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The Absorption Spectra of Acetylene, Ethylene and Ethane in the Far Ultraviolet

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An absorption spectrum of acetylene in the region 1520A to 1050A has been found. It appears at very low pressures. The analysis was made by obtaining the spectrum of acetylene made from about 50 percent heavy water. The small isotopic shifts of many bands revealed them to be vibrationless electronic transitions. These are arranged into two Rydberg series going to the same limit which corresponds to an ionization potential of 11.35 volts. The upper levels of the two series are designated as $np\Sigma$ and $np\Pi$ levels. The excitation and ionization are from the CC bond and only vibrations affecting this bond appear. The character of the vibrations present is deduced from the magnitude of the isotopic shifts. Strong predissociation occurs around 1520A. This yields a value of about 187 Cal/mole for the strength of the triple CC bond. A similar set of bands appears in ethylene in the region 1750A to 1200A. The bands are more diffuse than those in acetylene, and only one strong Rydberg series was discovered. The limit of the series corresponds to an ionization potential of 10.41 volts. The vibrational analysis is similar to that in acetylene. The spectrum of ethane is extremely diffuse and no analysis of it could be made. It is concluded that, as in methane, all the upper states are unstable.

A GREAT deal of data has been accumulated on the acetylene molecule in the ground state. It is known that the molecule is linear and symmetrical. The five frequencies in the unexcited state have been identified correctly and the infrared and Raman spectra of this molecule have been thoroughly worked out. Until recently there has been a scarcity of reliable data on the absorption of acetylene in the ultraviolet. Kistiakowsky[1] obtained a set of bands in the region 2400–2000A but was unable to obtain a satisfactory analysis of them. The author working with a vacuum grating spectrograph has obtained an extensive system of bands extending from $\lambda = 1520 - 1050$A. The bands were obtained in absorption, the source being a Lyman continuum. The appearance of the bands is somewhat complex and it was only by taking the absorption of heavy acetylene that sufficient clues were found to enable the analysis to be made. The spectrum yields a spectroscopic value for the ionization potential of acetylene, a plausible value for the energy of the triple CC bond and gives an insight into the absorption spectra in the far ultraviolet of many other polyatomic molecules which have been investigated more recently by the author.

The vacuum spectrograph used in this work was of the grazing incidence type, the angle of incidence being about 78°. The grating was a glass one of about 2 meters radius of curvature and ruled with 30,000 lines to the inch. The dispersion varied from 2.5A/mm at 1700A to 2A/mm at 1000A. The discharge tube used for obtaining the continuum was of the type designed by Collins and Price.[2] It was operated by the discharge of a condenser of about 3μf capacity charged to a potential of 15,000 volts through a capillary of 1 mm bore. The pressure was measured by means of a Pirani hot wire gauge. The advantage of this type of gauge was that it gave a continuous record of the pressure. This is very important in taking absorption photographs since unless the pressure does remain sensibly constant throughout the exposure the absorption bands tend to be blurred. Lines in the spectrum of molecular hydrogen were used as standards.

The method of obtaining the absorption spectrum of acetylene was as follows: Tank acetylene was purified by passing it through five spiral wash bottles containing water, chromic acid, mercuric chloride in HCl, copper nitrate in nitric acid and sodium hydroxide. It was then dried over P_2O_5 and led into the back of the spectrograph through a long fine capillary. The partial pressure of acetylene was never higher than 0.1 mm Hg in the high pressure pictures, and less than 0.001 mm in the low pressure ones, the path length being about 1.5 meters. Hydrogen was used as a conducting gas in the discharge tube.

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[1] Kistiakowsky, Phys. Rev. **37**, 277 (1931).

[2] Collins and Price, Rev. Sci. Inst. **5**, 423 (1934).

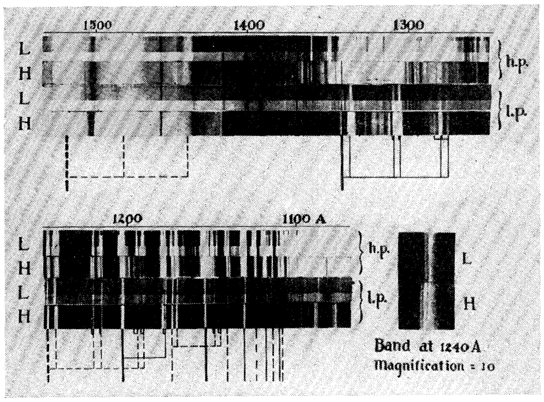

FIG. 1. The absorption spectrum of acetylene in the far ultraviolet.

As is seen from Fig. 1 a very rich absorption spectrum is obtained. It contains both diffuse and sharp bands. The bands obtained by Kistiakowsky round 2300A are sharp. The bands shown here round 1500A are very diffuse. At 1350A they are less diffuse and below this they become sharp again. Towards the shorter wavelengths they become very numerous and overlap, eventually reaching a limit at about 1050A. From this point on a continuous absorption starts. However, it becomes rapidly weaker and at about 800A the substance is again transparent. This transparency below 800A is also found for ethylene even when comparatively high pressures are used. It extends at least as far down as 150A, as observed by emission lines.

The bands can be conveniently divided into two classes.

Class I bands have a single head and are shaded towards the red. At low pressures and with very narrow slit widths (of the order of 0.001 inches) they appear as a single absorption line which is somewhat diffuse on the long wavelength side. They are, therefore, assumed to contain only P and R branches, and are designated as parallel bands.

Class II bands have two fairly sharp heads which are shaded towards the red. At low pressures they appear as a narrow absorption doublet having a separation of about 0.2A. The heads are apparently caused by the R and Q branches of the bands. A measurement of the separation of the heads gives a value for the moment of inertia of the molecule.

Taking the value of the moment of inertia of the molecule in the ground state to be 23.51×10^{-40} g cm^2 we obtain for the band at 1247A, $I = 25.00 \times 10^{-40}$ g cm^2 as compared with the value $I = 25.6 \times 10^{-40}$ g cm^2 obtained by Kistiakowsky for the bands round 2300A. The heads of the bands at shorter wavelengths have all about the same wave-number separation as that at 1247A. It thus appears that I changes considerably with the first electronic jump, the subsequent increases being comparatively small. The bands of class II are termed perpendicular bands. They contain P, Q and R branches.

Acetylene possesses five possible vibrational frequencies in both the upper and lower states. Because of the complexity of the spectrum great difficulty was experienced in trying to find these frequencies and then to assign them to the correct modes of vibration. The whole problem was, however, cleared up by obtaining the absorption of heavy acetylene which was made from a few drops of (60 percent) heavy water kindly supplied by Professor Taylor of Princeton University. A special type of generator was used for this purpose but it is not considered necessary to describe it in detail here.

The photographs for the heavy acetylene which contained about 45 percent C_2DH, 45 percent C_2H_2 and 10 percent C_2D_2 are shown in plate $I(H)$. A large number of the bands are apparently not shifted, but a closer investigation of the low pressure photographs shows that some of them suffer very small shifts. The microphotographs enlarged 20 diameters, show that the doublet at 1247A has now a third component on the short wavelength side, becoming a triplet. The increased relative intensity of the central component indicates that the long λ component of the heavy acetylene doublet overlaps the short λ component of that of light acetylene. The shift is very small, being only $0.30\text{A} \equiv 20$ wave numbers. Consequently these bands must be due to electronic transitions between the fundamental levels of the initial and final states. They suffer only a small isotopic shift due to the change in the difference of zero point energy between these two states.

light $\nu_L'' = \nu_e + \frac{1}{2}\sum\omega_L' - \frac{1}{2}\sum\omega_L''$

heavy $\nu_H'' = \nu_e + \frac{1}{2}\sum\omega_H' - \frac{1}{2}\sum\omega_H''$

$$\nu_H - \nu_L = \tfrac{1}{2}\{\sum(\omega_L'' - \omega_H'') - \sum(\omega_L' - \omega_H')\}.$$[*]

'' indicates the ground state.
' indicates the excited state.

It is assumed here that ν_e does not change appreciably in going over from light to heavy acetylene. Our subsequent analysis will justify this.

As the vibration frequencies in the ground state are greater than those in the upper state, the change $(\omega_L'' - \omega_H'')$ will be greater than the change $(\omega_L' - \omega_H')$ as both depend on approximately the same mass factors. Consequently $\nu_H - \nu_L$ is positive and there will be a shift towards the violet. The magnitude of the shift will be small and it is only on account of the high dispersion of the instrument that it could be detected. Only the fundamental electronic transitions of the bands of class II could be revealed this way. The ν_0's of the parallel bands were found by the apparent absence of shift and the fact that they fitted into a certain Rydberg series. [The head of the band of C_2DH fell in a region where the corresponding band of C_2H_2 was absorbing.]

The vibration bands are shifted by larger amounts and their second members are easily detected by the doubling of their shifts, vibrations of the same type all being shifted proportionally. There are some bands of appreciable intensity to the red side of all the very strong bands. These can be interpreted as transitions from an initial transverse vibrational state. The transverse vibrations in acetylene are of such small frequencies (605 and 730 wave numbers) that they must be present in appreciable quantities at room temperatures.

ANALYSIS OF THE BANDS

When the ν_0's of class I bands were taken it was found that they were represented fairly closely by the following Rydberg series:

$$\nu_0^n = 92{,}076 - R/(n-0.50)^2 \quad n = 3, 4, 5 \qquad \text{(I)}$$

and those of class II by

$$\nu_0^n = 91{,}950 - R/(n-0.95)^2 \quad n = 3, 4, 5. \qquad \text{(II)}$$

An idea of the accuracy with which the bands are represented by these formulas may be obtained by inspection of Table I: (The accuracy of the measurement of the bands varies considerably depending on whether they are sharp or diffuse. If the bands are sharp their heads can be measured to within a tenth of an Angstrom unit (~10 cm^{-1}). The measurements on the diffuse bands have a much greater probable error.)

TABLE I. *Observed and calculated frequencies of class I and class II bands.*

		CLASS I				CLASS II	
n	Int.	Wave	number	n	Int.	Wave	number
		Obs.	Calc.			Obs.	Calc.
3	10 *D*	74516	74518	3	10 *DD*	65790	65838
4	10	83140	83118	4	10	80116	80153
5	10	86665	86657	5	10	85226	85260
6	10	88431	88449	6	10	87636	87647
7	8	89464	89479	7	6	88946	88952
8	obscured			8	4	89743	89742
9	6	90560	90557	9	3	90260	90257
10	4	90860	90860	10	2	90610	90610

Both the series have approximately the same limit which coincides with the region where the continuous absorption starts. As many as ten members of each can be observed and measured. The subsequent members are somewhat obscured by overlapping and accurate measurements cannot be made on them.

The bands round 2300A investigated by Kistiakowsky would fall into this scheme by putting $n = 2$ in I, but as will be shown later this is probably a mere coincidence. The fact that they are observed at extremely high pressures indicates that the transition probability corresponding to them is extremely low whereas in the case of the bands which we have observed it is at least 100,000 times as great. Further Kistiakowsky's bands have *P*, *Q* and *R* branches. If they were fitted into our scheme they would fall into a class which contains only *P* and *R* branches.

A large number of facts, which come out of the vibrational analysis, go to show that one of the valence electrons between the two carbons is excited. Thus the two series may very probably be due to the different coupling of its orbital momentum with the internuclear axis. This leads to the designation of the upper levels of class I

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[*] In this formula the transverse frequencies have to be multiplied by two as they have two degrees of freedom.

bands as $p\Sigma$ levels and those of class II bands as $p\Pi$ levels; which is in agreement with the fact that the bands of class I contain only *P* and *R* branches, while those of class II contain *P*, *Q* and *R* branches. Further, G. H. Dieke[3] has calculated the differences between the energies of the $p\Sigma$ and $p\Pi$ levels for the various electronic states of helium, this being the only other molecule except N_2 for which such a large number of electronic states has been observed. As shown in Table II, there is a striking numerical agreement between the actual magnitude of these energy differences and those of helium.

TABLE II. *Comparison of energy differences of the $p\Sigma$ and $p\Pi$ levels in C_2H_2 and in He_2.*

$p\Sigma-p\Pi$	
C_2H_2	He^2
−8726	−8890
−3024	−2970
−1437	−1400
− 795	− 998 ?
− 518	?

The differences in the case of acetylene have not been corrected for zero point energy but it will be shown later that this does not alter the agreement appreciably. The differences are for the $p^3\Pi$ levels of helium.

From the limits of the Rydberg series the ionization potential of acetylene is calculated to be 11.35 electron volts probably correct to one-hundredth of an electron volt. The best and most recent determination by the methods of electron impact is due to Tate and Smith.[4] The value they give is 11.6±0.1 volts, which is in good agreement with the one given here. This is only one example of the possibility of obtaining accurate values of the I.P.'s of various molecules from their absorption spectra in the far ultraviolet. Other substances for which the author has been able to do the same thing are C_2H_4, CH_3OH, H_2CO, CH_3HCO, $(CH_3)_2CO$, O_2, CS_2, H_2S, SO_2, the methyl and ethyl halides and many others. The work on these substances is now in the process of publication.

ROTATIONAL STRUCTURE

The dispersion of the instrument is of course not high enough to resolve the rotational structure of the bands. One important thing however could be noticed in the case of class II bands.

A close inspection of one of the vibration bands accompanying the second member of this class reveals that its *R* branch is very slightly wider than that of the corresponding band for C_2DH. This is in agreement with the corresponding increase in moment of inertia of the C_2DH molecule and our assignment of *P*, *Q* and *R* branches to these bands. (The isotopic shifts were measured between the heads of the *Q* branches when this was possible.)

THE ANALYSIS OF THE VIBRATIONAL STRUCTURE

In the bands having low values of *n* a great deal of vibrational structure can be observed. As many as ten vibrational transitions accompany some of the fundamental electronic transitions. For bands having higher electronic quantum numbers, however, the vibrational structure is obscured by the overlapping of the subsequent electronic transitions. The vibrational analysis is greatly simplified by the magnitudes of the isotopic shifts. The shift of the ν_0 band due to the change in zero point vibrational energy is very small (20 cm^{-1}). In the particular case of acetylene the vibrational analysis could probably be made purely from the knowledge of the actual magnitude of this shift.

Fig. 2 shows the various vibrations possible in acetylene; the values of their frequencies in the ground state are those given by Sutherland.[5]

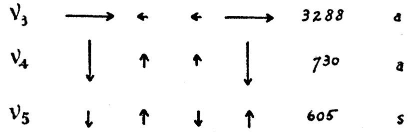

FIG. 2. Vibrations in acetylene.

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[3] G. H. Dieke, Zeits. f. Physik **57**, 71 (1929).

[4] J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932)

[5] Sutherland, Phys. Rev. **43**, 173 (1933).

The lengths of the arrows indicate qualitatively the relative displacements of the various atoms. (This can be derived from a purely mechanical treatment of a model.) It is seen that to a rough approximation: ν_2, ν_3 and ν_4 depend mainly on the CH linking and a rough calculation shows that they are approximately diminished by 11 percent in going from C_2H_2 to C_2DH. On the other hand, ν_1 and ν_5 depend mainly on the CC linking and are diminished by only about 5 percent by this substitution. Now it is very probable if the excited electron comes from the C≡C bond, that the CH bonds and therefore the frequencies ν_2, ν_3 and ν_4 will not be appreciably affected by the excitation. However, if it comes from the CH bond these frequencies will certainly be changed considerably. The latter possibility cannot occur as even small changes in the frequencies ν_2 and ν_3 would require a much larger shift in zero point energy than the 20 wave numbers observed; e.g., a 10 percent change would give rise to a shift in zero point energy of about 80 wave numbers.

In order to find the selection rules determining which vibrational transitions should occur, we must consider the influence of two factors: In the first place the symmetry of the molecule determines a selection rule. If the symmetry of the electronic eigenfunctions of the excited state is the same as that of the normal state, the selection rules are the same as those for the infrared bands. If the symmetry is different then different selection rules of the same character apply. It is not necessary to go into this here as only the symmetrical vibrations appear and for these there is no specific selection rule in either case.

Secondly, bands which might be allowed by the symmetry considerations may be nevertheless excluded for reasons which are analogous to those leading to the Franck-Condon principle for diatomic molecules. This means that if the CH distance is not affected by the electronic transition no transitions should occur which involve vibrations in the CH bond.

An inspection of the vibration diagram indicates that if an electronic jump occurs in the C≡C bond only the symmetrical vibrations ν_1 and ν_5 can be excited, and it will be shown that this is what happens in our case. It is supported by the fact that all the bands belonging to one particular electronic transition are of the same type, i.e., they are either all parallel or all perpendicular bands. This could only happen if both vibrations are symmetrical.

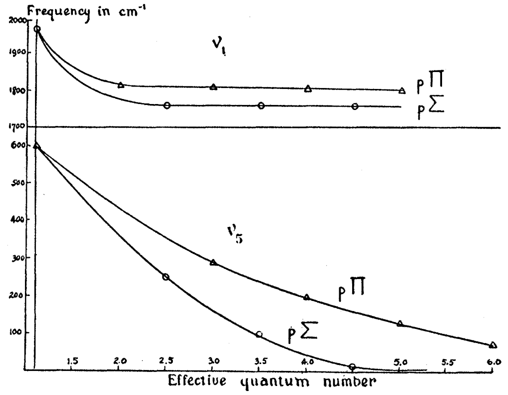

FIG. 3. Frequencies plotted against effective quantum number.

The observational facts are as follows: All the bands of class I and class II are accompanied by equally strong bands, a little to the short wavelength side of them. The separation of these accompanying bands from the ν_0 band decreases rapidly in the case of class I bands to almost zero with increase in electronic quantum number. In the case of class II bands, the diminution of the frequency difference is much slower. In both cases these bands must represent vibrations of the type ν_5 superimposed on the electronic transition. They could not represent a superposition of the vibration ν_4 as the change of ν_4 from 730 cm^{-1} in the ground state to the values of the differences observed would give rise to a much greater isotopic shift in the $\nu_0{}^n$ than that actually found. The frequency differences are plotted against the effective quantum number of the electronic state in Fig. 3. It is seen that smooth curves are obtained which can be extrapolated to 600 cm^{-1}, which is the value of ν_5 in the ground state.

THE ν_1 VIBRATION

Class I bands are accompanied also by bands lying about 1760 wave numbers to the short wavelength side. They have an observed isotopic shift of about 90 cm^{-1}. When the shift in ν_0 is taken into account the diminution in frequency difference is 110 cm^{-1}. The bands of class II are also accompanied by a similar set of bands lying about 1810 wave numbers to the short wavelength side of each number. The total diminution of the frequency difference is 90 cm^{-1} in this case. The magnitude of the shift which corresponds to a diminution of the wave-number separation by about 5 percent makes it certain that a vibration of the type ν_1 is involved. The values of the frequency are plotted against effective quantum number in Fig. 3. It is seen that, after the first electronic jump, the value of ν_1 remains appreciably constant in both $p\Sigma$ and $p\Pi$ states; this also occurs in the corresponding bands in helium. The differences in the absolute magnitude of ν_1 in the two states can be ascribed to the difference in the relative values of the force constants. This holds also for ν_5.

In both $p\Sigma$ and $p\Pi$ states, the frequency ν_1 appears equally intense in combination with the strong ν_5 transverse vibration. The frequencies $2\nu_1$ and $2\nu_1+\nu_5$ also appear quite strongly in some of the lower band systems. They are easily identified by the doubling of the isotopic shift.

This accounts for all the strong bands. There are, however, a number of bands lying to the red side of some of the strong bands, in particular the bands at 1340A and 1247A. They can be ascribed to transitions from the vibrational levels of the ground state. The difference 605 cm^{-1}, corresponding to a vibration of the type ν_5 in the ground state, is found fairly strongly and the values $\nu_4=730$ and $2\nu_5=1210$ are found somewhat more weakly. Most of the extremely strong bands have these weaker vibrations accompanying them and this seems the most plausible explanation for such bands.

THE PREDISSOCIATION OF THE λ1500 BAND

The bands observed by Kistiakowsky at about 2300A are sharp. They have been investigated still further in this laboratory by Professor G. H. Dieke, who has shown that even round 1900A they exhibit no signs of predissociation. Thus the continuous absorption reported by Kistiakowsky at about 2200 is due to impurities. The bands we have obtained are very diffuse round 1500A and even round 1300A are still slightly diffuse. Below this they are sharp.

If it is assumed that this diffuseness is caused by predissociation and further that this predissociation might be due to interaction with the normal state, then we find that the heat of dissociation of C_2H_2 into CH+CH must be slightly less than 8.1 electron volts or the energy of the triple bond is slightly less than 187 Cal./mole. This is in good agreement with the best chemical data. The value given by F. O. Rice[6] is about 200 Cal./mole, that given by R. G. W. Norrish[7] is 220 Cal./mole. However, it is generally accepted that these values are too high, and further the experiments from which they are obtained are not capable of great accuracy. In the above it is assumed that the molecule dissociates into normal CH radicals. An investigation of the energy values of excited CH shows that this must be so.

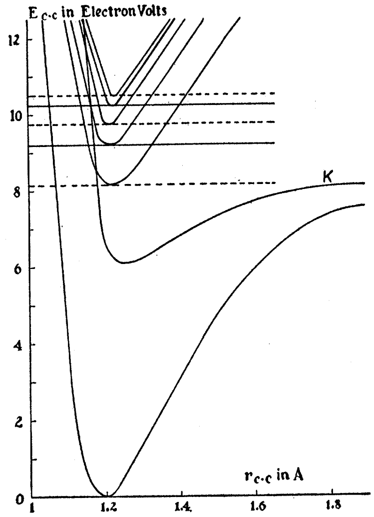

FIG. 4. Potential energy curves for the CC bond in C_2H_2

The assumptions mentioned at the beginning of the last paragraph are only justified by the resulting agreement obtained for the energy of the C≡C linking. In fact, the assumption that the excited state interacts with the normal state must be somewhat modified. This is seen from an inspection of the potential energy curves between the two carbon atoms, Fig. 4.

Approximate Morse[8] curves can be obtained for this potential in the following way. The various constants of the acetylene molecule are

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[6] F. O. Rice and W. R. Johnston, J. Am. Chem. Soc. **56**, 214 (1934).

[7] R. G. W. Norrish, Trans. Faraday Soc. No. 152, 106, January, 1934.

[8] P. M. Morse, Phys. Rev. **34**, 57 (1929).

TABLE III. *Frequencies of the observed bands in C_2H_2 and their assignments.*

TYPE	INTENSITY		FREQUENCY	ASSIGNMENT				
	h.p.	l.p.		n	v_1	v_5	$(v_4)_0$	$(v_5)_0$
L	100 *DD*	50 *DD*	65790	$3p\Pi$	0	—	0	0
“	100 *DD*	50 *DD*	67610	“	1	—	0	0
“	100 *DD*	30 *DD*	69430	“	2	—	0	0
H p	2	0	72335	$3p\Sigma$	0	0	−?	
L “	4	0	73148	“	0	0	−1	−1
H “	5	1	305	“	0	0	−?	
L “	10	1	408	“	0	1	−1	−1
H “	10	1	781	“	0		−?	
L “	10	2	74020	“	0	1	−1	0
L “	10	4	510	“	0	0	0	0
“ “	100	10	750	“	0	1	0	0
“ “	10 *D*	1 *D*	990	“	0	2	0	0
“ “	10 *D*	4 *D*	75235	“	0	3	0	0
H “	10	1	550	“	1	0	0	−1
L “	10	1	640	“	1	0	0	−1
H “	10	1	800	“	1	1	0	−1
L “	10	1	872	“	1	1	0	−1
H “	obsc.	10	76170	“	1	0	0	0
L “	10	8	266	“	1	0	0	0
H “	obsc.	10	400	“	1	1	0	0
L “	20	10	497	“	1	1	0	0
L “	5	1	77427	“	2	0	0	−1
“ “	5	2	667	“	2	1	0	−1
H “	10	3	800	“	2	0	0	0
L “	10	5	008	“	2	0	0	0
H “	10	1	040	“	2	1	0	0
L “	10	1	256	“	2	1	0	0
	2	0	78790	$4p\Pi$	0	0	−1	−1
	3	0	79076	“	0	1	−1	−1
	3	0	400	“	0	0	−1	0
	3	0	510	“	0	0	0	−1
	3	0	662	“	0	1	−1	0
L s	50	10	80110	“	0	0	0	0
H s	50	10	130	“	0	0	0	0
H & *L s*	100	10	400	“	0	1	0	0
L “	2 *D*	0	81200	“				
L “	2 *D*	0	390	“				
L “	4	0	700	“				
*H** “	3	0	770	“	1	0	0	0
H “	10	5	830	“	1	0	0	0
L “	10	10	925	“	1	0	0	0
*H** “	3	0	82050	“	1	1	0	0
H “	5	2	110	“	1	1	0	0
L “	10	4	210	“	1	1	0	0
H “	8	2	83630	“	2	0	0	0
L “	8	2	730	“	2	0	0	0
H “	8	2	860	“	2	1	0	0
L “	8	2	84020	“	2	1	0	0
H & *L p*	50	10	83120	$4p\Sigma$	0	0	0	0
p	50	10	190	“	0	1	0	0
H “	30	10	760	“	1	0	0	0
*H** “			“	“	1	1	0	0
L “	8	2	880	“	1	0	0	0
H “			“	“	1	1	0	0
L “	10	7	952	“	1	1	0	0
L “	obsc.		85630	“	2	0	0	0
L s	20	10	85230	$5p\Pi$	0	0	0	0
H “	20	10	250	“	0	0	0	0
H & *L s*	30	10	430	“	0	1	0	0
H “	10	8	86950	“	1	0	0	0
L “	10	8	87046	“	1	0	0	0
L “	6	3	242	“	1	1	0	0
L p	50	10	86665	$5p\Sigma$	0	0	0	0
L “	10	5	88431	“	1	0	0	0
L “	obsc.		90205	“	2	0	0	0
L s	30	10	87635	$6p\Pi$	0	0	0	0
L “	2		776	“	0	1	0	0
L “	2		89447	“	1	0	0	0
L p	30	10	88430	$6p\Sigma$	0	0	0	0
	obsc.		90200	“	1	0	0	0
	20	8	88946	$7p\Pi$	0	0	0	0
	6	0	89020	“	0	1	0	0
	4	0	90760	“	1	0	0	0
	10		89464	$7p\Sigma$	0	0	0	0
	10	4	89743	$8p\Pi$	0	0	0	0
			91560	“	1	0	0	0
	10	5	90100	$8p\Sigma$	0	0	0	0
	8	3	90260	$9p\Pi$	0	0	0	0
	5	1	92085	“	1	0	0	0
	8	2	90560	$9p\Sigma$	0	0	0	0

defined below. The values given are those obtained by Mecke[9] for the ground state.

$$\underset{}{\mathrm{H}}\overset{k_1}{\underset{r_{\mathrm{CH}}}{\text{——}}}\mathrm{C}\overset{k_2}{\underset{r_{\mathrm{CC}}}{\text{——}}}\mathrm{C}\overset{k_1}{\underset{r_{\mathrm{CH}}}{\text{——}}}\mathrm{H}$$

k_1 = force constant between H and C = 20 volts,

k_2 = force constant between C and C = 69 volts.

$\nu_{\mathrm{CH}} = k_1(1/\mathrm{C}+1/\mathrm{H}) = 3200\ \mathrm{cm}^{-1}$,

$\nu_{\mathrm{CC}} = 2k_2/\mathrm{C} = 2100\ \mathrm{cm}^{-1}$,

$r_{\mathrm{CH}} = 1.08\ \mathrm{A} \qquad r_{\mathrm{CC}} = 1.19\mathrm{A}$.

We can calculate the values of r_{CC} in the upper states from the corresponding moments of inertia which are obtained from the separation of the band heads. This can be done on the assumption that r_{CH} does not vary. It can only be done for the bands of class II. In these we find an increase in r_{CC} over the value in the normal state of about 0.03A, the value 1.24A remaining fairly constant for all the members of the class. This small difference in r_{CC} in the upper and lower states is in agreement with the fact that long vibrational progressions are not obtained. The bands observed by Kistiakowsky round 2300A have a somewhat larger value for r_{CC} (1.26A).

The value of ν_{CC} in the ground state is practically equal to ν_1 and for the upper state it can also be taken to be equal to the value of ν_1 found in these cases. The heats of dissociation in the upper states are unknown, but for the purpose of calculating the potential curves they can be taken to be about 7 electron volts or 160 Cal./mole (i.e., = the strength of the double CC bond). That in the lower state must be equal to the strength of the triple CC bond, and is approximately equal to 8.2 electron volts or 200 Cal./mole. It is to be stressed that these values are only taken so that rough ideas of the shape and position of the potential curves can be obtained.

The potential curves obtained in this way are shown in Fig. 4. It is seen that there is no possibility of the intersection of the potential curves of the upper and lower states and to

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[9] Mecke, Zeits. f. physik. Chemie **B17**, 1 (1930).

explain the predissociation of the band at 8.1 electron volts into normal CH radicals we have to postulate the curve K. This curve must go to the heat of dissociation of the normal state. It may extend down as far as 6.1 electron volts and may possibly represent the upper state of the bands observed by Kistiakowsky round 2300A. Certainly the extremely low transition probability of these bands seem to make this a likely explanation. The possibility that the predissociation does correspond to a dissociation of the type described above must be admitted from the close agreement of the bond strength predicted this way and that obtained from chemical data. Further in the case of polyatomic molecules there are a large number of instances of photodissociation into normal radicals by means of predissociation due to interaction with the initial state, e.g., formaldehyde shows one region of predissociation around 2750A corresponding to about 105 Cal./mole which is the heat of dissociation of the CH bond; also another around 1745A or about 164 Cal./mole corresponding to the breaking of the CO bond. Similar cases occur in all ketones. In the case of a polyatomic molecule predissociation may occur over a far wider range than is found for diatomic molecules. This is due to the fact that the resulting radicals may have various amounts of vibrational and rotational energy as well as electronic energy which is the only kind present in the predissociation of a diatomic molecule. This kind of explanation accounts for the partial predissociation of the λ1350 band which is considerably removed from the main region of predissociation.

Table III giving the frequencies of the bands observed in C_2H_2 along with their assignments is appended. When the bands are clearly (a) single headed they are marked p; (b) double headed they are marked s. The v's refer to the number of quanta of the respective vibrations present $L \equiv C_2H_2$, $H \equiv C_2DH$, $H^* \equiv C_2D_2$.

THE ABSORPTION SPECTRUM OF ETHYLENE

The analysis given here for acetylene has also thrown considerable light on the ultraviolet absorption spectrum of ethylene. This spectrum which starts at about 1744A was obtained in the same way as that of acetylene and at about the same pressures. In this case only one strong series was observed which may be related to the fact that the molecule is no longer linear and the orbital momentum of the excited electron cannot be resolved along the internuclear axis any more.

The ν_0^n's of the higher members of the series fit fairly well into the Rydberg series

$$\nu_0^n = 84{,}400 - R/(n+0.0)^2. \quad n = 2, 3, 4, \text{etc.}$$

The degree of accuracy with which this formula represents the bands is given in Table IV. The limit corresponds to an ionization potential of 10.41 volts which agrees fairly well with the value 10.0±? given by Kallman and Dorsch[10] as determined by the methods of electron impact.

TABLE IV. *Comparison between calculated and observed values for the separation between successive members of the absorption spectrum of ethylene.*

n	Int.	Wave number	Separation between successive members (cm^{-1})	
			Obs.	Calc.
2	10 *D*	57360	14810	15241
3	10 *DD*	72170	5410	5334
4	8	77580	2480	2469
5	7	80060	1320	1341
6	5	81380	800	808
7	3	82180		

The vibration pattern of the first electronic band is similar to that in acetylene and it is therefore assumed that the same types of vibration ν_1 and ν_5 are excited.

The frequencies and assignments of the strong bands are given in Table V. The value of ν_5 decreases to practically zero in the first few electronic states while the value of ν_1 also decreases

TABLE V. *Frequencies and assignments of the strong absorption bands in ethylene.*

I	ν cm^{-1}	n	v_1	v_5	I	ν cm^{-1}	n	v_1	v_5
10 *D*	57360	2	0	0	8	77580	4	0	—
10 *D*	57840	2	0	1	8	77880	4	1	—
10 *D*	58700	2	1	0	5	78170	4	2	—
10 *D*	59170	2	1	1					
8 *D*	60030	2	2	0	7	80060	5	0	—
8 *D*	60500	2	2	1	7	80290	5	1	—
6 *DD*	61370	2	3	0	obscured		5	2	—
6 *DD*	61830	2	3	1					
10 *DD* double	72170	3	0	—	5	81380	6	0	—
“ “ “	72980	3	1	—	5	81600	6	1	—
8 “ “	76370	3	2	—	4	81800	6	2	—
					3	82180	7	0	—

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[10] Kallman and Dorsch, *Abhandlung für Kaiser Wilhelm Institut*, Vol. 12 (1929).

to a very small value as n becomes large. Table VI shows the values of these frequencies in the different electronic states. The values of ν_1 and ν_5 in the ground state are assumed to be 1623 cm^{-1} and 1342 cm^{-1}.[11]

TABLE VI. *Values of ν_1 and ν_5 frequencies.*

n	2	3	4	5	6
ν_1	1340	800	300	230	200
ν_5	480	150	—	—	—

A large number of weak diffuse bands were obtained which have not been classified. Some of them undoubtedly correspond to other electronic series.

THE ABSORPTION OF ETHANE

At very low pressures (0.01 mm) the absorption of ethane consists of extremely diffuse bands starting at 1350A and going down below 1000A. The bands are far too diffuse for any analysis to be attempted. In this respect they resemble methane.[12] The low pressure bands in methane start at 1300A; at somewhat higher pressures they extend up to 1450A. Those of ethane behave in the same way and move to a limiting value of around 1500A with increase in pressure. On account of the extreme diffuseness of the bands in ethane it is assumed that as in methane all the upper electronic states are unstable.

In conclusion the author wishes to express his gratitude to Dr. G. H. Dieke for his generous help and numerous suggestions in connection with both the experimental and theoretical aspects of this work.

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[11] Mecke, Zeits. f. physik. Chemie **B17**, 16A (1932).

[12] A. B. F. Duncan, J. Chem. Phys. **2**, 851 (1934).

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Artificial Radioactivity Produced by the Deuteron Bombardment of Nitrogen[1]

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This paper describes the work leading to the discovery and investigation of radio-oxygen, and also includes some incidental results on other nuclear disintegrations. It is shown that nitrogen bombarded with deuterons gives rise to a radioactive substance which emits positive electrons of maximum energy 1.2 mv, has a half-life of 126±5 sec., and is found by chemical analysis to be an isotope of oxygen. The nuclear cross section for the activation of nitrogen at 2 mv deuteron energy is 6×10^{-27} cm^2; that for the activation of carbon is three times as great. The neutrons expected to accompany the formation of radio-oxygen were found to be present. These results were obtained using gaseous nitrogen as a target; in some of the experiments use was made of the fact that the active product can be deposited on a metal surface by recoil.

EXPERIMENTAL ARRANGEMENT

DEUTERONS were accelerated to a kinetic energy of about 2 mv in an apparatus described elsewhere.[2] A brass tube was set into the side of this apparatus in such a position as to intercept the deuteron beam, which passed into the atmosphere through a vacuum-tight window[3] as shown in Fig. 1. The target to be

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* Now at Cornell University.

[1] A preliminary report of this work was given by M. S. Livingston and E. McMillan, Phys. Rev. **46**, 437 (1934).

[2] E. O. Lawrence and M. S. Livingston, Phys. Rev. **45**, 608 (1934).

[3] The window used for admitting the deuteron beam was so satisfactory that it seems worth while to describe it in some detail. It consisted of a sheet of 0.0001″ thick aluminum foil (procured from the American Platinum Works) mounted with wax on a brass plate, covered as closely as possible with one mm holes over an area of 1×1.5 cm. A wax to be used for this purpose must have a high melting point (the window becomes quite warm under the deuteron bombardment), it must flow freely when melted, and it must stick firmly to a clean metal surface when cold. These requirements are satisfied by rosin, with just enough Venice turpentine added to make it sticky, as determined by trial. The window was mounted by heating the supporting grid to a temperature above the melting point of the wax, covering it with a thin coat of wax and blowing off the excess, and then putting on the foil, touching it at one edge first and

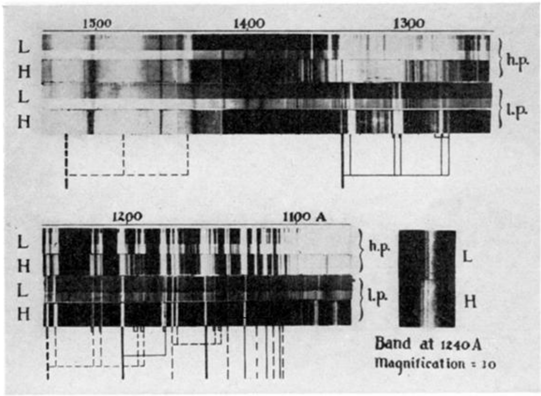

FIG. 1. The absorption spectrum of acetylene in the far ultraviolet.