

ULTRAVIOLET ABSORPTION SPECTRA OF ACETYLENE AND FORMALDEHYDE.

BY G. HERZBERG (*Darmstadt*).

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Photochemical reactions are produced only by radiations which bring the molecules into states of an electron configuration other than that of the ground state. Radiations which only excite rotations or vibrations of the molecule (infra-red or red absorption spectra) in general cannot lead to photochemical decomposition. If the potential curve of the upper electronic state involved is one of repulsion¹ a continuous absorption spectrum occurs which corresponds to immediate dissociation of the molecule into its constituents having more or less kinetic and excitation energy. If the upper electronic state has a minimum of potential energy somewhere near that of the ground state the molecule may either not decompose but go back to the ground state with emission of radiation, or decompose by collision or by radiationless transfer without collision (predissociation).²

In this way the *photochemical dissociation processes* of *diatomic* molecules have, to a great extent, been explained. As to *polyatomic* molecules, however, very little has been done so far. The continuous and diffuse absorption spectra exhibited by these molecules in the gaseous state³ in addition to discrete absorption bands, evidently correspond also to photochemical dissociation: a detailed explanation has not yet, however, been given in most cases.

In order to obtain a better knowledge of the photochemical dissociation processes in polyatomic molecules it is necessary, in the first place, to get better information as to the electronic levels of polyatomic molecules; that is to say one has to investigate the *electronic band spectra* (ultraviolet absorption spectra) of these molecules. Until now none of these spectra has been completely explained. The electronic band spectra of some of the simplest polyatomic molecules even are completely unknown because they lie in the far ultraviolet.

With this in view G. Scheibe and the author⁴ have recently investigated the far ultraviolet absorption spectra of the *methyl halides*. The discrete absorption bands they found in the far ultraviolet correspond to transitions into stable electronic states of these molecules lying very high above the ground level.⁵ There was, however, a region of continuous absorption lying

¹ At least for nuclear distances of the same order of magnitude as that of the potential minimum of the ground state.

² Pre-dissociation and related phenomena will be discussed in a forthcoming review of the author in the *Ergebn. exakten Naturw.*

³ In the liquid or solid state continuous bands occur very often, but must not correspond to photochemical dissociation.

⁴ G. Herzberg and G. Scheibe, *Trans. Farad. Soc.*, **25**, 716, 1929, and *Z. physik. Chem.*, **B 7**, 390, 1930.

⁵ The frequency of vibration in two of the upper states of CH_3I is 1090 cm.^{-1} and 1080 cm.^{-1} respectively, corresponding to a transverse vibration of the H-atoms in the CH_3 group. So far no other frequency of the excited state could be analysed. Exposures taken at higher pressures revealed two frequencies of the ground-state, namely, 1250 and 520 cm.^{-1} . The first also found by Bennet and Meyer (*Physical Rev.*, **32**, 888, 1928) in the infra-red presumably is a transverse vibration of the H-atoms in the ground state, corresponding to that of the excited state. The latter frequency was also observed by Dadieu and Kohlrausch (*Wien. Ber.*, **139**, 77, 1930) and is a valency vibration $\text{CH}_3\rightleftharpoons\text{I}$ cf. below).

at *longer* wavelengths than the discrete bands. It was shown that this continuous absorption corresponds to the *photochemical dissociation of the halide* into normal CH_3 and slightly excited halogen (2P) or into slightly excited CH_3 and normal halogen (2P) with various amounts of kinetic energy. The maximum of continuous absorption corresponds to dissociation with very high kinetic energy (about 2 volts = 46 kal./mol. in the case of CH_3I). The upper electronic state involved is one of nearly pure repulsion.⁶

For the same reasons as given above the author has taken absorption spectrograms of two other simple polyatomic molecules, namely *acetylene* (C_2H_2) and *formaldehyde* (H_2CO). Acetylene has also been chosen for investigation because of the very simple fine structure found by Mecke and co-workers^{6a} in the infrared. Mecke has already pointed to the close similarity to be expected between C_2H_2 and N_2 because both have the same number of electrons. Such a similarity is also to be expected between H_2CO and O_2 , especially with regard to the electronic levels.⁷ There are of course other polyatomic molecules which resemble certain diatomic molecules in the same manner as above. It is hoped to investigate some of these later.

The experimental procedure was quite the same as that in the previous paper⁴ except that a two meter vacuum spectrograph was used.⁸

Acetylene.

C_2H_2 has no absorption until λ 2070 at pressures up to 30 mm. and 20 cm. length of the absorption tube. Here a system *A* of very weak absorption bands extends to shorter wavelengths with increasing intensity.^{8a} The regularities are not obvious. The distance of the main bands is 1365 and 865 cm.^{-1} . Another very strong system *B* of absorption bands begins at about λ 1540—depending on the pressure. Unfortunately, in this region the continuous spectrum of hydrogen which served as background has already faded away, and there is only the many line spectrum of hydrogen. Nevertheless, the discrete structure of this strong absorption is quite clearly to be seen on the plates. The distance of the main bands is about 1710 cm.^{-1} . The structure of these bands will further be investigated with a Lyman source of continuous radiation as background.

It seems to the author that the strong system *B* corresponds to the Lyman-Birge-Hopfield bands, the first ultra-violet absorption system of N_2 beginning at about 1450 Å.U. The shift to longer wavelengths is what

⁶ Cf. Fig. 11 of the above-mentioned paper.

^{6a} K. Hedfeld and R. Mecke, *Z. Physik*, **64**, 151, 1930, W. H. J. Childs and R. Mecke, *ibid.*, 162, 1930, R. Mecke, *ibid.*, 173, 1930.

⁷ It is well known that all diatomic hydrides show a pronounced similarity to the united atom.

⁸ This vacuum spectrograph was designed by Dr. Skinner and built in the workshop of the H. H. Wills Physics Laboratory (Bristol) where the work was carried out.

^{8a} Shortly after this paper had been sent away a paper by Kistiakowsky (*Physical Rev.*, **37**, 276, 1931) appeared on the ultraviolet absorption spectrum of acetylene. Kistiakowsky used absorption tubes of 2 m. length and atmospheric pressure of C_2H_2 . So he got absorption bands at λ 2400. There seems little doubt to me that his bands are the continuation of those discussed here to longer wavelength. I found that on increasing the pressure from 1 to 30 mm. the long wavelength limit shifted considerably to longer wavelength, so that it is quite possible that at atmospheric pressure and 2 m. length of absorption tubing the limit is at λ 2400.

one might expect in going from a diatomic to a polyatomic molecule. The weak system *A* is believed to correspond to the transition from the normal $^1\Sigma$ to the first excited $^3\Sigma$ level of N_2 , a transition which is absolutely forbidden in N_2 but which might occur weakly in C_2H_2 . The distance of the main bands in both systems *A* and *B* is not in contradiction to this analogy. Anyhow the existence of two different stable electronic levels in C_2H_2 is proved by the observation of the two band systems *A* and *B*. As to the energies of dissociation and products of dissociation in these states nothing definite can be said until now because the vibrational analysis of the bands is rather difficult in consequence of the existence of several vibrations and is not yet finished.

At higher pressures a continuous absorption sets in at about λ 1880. It is not absolutely certain whether this is really due to C_2H_2 and not to an impurity. In the first case it might correspond to a dissociation of C_2H_2 into two normal CH-radicals. But this would lead to a pretty low value for the binding energy of the C—C bond. The possibility that it corresponds to a photochemical dissociation into HC—C and H seems rather more likely.

Formaldehyde.

The absorption spectrum of H_2CO in the near ultra-violet has already been investigated by V. Henri and S. A. Schou.⁹ They have found

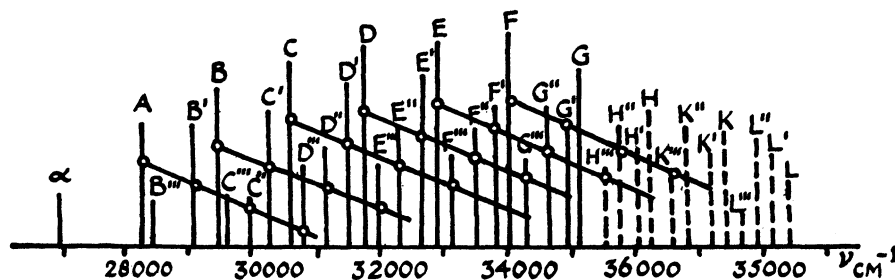


FIG. 1.

a system of discrete absorption bands beginning at about λ 3570 with clearly resolved fine structure due to the small moment of inertia round the $C=O$ axis. At a certain point the fine structure of these bands disappears, the bands become diffuse (predissociation) and then gradually mix into a continuous absorption. On the author's plates the discrete and diffuse bands are also present, whereas the continuous absorption is absent or very weak. A good spectrogram of these bands has already been published by Henri and Schou. The distance of the main bands, which they call *A*, *B*, *C* . . . is 1187 cm.^{-1} and is gradually decreasing. Each of these is accompanied by a somewhat weaker band *B'*, *C'*, . . . on its long wavelength side (cf. Fig. 1 for a diagrammatic representation of the bands) except that the *A* band has no such companion. This fact is very important for a correct interpretation of the vibrational structure of this band system, but has not been regarded by Henri and Schou. They, therefore, interpreted the main and satellite bands in the manner shown in Fig. 2. The larger vibrations of the upper level are numbered by the quantum number ν' the smaller ones by w' . For every vibrational level

⁹ V. Henri and S. A. Schou, *Z. Physik*, **49**, 774, 1928.

v' the values $w' = 0, 1, 2, \dots$ are possible. According to Henri and Schou the main bands A, B, . . . correspond to transitions from the vibrationless¹⁰ level of the ground state ($v'' = 0, w'' = 0$) to the levels $v' = 0, 1, 2, \dots$ with $w' = 1$ of the upper electronic state, the satellite bands correspond to similar transitions only with $w' = 0$, so that the distance $B'B$ (361 cm.^{-1}), $C'C$, . . . is the second vibration in the upper level. The transition $v'' = 0, w'' = 0 \rightarrow v' = 0, w' = 0$ is not observed according to this interpretation. No plausible reason can be given for this. Therefore, we give another interpretation in Fig. 3 (also indicated in Fig. 1) which immediately explains why the first main band has no satellite. Correctly speaking, according to this new interpretation B' is the satellite of A, C' that of B, etc., so that the main bands A, B, . . . correspond to transitions to different v' levels with $w' = 0$ whereas B', C', \dots have $w' = 1$ ($v' = 0, 1, \dots$). Bands with $w' = 2, 3, \dots$ are also present, though the intensity decreases rapidly in a w' progression. Whereas

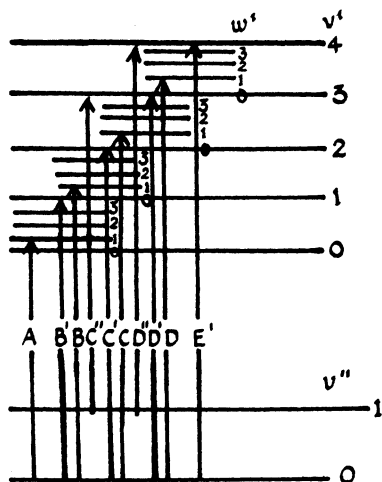


FIG. 2.

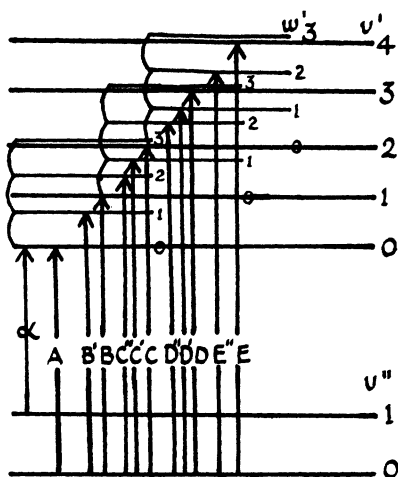


FIG. 3.

according to the new interpretation the larger vibrational frequency is rather the same as according to Henri and Schou namely 1187 cm.^{-1} the smaller one is now 830 cm.^{-1} (distance AB', BC', \dots) against 360 cm.^{-1} of Henri and Schou.

The superiority of the new interpretation is further shown by the fact that it is no longer necessary to assume that certain bands correspond to transitions from the higher vibrational states of the ground state to the upper state, as was done by Henri not only in this case (e.g. bands $C'', D'' \dots$) but also in many other cases. According to the Boltzmann factor such bands ought to be extremely weak compared with those corresponding to the vibrationless state, a condition not at all fulfilled in Henri's analysis.

A band which however certainly is a transition from the first vibrational level of the ground state is the very weak one called α by Henri and Schou (see Fig. 1). It lies on the long wave-length side of band A. The distance

¹⁰ We neglect the half-quantum zero-point vibrational energy of the quantum mechanics because it does not alter the conclusions.

1300 cm.⁻¹ should be a vibrational frequency of the ground state^{10a}. A similar interpretation applies to the very weak bands B''' , and C''' .

A rigorous test of this new analysis cannot be made unless the fine structure of the bands is analysed, because they are very wide and without pronounced heads. In fact Henri and Schou have analysed the fine structure, but there are several inconsistencies in their analysis, e.g. the values

$$B'' = \frac{h}{8\pi^2 c I''} \quad (I'' = \text{moment of inertia of the lower state}) \text{ for the } A, B, C,$$

. . . bands decrease just in the same manner as the B' values, though all these bands even according to Henri and Schou have the same lower level.¹¹ Therefore it is proposed to reinvestigate the fine structure. Besides an exact constancy of the first quantum of vibration w' for different values of v' cannot be required because the superposition of two frequencies is not exactly the sum of both (cf. also below). The differences AB' , BC' , . . . as calculated from Henri's data in fact increase.

If we follow the analogy between H_2CO and O_2 it seems probable that the Henri-Schou bands correspond to the Schumann-Runge bands of oxygen. The shift to longer wavelengths is again in agreement with what one might expect for a polyatomic molecule.

Raman effect and infra-red investigations have revealed the existence of two types of vibrations in polyatomic molecules¹² *valency vibrations* and *transverse vibrations*, i.e., vibrations in the direction of a chemical bond and perpendicular to it (stretching and bending of the bond). The larger frequency 1187 cm.⁻¹ observed in the excited state of H_2CO is presumably the valency vibration of $CH_2 \longleftrightarrow O$, i.e., it is analogous to the vibration $O \longleftrightarrow O$ of oxygen in the upper $^3\Sigma$ state of the Schumann-Runge bands, whereas the smaller frequency 830 cm.⁻¹ of H_2CO is probably the transverse vibration of the H-atoms ($H \longleftrightarrow H$). Both observed vibrations cannot be $C \longleftrightarrow H$ vibrations because this always has been found to be about 3000 cm.⁻¹, a value which cannot be altered very much for the excited state, because the excitation lies in the $C \equiv O$ bond. The transverse vibration of the H-atoms, which for the normal state usually is found to be about 1300-1500 cm.⁻¹ may well be lowered by the excitation in the $C \equiv O$ bond because the corresponding potential curve is determined by the position of the O nucleus. A transverse vibration of the O nucleus presumably would give a much smaller frequency than those observed.

The fact that the larger vibration decreases in the same manner as in a diatomic molecule, whereas the smaller one remains constant or even increases with increasing vibrational quantum number is further support for our interpretation of the two vibrations. Diatomic molecules have only one valency vibration which decreases with increasing quantum number. The potential curve for transverse vibrations is composed of two repulsion curves (repulsion from the two neighbouring atoms), i.e., it may be on both sides steeper than a parabola and so the frequency of vibration may well increase with increasing quantum number, as it does according to Henri and Schou's data.

The rapid decrease of intensity in a w' group ($v' = \text{const.}$) and the slow increase and decrease of intensity in a v' group is easily explained by Franck's principle, if one considers the potential curves of Fig. 4 and

^{10a} Similar bands have been found in the case of CH_3I (cf. notes 4 and 5).

¹¹ Cf. also the infra-red investigations of E. O. Salant and W. West (*Physical Rev.*, **33**, 640, 1929).

¹² Cf. e.g. D. H. Andrews, *Physical Rev.*, **36**, 544, 1930, and R. Mecke, *Z. Physik*, **64**, 173, 1930.

remembers that the potential curves are the narrower the larger the quantum of vibration.

As in O_2 the dissociation¹³ by increasing the vibrational energy in the upper state of the Henri-Schou bands presumably leads to normal O and excited CH_2 or excited $O(^1D)$ and normal CH_2 , the excitation being of the order of a few volts.¹⁴ The total amount of energy for this dissociation from the ground state is found by extrapolation to be $69,000\text{ cm.}^{-1}$ or 195 k.cal./mol. From chemical heats of combustion one gets a value 155 k.cal./mol. for the dissociation into normal O and normal CH_2 , so that the energy of excitation is of the right order corresponding presumably to O^1D .

The beginning of predissociation ($\lambda\ 2750$)¹⁵ corresponds to the overlapping of another electronic level which is continuous in that region (α' of Fig. 4). As pointed out by the author¹⁶ the beginning of predissociation only gives an upper limit to the dissociation energy of the normal molecule. This limit is 105 k.cal./mol. It therefore cannot correspond to the dissociation $CH_2 + O$ but must be $H_2CO \rightarrow H + HCO$,¹⁷ as was shown by Mecke some time ago.^{17a} The photochemical dissociation of H_2CO in the region of pre-dissociation and even near its limit occurs with rather large amounts of kinetic energy, the energy of the same dissociation ($H_2CO \rightarrow H + HCO$) calculated from chemical data being 92 k.cal./mol.

Even at a somewhat high pressure (50 mm.) no absorption was noted in H_2CO between $\lambda\ 2500$ and $\lambda\ 1650$. At $\lambda\ 1650$ a very strong discontinuous absorption begins (at lower pressures at $\lambda\ 1560$). Unfortunately as in C_2H_2 the many line spectrum of hydrogen prevents an accurate measurement of the bands. But three bands are clearly defined, the distance of which is 1180 cm.^{-1} .¹⁸ These bands are the transition of the molecule to a new stable electronic level of high energy. But though it is stable if left by itself, it will not be stable against collisions with other molecules and, therefore, will be active photochemically, the different energies of dissociation of the normal molecule being much smaller than its energy content. The same considerations, of course, apply to the upper state of the B bands of C_2H_2 .

Hitherto no state of O_2 analogous to the above-mentioned state of H_2CO has been found. It should lie still further in the ultra-violet. It might be,

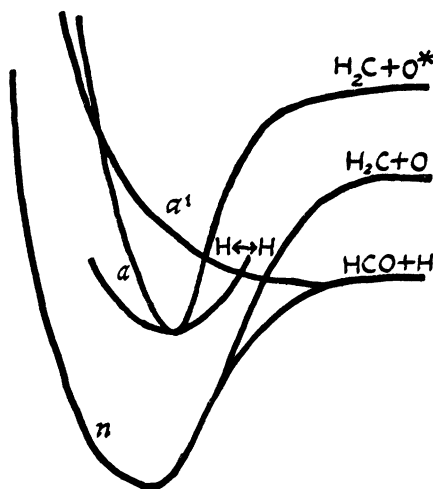


FIG. 4.

¹³ G. Herzberg, *Z. Physik. Chem.*, **B 4**, 223, 1929.

¹⁴ In the case of oxygen the excitation is 1.96 volt , cf. 16.

¹⁵ The limit is not sharp.

¹⁶ G. Herzberg, *Z. Physik. Chem.*, **B 10**, 189, 1930; *Z. Physik*, **61**, 604, 1930.

¹⁷ The reason that no such predissociation can occur in the case of oxygen is obvious.

^{17a} R. Mecke, *Nature*, **125**, 526, 1930.

¹⁸ The structure of these bands also will further be investigated with a Lyman continuous spectrum as background.

however, in this case (and in that of C_2H_2 as well) that the far ultraviolet bands correspond to an electron jump of the C—H bond.

I hope to discuss this matter further and in more detail when the analysis of the bands discussed above has been completed.

Summary.

The ultraviolet absorption spectra of C_2H_2 and H_2CO are investigated with a 2 m. vacuum spectrograph. Both of these molecules show two regions of discontinuous absorption corresponding to two stable excited electronic levels of these molecules. The longer wavelength system of H_2CO has already been discovered by Henry and Schou. Their vibrational analysis is corrected here. The vibrations and photochemical processes in the different states of these molecules are discussed.

The spectrograms underlying the above discussion were taken during my stay at the H. H. Wills Physical Laboratory (Bristol). I wish to express my sincere thanks to Professor A. M. Tyndall for the kindness with which he placed every facility at my disposal and for his constant interest. I am also indebted to the staff of this institute for kind help.

Finally, I desire to thank the Notgemeinschaft der Deutschen Wissenschaft for a Forschungsstipendium given to me whilst I worked out the above results.

*Darmstadt (Germany), Physikalisches Institut der
Technischen Hochschule.*