin and the band-head separations with almost the same accuracy, though the calculated line positions were not always as good as the measured positions.

The gyrovibronic-origin separations of the band pairs give a useful check on the rotational constants, since, by division by 4 or 8, they afford independent and fairly accurate estimates of the quantity $\{A - \frac{1}{2}(B + C)\}$. These values are given in Table 18. For acetylene, the origin separation is taken as the observed Q-head separation. For dideuteroacetylene, owing to incomplete resolution, the Q heads were somewhat poorly defined and therefore we thought it better in this case to use the experimentally well-defined R heads.

(g) *The Forbidden Progressions* D *and* G.—The D bands are weak satellites on the high-frequency side of the C bands, and the G bands are still weaker satellites on the same side of the B bands. We assign the D bands, which are not weakened by cooling, to transitions from the vibrationless ground state Σ_g^+ for which $K'' = 0$, to the upper gyrovibronic state for which $K' = 2$, and the G bands, which are temperature sensitive, to transitions from the lowest Π_g vibronic state, for which $K'' = 1$, to the upper gyrovibronic state for which $K' = 3$ (Fig. 12, p. 2733). In both cases $\Delta K = 2$, in contravention of the K selection rules of the symmetric top (eqn. 15, p. 2719).

TABLE 18. *Values of* $\{A - \frac{1}{2}(B + C)\}$ *in* cm.$^{-1}$ *from band-pair separations.*

		C_2H_2 (from Q heads)			C_2D_2 (from R heads)		
Band-pair		B − A	H − E	F − J	B − A	H − E	F − J
v	1	12·70	12·80	12·70	—	—	—
	2	14·17	14·04	14·00	8·52	—	8·45
	3	15·45	15·35	—	9·12	8·92	9·05
	4	16·72	16·39	—	9·72	9·38	9·65
	5	—	16·86	—	10·10	9·86	10·02
	6	—	—	—	10·20	—	—

The strongest evidence for our assignment of these bands relates to their positions. This is so consistent among lower-state progressions differing with respect to the number of upper-state vibrational quanta, all of which have slightly different energies, that one cannot doubt that the bands really belong to the gyrovibronic patterns into which the lower-state progressions are elaborated by the asymmetric-top character of the upper state. The best defined points for measurement in these weak bands are their R heads, the positions of which we can calculate to within about 1 cm.$^{-1}$ of the observed intensity maxima, from our rotational constants.

The forms of the bands are interesting, although, owing to low intensities, they could not be studied in detail. However, the D bands are certainly single-headed, presumably having no Q branch: they constitute, indeed, the only obvious series of single-headed bands in the spectrum. Some at least of the G bands appear to be double-headed, but with a peculiarly narrow spacing, about 2·5 cm.$^{-1}$, between the intensity maxima: it seems that these bands have Q branches.

If we were dealing with symmetric-top states only, we would be tempted to diagnose (eqns. 13 and 14, p. 2719) transitions, which, when they start from a Σ_g^+ vibronic state give bands without Q branches, but when they originate in a Π_g state produce bands with Q branches, as following those *J* selection rules which apply when $\Delta K = 0$, and therefore as involving electronic oscillations parallel to axis *a* (eqn. 15, p. 2719). We are actually dealing with an asymmetric top, which the concept of *K* is extended to cover, even though it can be numerically defined therefor only by the limit into which it goes when the top becomes symmetric. Thus, in our case, the *K* rules of the symmetric top are not expected to hold strictly; and, in particular, the conditions for transitions with electric oscillations parallel to *a* are broader than is indicated above. If both upper and lower states are regarded as asymmetric tops, general or limiting, then either a rotational state of top-species *A* must combine with one B_a, or a rotational state B_b must combine with one B_c (eqn. 16, p. 2719). As one of our states belongs to the limiting case of no asymmetry, a more specific expression of the condition is that a Σ rotational state of the linear molecule must combine with either an *A* or a B_a state of the bent molecule, whilst a Π linear state must combine with either a B_b or a B_c bent state (Table 15, p. 2720). These combinations are permitted when ΔK is even, and, in particular, when $\Delta K = 2$ (Fig. 5, p. 2721). It can also be argued, conversely, that transitions with $\Delta K = 2$ must involve electronic oscillations parallel to *a*.

The conclusion that the forbidden ($\Delta K = 2$) bands D and G have their electric oscillations of transition parallel to *a*, whereas all the allowed ($\Delta K = \pm 1$) bands have their oscillations parallel to *c*, is consistent with the observation that the forms of the D and G bands are strikingly different from those of all the other bands. Regrettably, we cannot analyse the differences in a more detailed way, for lack of sufficiently strong photographs.

What is forbidden about these bands is not that $\Delta K = 2$, a difference allowed to an asymmetric top, but that the overall selection rules, which must be obeyed in all circumstances (eqns. 20 and 21, pp. 2722, 2723), and the asymmetric-top rules mentioned above,* are not simultaneously satisfied for combinations of the lower vibronic states with the relevant vibronic states of an upper electronic state A_u (Fig. 5, p. 2721). Yet the band-systems to which the D and G bands are shown by their positions to belong, certainly depend on transitions to vibronic states of an electronic state A_u (Section 3d, p. 2734). However, the asymmetric-top and the overall selection rules would be obeyed, with $\Delta K = 2$, if the upper electronic state were of species B_u (Fig. 5). We conclude that some perturbation is mixing a small amount of B_u character with the A_u electronic state of the *trans*-bent acetylene molecule.

A conceivable electronic state from which the B_u character might be borrowed is suggested by our correlation diagram (Fig. 3, p. 2715). Our upper electronic state A_u is clearly to be identified with the lower of the two A_u states represented on the left of the diagram. Transitions from the electronic ground state to this state are allowed only in consequence of *trans*-bending, but become forbidden as the molecule is straightened (and remain forbidden with *cis*-bending). The energy curve of this state is seen to be intersected, at a certain degree of *trans*-bending, by the much steeper curve of a B_u electronic state, to which transition from the electronic ground state is allowed, not only in all bent configurations, but also in the limit of no bending, when the energy is very much higher. The ultra-violet spectrum of this upper state might well be a continuum, the energy curve being more a wall than a hollow; but as the energy must neighbour that of the A_u state over a range of the configurations through which the molecule must pass during excitation from the electronic ground state, some electronic resonance between the two states seems possible, provided that a suitable mixing perturbation can be found. As noted already (Section 1b, p. 2726), the presence of a continuous spectrum underlying our band spectrum is not excluded by our observations.

The mixing potential has to have B_g symmetry (Table 4, p. 2711). The condition that it must make no noticeable difference to band positions, excludes a vibration; and anyway, no single vibration has B_g symmetry (Fig. 4, p. 2715). It could be a rotation, since, for all we know, line positions in the B and G bands may be displaced; and rotation round axis a has B_g symmetry. Though we cannot prove it, this seems the best speculation at present. We are attracted to it by the knowledge that molecular rotation round a, and electronic orbital motion, must be coupled together by the yoke they share as common carriers of the angular momentum in straight-to-bent transitions. The coupling energy could be due to Coriolis forces.

In the spectrum of dideuteroacetylene the D bands cannot be seen, probably because they are obscured by the q and p bands which overlap each C band.

(h) *The Minor Progressions.*—Corresponding to the main progressions, A, B, C, . . ., we find, shifted to higher frequencies in the spectra of acetylene and dideuteroacetylene, much weaker progressions, labelled a, b, c, . . ., respectively; and, shifted to still higher frequencies in the spectrum of dideuteroacetylene, a further series of not quite such weak progressions, which we label p, q, r, . . ., respectively. The progressions a, b, c, . . ., are weaker relatively to the main progressions in the spectrum of acetylene than in that of dideuteroacetylene. In the spectrum of acetylene the progressions p, q, r, . . ., could not be found. In the spectrum of dideuteroacetylene, the positions of the bands, which, if observed, we would have labelled h, are covered by the stronger observed bands t. The correspondences are indicated in the following scheme:

Main progns.	....	A	B	C	E	F	H	J	K	L	Approx. shift (cm.$^{-1}$)
Minor progns.	C_2H_2	a	b	c	e	f	h	j	k	l	+ 1380
	C_2D_2	a	b	c	e	f	—	j	—	—	+ 1300
	C_2D_2	p	q	r	t	u	w	y	—	—	+ 2200

In any vertical column of this scheme, the progressions show the same sort of dependence of intensity on temperature: progressions c and r are not weakened by cooling, whilst

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* Asymmetric-top rules should not be broken by a symmetric top, which is only a limiting case.

a, b, p, and q are weakened, e, h, t, and w are weakened more, and f, j, u, and y more still. Thus it is clear that the common frequency shift applying to each horizontal row in the above scheme represents a vibration frequency of the upper electronic state.

As we are dealing throughout, not with single bands, but with progressions, in intervals of about 1000 cm.$^{-1}$ in acetylene and about 800 cm.$^{-1}$ in dideuteroacetylene, there might have been some dubiety concerning the frequency shifts entered to the right of the above scheme of progressions. However, we can be sure that the first figure should indeed be 1380 cm.$^{-1}$, and not 380 cm.$^{-1}$ or 2380 cm.$^{-1}$, because, in the acetylene spectrum, we can find the first bands, a_0, b_0, c_0, . . ., of the minor progressions, as well as those A_0, B_0, C_0, . . ., of the major ones. Although we cannot do this in the spectrum of dideuteroacetylene, because of the small intensities at low quantum numbers, we have deduced the origin of the band system (next section), and therefore the correlation, as between acetylene and dideuteroacetylene, of the origins and band quantum-numbers. Thus, the analogies between the spectra point, with a high degree of probability, to the conclusion that the relevant dideuteroacetylene shift is about 1300 cm.$^{-1}$, as entered above, and is not more or less than this by the progression interval 800 cm.$^{-1}$. No such correspondence between the spectra helps us to define the frequency of dideuteroacetylene relevant to the progressions, p, q, r, . . ., the observed bands of which would allow it to be taken near 600 cm.$^{-1}$, or near 1400 cm.$^{-1}$, or near 2200 cm.$^{-1}$. However, we can account satisfactorily for the appearance of these progressions in the spectrum of dideuteroacetylene only on the basis that the common shift which characterises them is near 2200 cm.$^{-1}$, as is noted above.

After the totally symmetrical bending vibration $A_g(\alpha)$, the two vibrations of the upper state which should appear most strongly in these spectra are the two totally symmetrical stretching vibrations A_g(C) and A_g(H). Even harmonics of non-totally symmetrical vibrations are symmetry-allowed, but should appear much more weakly, if at all. We assign the approximate frequencies, 1380 cm.$^{-1}$ in acetylene and 1300 cm.$^{-1}$ in dideuteroacetylene, to the upper-state carbon-bond-stretching vibration A_g(C). The isotopic difference of frequency is consistent with assignment to a carbon vibration. On the Franck–Condon principle, progressions in successive quanta of vibration A_g(C) cannot be expected to increase in intensity with increasing quantum number at a rate comparable to that of progressions in the $A_g(\alpha)$ vibration. And thus, as we proceed towards higher frequencies, progressions in the A_g(C) vibration will soon get lost beneath the rapidly strengthening bands of the $A_g(\alpha)$ progressions. Thus we account for the fact that we have not been able to observe a second quantum of the A_g(C) vibration.

The approximate frequency 2200 cm.$^{-1}$ of dideuteroacetylene is attributed to the hydrogen-stretching vibration A_g(H). This is a form of motion, which, in the bent molecule, is bound to be accompanied by small angular changes, which would not much reduce the frequency, but would lend the vibration an appreciable intensity in the spectrum. In acetylene the smaller hydrogen masses would lead to less bending and smaller intensities; but we think that the main reason why we do not observe the system of minor progressions, p, q, r, . . ., in the spectrum of acetylene is that their displacement from the main progressions would, according to our assignment of the responsible vibration, be about 3000 cm.$^{-1}$, so that each band of any such minor progression would approximately agree in position with a very much stronger band of main progression, a band having three extra quanta of the intensifying vibration $A_g(\alpha)$. In fact, we observe in a number of the main bands, C_4 and C_5 for instance, disturbances to the rotational structure, or to the whole band position, which suggest a Fermi effect following accidental coincidences of upper vibronic states of like symmetry. By an examination of such perturbations in the C progression, we have arrived at the opinion that the fundamental frequency of the A_g(H) vibration in C_2H_2 is indeed close to 3000 cm.$^{-1}$. We do not find a second quantum of this vibration, either in the spectrum of acetylene or in that of dideuteroacetylene. The reason why we should not expect to do so is as given in the preceding paragraph, but is still more cogent in its application to this case, since higher frequencies are involved.

(i) *Origin of the Band-system.*—In the spectrum of acetylene, no member of the C progression has been found at lower frequencies than that of the band labelled C_0. Its

R-head is at 42,225·5 cm.$^{-1}$, and its gyrovibronic origin is calculated from the rotational analysis to be at 42,209·1 cm.$^{-1}$. No member of the heat-strengthened progressions A and B has been observed on the low-frequency side of the bands labelled A_0 and B_0. Bands of the weaker progressions E and H have been found down to E_0 and H_0 near 41,000 cm.$^{-1}$, and various other weak bands are recorded down to 40,500 cm.$^{-1}$. Thus it seems certain that C_0 is really the first band of the C progression, and therefore that the quantum numbers indicated by subscripts in the labels of all the acetylene bands have been correctly assigned.

A small part of the energy at the gyrovibronic origin of the band C_0 is due to the one K-unit of rotation in the upper state (Fig. 12, p. 2733). Correcting for this by deduction of the appropriate value of $\{A - \frac{1}{2}(B + C)\}$, we find (Table 17, p. 2735) for the vibronic origin of C_0, which is also the electronic origin of the whole band-system of acetylene, the value 42,197·7 cm.$^{-1}$.

The spectrum of dideuteroacetylene presents the difficulty that, owing to its small intensity at the low-frequency end, we could not observe the early members of the progressions. On the assumption, for the moment, that we have assigned quantum numbers correctly to the observed bands, the situation with respect to the C progression is that bands C_1 and C_0 have not been observed; however, we can deduce their positions very approximately by extrapolation from the observed positions of the bands C_6 to C_2. This leads us to expect C_1 at 43,124 cm.$^{-1}$ and C_0 at 42,280 cm.$^{-1}$. These extrapolated figures, like the observations from which they are derived, refer to R-heads. According to calculations based on rotational constants of dideuteroacetylene given later, the band origins should lie 13 cm.$^{-1}$ lower. It follows that the gyrovibronic origin of band C_0 is at 42,267 cm.$^{-1}$. Some of this energy is due to rotation, and, allowance being made for this, we find for the vibronic origin of the C progression, which is the electronic origin of the band-system in dideuteroacetylene, the value 42,260 cm.$^{-1}$.

The relation of this figure for dideuteroacetylene to that derived above for acetylene is so reasonable as to leave no doubt that quantum numbers have been assigned, and the electronic origin for dideuteroacetylene has been located, correctly. Our closest guide is that of benzene. The difference of zero-point energy between benzene and hexadeuterobenzene in the electronic ground state is 4100 cm.$^{-1}$; and, in an excitation by 38,000 cm.$^{-1}$, this difference drops by 5%, with the result that the origin of the band-system of hexadeuterobenzene is displaced to a higher frequency than that of benzene by 200 cm.$^{-1}$ (Garforth, Ingold, and Poole, *J.*, 1948, 515). The difference of zero-point energy between acetylene and dideuteroacetylene in the electronic ground state is 1156 cm.$^{-1}$ (Table 9, p. 2716). Naively, we might expect that an excitation of 42,000 cm.$^{-1}$ would reduce the difference by 5½%, thus to displace the origin of the band-system of dideuterobenzene to higher frequency than that of acetylene by 64 cm.$^{-1}$. The displacement deduced above is in the expected sense and amounts to 62 cm.$^{-1}$. Discrepancies of hundreds of cm.$^{-1}$ would have arisen if any quantum numbers had been misassigned.

(j) *The Intensity of the Band-system.*—In acetylene at ordinary temperature about 88% of the molecules are in the vibrationless electronic ground state Σ_g^+. Nearly all of those excitations to the bent electronic state A_u which start without vibrations, end to give the bands of progression C, the other progressions having a vibrationless starting state, D and c, being relatively quite weak. Hence the intensity of the C progression, calculated with due allowance for the proportion of molecules available to produce it, can be taken as an approximation to the intensity of the whole electronic transition.

As mentioned in Part III (p. 2717), we have measured, by the method described in Part II (p. 2707), the intensities of the bands of this progression from C_1 to C_5. The results, expressed as oscillator-strengths, which allow for the circumstance that not all the molecules present are in the relevant initial state, are given in Table 19. From the variation of oscillator-strength with quantum number, we have calculated, in the simplified way outlined in Part III (p. 2717), the overlap parameter q, which is the displacement of origin of the appropriate vibrational co-ordinates in the combining states. As there are three vibrations in the totally symmetric species of the bent state, q is a somewhat involved function of its geometry: indeed, in order to deduce this function, it is necessary to know the force system. But the determination of q from band intensities allows us to use the sum rule, and thus to calculate, as described in Part III (p. 2717), from the intensity of each measured band, the intensity of the whole C progression. The results of these calculations are seen to be fairly consistent from the following:

Oscillator-strengths (f) *of* C *bands and of* C *progression.*

Band	C_1	C_2	C_3	C_4	C_5
$10^5 f$ measured for band	0·0042	0·036	0·145	0·51	1·2
$10^5 f$ calc. for progression	7·9	9·5	8·2	8·4	6·4

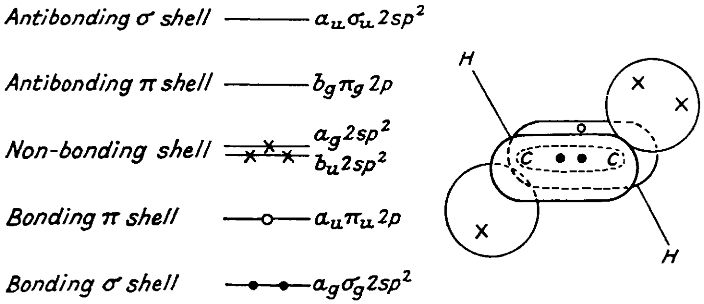
The oscillator-strength of the C progression is thus about 8×10^{-5}, this figure containing an allowance for the circumstance that, under the conditions of measurement, not all the molecules are in the starting state. The same figure, preferably in its rounded form 1×10^{-4}, should represent an approximation to the oscillator-strength of the whole electronic transition.

An ordinary allowed electric-dipole transition often has an oscillator-strength of 0·1—1. The result that our transition is 10^3—10^4 times weaker is not due to its being forbidden in any way by the symmetry of the combining states. The transition is what we might call "Franck–Condon-forbidden." In other words, the change of shape is so drastic (as we shall particularise later) that the transitions are far from being "vertical" transitions in the Franck sense. Quantally, this diminishes their probability. Classically, the electron-jump is reduced to slow motion by the need to wait for the nuclei.

(4) PHYSICAL NATURE OF THE EXCITED STATE

(a) *Electronic Properties.*—Here we shall collect the conclusions which have already been reached, though some have not yet been put into words. The upper electronic state of the near-ultra-violet band-system of acetylene has the *trans*-bent stereochemical configuration, and the electronic wave-function has the symmetry of the model of the molecule, except that it changes sign across the molecular plane, to which the oscillatory transition moment is perpendicular.

FIG. 13. *Schematic representation of orbital occupancy in the upper electronic state of the near-ultra-violet band-system of acetylene. The carbon atoms are bound by three shared electrons and possess* 1·5 *unshared electrons each in* trans-*related groups, weak resonance being assumed between the non-bonding atomic orbitals sketched, to give the molecular non-bonding orbitals named.*



The electronic configuration adopted in the bent upper state by the six electrons of the original carbon triple bond is as shown schematically in Fig. 13. On the left an orbital energy diagram indicates the occupancy of the successive shells, while the sketch on the right is a reminder of the general geometrical relation of the occupied orbitals. As the antibonding shells are unoccupied, the configuration represents a 3-electron C–C bond, and we ought to expect its length and force-constant to correspond to a bond-multiplicity of 1·5. The two carbon atoms between them have three essentially unshared electrons, and, allowing for the expected weak resonance between the non-bonding atomic orbitals, we may say that each carbon atom has 1·5 unshared electrons. The two groups of unshared electrons are *trans*-related, and, in the light of dispersion theory, this has an important bearing on the directed polarisability of the carbon atoms of normal acetylene.

(b) *Geometrical Properties.*—The rotational constants A for the electronic upper state of acetylene in several different states of vibration are given in Table 17. They may also be obtained by the nearly independent method of adding to the values of $\{A - \frac{1}{2}(B + C)\}$ given in Table 18 the relatively small and nearly constant values of $\frac{1}{2}(B + C)$ obtained from Table 17. The mean values of A obtained in these ways are given in Table 19, and,

TABLE 19. *Mean rotational constants* A (*in cm.*$^{-1}$) *for the bent excited states of acetylene and dideuteroacetylene.*

v	0	1	2	3	4	5	6
C_2H_2	12·50	13·81	15·14	16·34	17·70	—	—
C_2D_2	—	—	9·31	9·86	10·41	10·82	11·03

as shown in Fig. 14, they plot to a good straight line, from which smoothed values can be read. Slightly better values of the other rotational constants, B and C, than those in Table 17, may be similarly deduced by plotting.

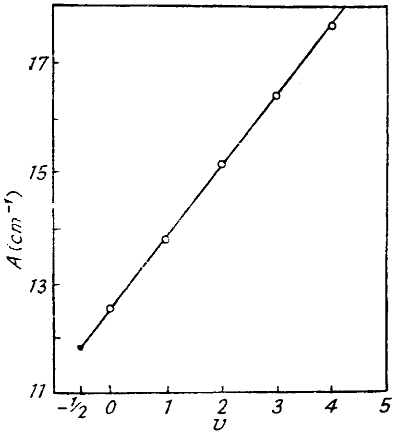


FIG. 14. *Variation of the rotational constant* A *of the* trans-*bent electronic upper state of acetylene with the quantum number* v *of its totally symmetrical bending vibration.*

The values adopted as a result of these procedures for $A^{(0)}$, $B^{(0)}$, and $C^{(0)}$, the rotational constants of the vibrational ground state of the electronically excited molecule are:

$$A^{(0)} = 12{\cdot}50, \qquad B^{(0)} = 1{\cdot}127, \qquad C^{(0)} = 1{\cdot}033 \text{ cm.}^{-1}$$

The corresponding moments of inertia are:

$$10^{40}I_a^{(0)} = 2{\cdot}24 \qquad 10^{40}I_b^{(0)} = 24{\cdot}83 \qquad 10^{40}I_c^{(0)} = 27{\cdot}09 \text{ g.-cm.}^2$$

We note that $10^{40}(I_a^{(0)} + I_b^{(0)}) = 27{\cdot}07$ g.-cm.^{2}, which agrees so nearly with $10^{40}I_c^{(0)}$ as to establish the planarity of the excited molecule.

If α is the angle by which each C–H bond in the *trans*-bent excited molecule is turned out of the produced line of the C–C bond, then the moments of inertia are given by the formulæ:

$$I_a = \tfrac{1}{2}(m_C + m_H)r_{CC}^2 \sin^2\theta + 2m_Hr_{CH}^2\sin^2(\alpha - \theta) - 2m_Hr_{CC}r_{CH}\sin\theta\sin(\alpha - \theta)$$
$$I_c = \tfrac{1}{2}(m_C + m_H)r_{CC}^2 + 2m_Hr_{CH}^2 + m_Hr_{CC}r_{CH}\cos\alpha$$
$$I_b = I_c - I_a$$

Here m_C and m_H are the atomic masses, and r_{CC} and r_{CH} the bond lengths, while θ, the angle between the C–C bond and the principal axis of inertia a, is given by

$$\tan 2\theta = \frac{m_Hr_{CH}^2 \sin 2\alpha + m_Hr_{CC}r_{CH} \sin\alpha}{\tfrac{1}{4}(m_C + m_H)r_{CC}^2 + m_Hr_{CH}^2\cos 2\alpha + m_Hr_{CC}r_{CH}\cos\alpha}$$

Various bond lengths and bond angles were assumed and the corresponding moments of inertia were calculated, until agreement with the spectroscopically determined values were obtained. Some of these calculated values are in Table 20, line (6) of which represents our best approximation.

Actually, the three geometrical parameters, r_{CC}, r_{CH}, and α, cannot uniquely be determined from the moments of inertia of excited acetylene only, because, in this planar molecule, but two of the three moments are independent. We could, for example, change r_{CH} slightly from 1·08 Å, and make compensating adjustments in r_{CC} and α. However, the choice $r_{\mathrm{CH}} = 1{\cdot}08$ Å can be supported by reference to the spectrum of dideuteroacetylene. Here we have values of $\{A - \frac{1}{2}(B + C)\}$ for various vibrational quantum numbers v. The unimportant part of this, $\frac{1}{2}(B + C)$, which we know to be practically independent of v, can be computed sufficiently well from the calculated moments of inertia I_b and I_c of Table 20. This leaves the main term A, essentially spectroscopic in its mode of determination, as already recorded in Table 19. This quantity depends markedly on v; but a graphical extrapolation, which is not quite linear, probably because of the use of R-heads, instead of Q-heads, in the measurements of $\{A - \frac{1}{2}(B + C)\}$ in this spectrum, allows us to deduce $A^{(0)}$, and thence that $10^{40}I_a^{(0)} = 3{\cdot}50$ g.-cm.^{2}, in agreement with the calculated value in line (10) of Table 20.

TABLE 20. *Calculated moments of inertia (I in g.-cm.^{2}) of the* trans-*bent molecule : comparison with spectroscopic values.*

	r_{CC}	r_{CH}	α	θ	$10^{40}I_a$	$10^{40}I_b$	$10^{40}I_c$
				Acetylene			
(1)	1·40	1·06	63°	9° 42′	2·35	24·84	27·19
(2)	1·40	1·08	63°	9° 57′	2·43	24·95	27·38
(3)	1·39	1·08	62°	10° 1′	2·37	24·76	27·14
(4)	1·38	1·08	62°	10° 7′	2·36	24·46	26·82
(5)	1·38	1·08	60°	10° 1′	2·25	24·72	26·97
(6)	1·383	1·08	59° 50′	9° 58′	2·24	24·84	27·08
				Spectrosc.	2·24	24·83	27·09
				Dideuteroacetylene			
(7)	1·40	1·06	63°	14° 50′	3·99	34·16	38·16
(8)	1·39	1·08	62°	16° 55′	3·75	31·26	35·00
(9)	1·38	1·08	60°	16° 45′	3·53	31·42	34·96
(10)	1·383	1·08	59° 50′	16° 40′	3·51	31·49	35·00
				Spectrosc.	3·50	—	—

The significance of this check may be explained as follows. Suppose that we have been taking r_{CH} too small in acetylene. Then all three moments of inertia must be too small. But we can make them right by taking, judiciously, r_{CC} too large and α too wide. However, when we now take r_{CH} equally too small in dideuteroacetylene, we are bringing in from the periphery of the molecule towards its centre of gravity twice as much mass as before, and therefore the same adjustments in r_{CC} and α will not compensate.

We conclude that the geometrical form of the *trans*-bent molecule is given approximately by the following figures :

$$r_{\mathrm{CC}} = 1{\cdot}383\ \text{Å} \qquad r_{\mathrm{CH}} = 1{\cdot}08\ \text{Å} \qquad \angle\mathrm{CCH} = 120{\cdot}2^\circ$$

The value for the valency angle implies that the change of σ-bond hybridisation from linear to plane-trigonal during the electronic excitation is complete. It is consistent with our conclusions concerning the configuration to which the π electron system is excited, a configuration involving a 3-electron C–C bond, that the length of the C–C bond is almost as in benzene, the geometrical parameters of which are usually given as $r_{\mathrm{CC}} = 1{\cdot}39$ Å, $r_{\mathrm{CH}} = 1{\cdot}08$ Å, $\angle\mathrm{CCH} = 120^\circ$.

In Fig. 15 the nuclear distributions of the normal and the excited molecule of acetylene are drawn to scale with coincident axes of inertia. From the drawing one can see in what directions and how far the atoms have to move when excitation takes place from one vibrationless form to the other as at the origin of the band system. It is easy to appreciate from this diagram why the Π_g or $\mathrm{A}_g(\alpha)$ vibration is so very much more intensity-giving than either of the other vibrations $\Sigma_g^+(\mathrm{C})$ or $A_g(\mathrm{C})$, and $\Sigma_g^+(\mathrm{H})$ or $A_g(\mathrm{H})$, which on grounds of symmetry alone, are equally competent to form bands.

(c) *Elastic Properties.*—From the Tables in Part V (following paper), it is possible directly to read the fundamental frequencies of the vibrations $A_g(\alpha)$ and $A_g(\mathrm{C})$ of the excited acetylene molecule, that is, the size of the first quantum of each of these vibrations in the absence of all other vibrations. The same two fundamental frequencies can be determined with fairly close approximation for excited dideuteroacetylene from higher harmonics of $A_g(\alpha)$, and from combination frequencies of $A_g(\alpha)$ with $A_g(C)$, by back-extrapolation over the first two quanta of $A_g(\alpha)$. A similar procedure of extrapolations allows us to find the fundamental frequency $A_g(H)$ of excited dideuteroacetylene. These frequencies are in Table 21.

TABLE 21. *Totally symmetrical fundamental frequencies* ($cm.^{-1}$) *of the* trans-*bent excited states of acetylene and dideuteroacetylene.*

	$A_g(\alpha)$	$A_g(C)$	$A_g(H)$
A_u state of C_2H_2	1049	1380	(3020, 2980)
„ „ C_2D_2	844	1310	2215

We have no similarly direct method of deducing the fundamental frequency $A_g(H)$ of excited acetylene, but we have two rough and indirect methods, which agree tolerably well, and give a mean result of 3000 $cm.^{-1}$. The first method is based on the hypothesis that the perturbations, observed in C bands above C_3, are due to Fermi resonance with transitions involving the development in absorption of one quantum of the vibration $A_g(H)$. By noting the magnitudes and directions (up in C_4 and down in C_5, for example) in which line positions are shifted from the expected positions, and allowing an effect of anharmonicity on $A_g(\alpha)$–$A_g(H)$ combination frequencies in acetylene on the basis of what we know of such an effect in dideuteroacetylene, we can approximately locate the unperturbed positions of the perturbing bands, and thereby deduce that the fundamental frequency of the vibration $A_g(H)$ of acetylene is about 3020 $cm.^{-1}$. The other method is to use the product rule of Teller and Redlich in its application to the excited acetylene molecule. This theorem requires that the ratio of the A_g frequency-products of the light and the heavy molecule shall be twice the square-root of the ratio of their moments of inertia around axis *c*. Taking the moments of inertia from Table 20, we can easily deduce that the acetylene frequency $A_g(H)$ required to give the right product ratio is 2980 $cm.^{-1}$.

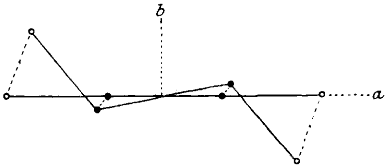


FIG. 15. *The linear normal and* trans-*bent excited molecules of acetylene on the same scale and with coincident axes of inertia.*

From the carbon stretching frequencies, we can deduce that the carbon-bond force-constant of excited acetylene is $7{\cdot}2 \times 10^5$ dynes/cm. Since the usually given force constant for a single carbon bond is $4{\cdot}5 \times 10^5$, and for a double bond $9{\cdot}8 \times 10^5$ dynes/cm., the value at which we have arrived, namely, the mean of these, seems a fortunate one to be able to offer for a three-electron bond. The value for normal benzene is $7{\cdot}6 \times 10^5$ dynes/cm. From the hydrogen-stretching frequencies, the force constant of the C–H bond of the excited acetylene molecule is computed to be $5{\cdot}0 \times 10^5$ dynes/cm. This should be compared with the CH constants of those normal molecules, such as benzene and ethylene, whose structures are based on plane-trigonal hybridisation : for both the CH force-constant is given as $5{\cdot}1 \times 10^5$ dynes/cm. The calculated bending force-constant of excited acetylene is somewhat sensitive to the precise method of calculation, but in view of the incompleteness of our knowledge of the potential-energy function, the simplest possible method (assuming independent hydrogen motions with non-stretching bonds) is not demonstrably worse than any other. It gives for the bending moment constant of excited acetylene 8×10^{-12} dyne-cm./radian. The value for planar hydrogen-bending motion in benzene, the most nearly comparable normal molecule with respect to *both* bonds forming the variable angle, is given also as 8×10^{-12} dyne-cm./radian.

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