347. *Magnetic Perturbation of Singlet–Triplet Transitions. Part IV.* Unsaturated Compounds.*

By D. F. Evans.

Singlet–triplet absorption bands induced by oxygen at high pressure have been observed with ethylene and deuteroethylenes, butadiene, hexatriene, and a number of other conjugated olefins, and also diacetylene and a variety of substituted diacetylenes. The ethylene bands are the same as those obtained by Reid [1] for long path lengths of liquid ethylene. With butadiene and hexatriene, transitions to a second excited triplet level are also observed. Ethylene and acetylene (but not ethane) considerably perturb the Herzberg ($^3\Sigma_u^+$–$^3\Sigma_g^-$) bands of oxygen, and apparently increase their intensity.

In the present work the singlet–triplet absorption spectra of a variety of olefinic and acetylenic compounds have been studied, by using the perturbing effect of oxygen under pressure.[2] The results for olefins illustrate the versatility of the oxygen perturbation technique, since no unambiguous data on the triplet levels of simple olefinic substances have previously been obtained. Lewis and Kasha [3] reported phosphorescence emission near 4000 Å for halogenated ethylenes, but according to Kasha and McGlynn [4] these results are not authentic. Extremely weak absorption bands in the region 2600—3400 Å were observed by Reid [1] for long path lengths of liquid ethylene. These were tentatively assigned as singlet–triplet bands, but the possibility that they were due to an extension of the *N*–*V* bands at shorter wavelengths, or to impurities,[5] was not excluded. In their later review, Kasha and McGlynn [4] claimed that an assignment by Snow and Allsopp [6] of a weak absorption band near 2100 Å in gaseous ethylene was the first authenticated singlet–triplet absorption in complex molecules. Snow and Allsopp did not, however, in fact, claim to have observed singlet–triplet absorption in ethylene itself, but only in cyclohexene and trimethylethylene. Potts[7] observed weak bands in the region 2500—2100 Å for alkylethylenes in rigid glasses at low temperatures and, following Snow and Allsopp, tentatively assigned these as singlet–triplet bands. And finally, Lewis and Kasha [3] reported on the lowest triplet level of lycopene on the basis of the phosphorescence emission of all-*trans*-lycopene which had been converted into *cis*-isomers by heating it with iodine.

From the present results only the assignment due to Reid seems to be correct.

The phosphorescence emissions of a number of polyacetylenes have been observed by Beer.[8] No phosphorescence was obtained with hexa-2,4-diyne (dimethyldiacetylene), and accordingly the singlet–triplet absorption spectra of tetra-1,3-diyne (diacetylene) and a number of its derivatives have been studied.

Experimental

Apparatus and Techniques.—Measurements were made on a recording spectrophotometer (Perkin–Elmer Spectracord 4000), with the high-pressure cell and techniques previously described.[1] In the measurements on acetylene, ethylene, and the deuterated ethylenes at high pressures, a known volume of the purified gas was condensed in a metal tube (fitted with a diaphragm valve) which was attached to the high-pressure cell. The diaphragm valve was closed, and after the gas had vaporized the needle valve of the high-pressure cell was also closed. The cell, now containing a known pressure of the gas, was disconnected and the

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* Part III, *J.*, 1959, 2753.

[1] Reid, *J. Chem. Phys.*, 1950, **18**, 1299.

[2] Evans, *J.*, 1957, 1351.

[3] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100.

[4] Kasha and McGlynn, *Ann. Rev. Phys. Chem.*, 1956, **7**, 403.

[5] Wilkinson and Mulliken, *J. Chem. Phys.*, 1955, **23**, 1895.

[6] Snow and Allsopp, *Trans. Faraday Soc.*, 1934, **30**, 93.

[7] Potts, *J. Chem. Phys.*, 1955, **23**, 65.

[8] Beer, *J. Chem. Phys.*, 1956, **25**, 745.

spectrum recorded. The cell was then attached to an oxygen cylinder containing oxygen at a higher known pressure. The needle valve was opened for a few seconds and quickly closed to avoid appreciable diffusion of the gas out of the cell, and the spectrum again recorded. Diacetylene was measured at atmospheric pressure, and also at a higher pressure (~4 atm.) which was obtained by condensing some liquid diacetylene in the cooled cell. Complete vaporization occurred when the cell was filled with oxygen under pressure and subsequently allowed to warm to room temperature. (The vapour pressure of diacetylene at 20° c in the absence of oxygen under pressure is ~1·5 atm.[9])

Since many of the compounds studied react slowly with oxygen, the possibility that some of the observed spectra were due to reaction products was carefully considered. The criteria used to eliminate this possibility were that the intensity of the new absorption bands observed should not vary with time and, for the solution measurements, that these bands should disappear when the oxygen was removed. For many compounds, additional measurements were made after the original sample had been repurified. Appreciable irreversible absorption was observed only with diacetylene which, even in the absence of oxygen, rapidly polymerises in solution (but only very slowly in the gas phase). This irreversible absorption showed no structure in the wavelength region studied.

Only one measurement was made on an acetylene–oxygen mixture at high pressures (acetylene ~20 atm., oxygen 100 atm.). When the needle valve was opened to release the pressure, a violent explosion occurred which reduced the quartz windows of the cell to fine dust and blew off the stainless steel end-plates at high velocity. Subsequent measurements on acetylene–oxygen mixtures were therefore made photographically at lower pressure (~4 atm.) with a cell with a long path length. This cell consisted of a 6·4 m. long iron pipe (2 cm. int. diameter) to which quartz windows were cemented with Araldite. The spectra were taken on a Hilger small quartz spectrograph, with a hydrogen discharge lamp and Ilford Q_1 and process plates.

Materials.—Ethylene, butadiene, and acetylene (from cylinders) and diacetylene (from aqueous sodium hydroxide and 1,4-dichlorobut-2-yne [10]) were purified by repeated bulb-to-bulb distillation in a vacuum. *trans*-Dideuteroethylene was prepared by the reduction of dideuteroacetylene (from deuterium oxide and baked-out calcium carbide) with chromous chloride solution.[11] The crude gas was passed successively through ammoniacal silver nitrate solution, dilute acid, and a trap at −78°, and was finally purified by bulb-to-bulb distillation in a vacuum. The infrared spectrum was in good agreement with that given by Crawford, Lancaster, and Inskeep,[12] and, in particular, bands due to ethylene or other deuteroethylenes could not be detected. Tetradeuteroethylene was obtained by treatment of tetradeuteroethylene dibromide (Merck's, isotopic purity >99%) with zinc dust in moist dioxan,[13] and was purified by passage through a trap at −78°, and by distillation in a vacuum. The only impurity that could be detected from the infrared spectrum was ~3% of C_2HD_3. Hexa-1,3,5-triene was prepared as directed by Woods, Bogliano, and Duggan,[14] and purified by fractional distillation and fractional freezing. The product so obtained has the *trans*-configuration.[15] The remaining compounds were prepared and purified by standard procedures.

RESULTS AND DISCUSSION

The spectra obtained for mixtures of oxygen with ethylene, *trans*-dideuteroethylene, and tetradeuteroethylene are shown in Fig. 1. The main features are the same in all three cases. A regular series of rather broad bands on a continuous background is observed in the region 3500—2800 Å. The average separation between the bands is ~1000 cm.$^{-1}$, and the absorption seems to be tending towards a maximum at about 2700 Å. Below about 2800 Å an additional absorption, associated with rather sharper bands, is apparently superimposed. The latter absorption, which rapidly increases in intensity towards shorter wavelengths, occurs in a region where pure oxygen itself absorbs, and is discussed later.

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[9] Tanneberger, *Ber.*, 1933, **66**, 486.
[10] Armitage, Jones, and Whiting, *J.*, 1951, 44.
[11] Patterson and du Vigneaud, *J. Biol. Chem.*, 1938, **123**, 331.
[12] Crawford, Lancaster, and Inskeep, *J. Chem. Phys.*, 1953, **21**, 678.
[13] Wilson and Wylie, *J.*, 1941, 601.
[14] Woods, Bolgiano, and Duggan, *J. Amer. Chem. Soc.*, 1955, **77**, 1800.
[15] Lippincott, White, and Sibilia, *J. Amer. Chem. Soc.*, 1958, **80**, 2926.

The frequencies of the observed bands in the region 3500—2800 Å are given in Table 1, together with those obtained by Reid [1] for long path lengths (1·25—2·5 m.) of liquid ethylene. The close agreement between the present results for ethylene, and those of Reid, shows that the same transition is certainly involved. (The longest wavelength band at 3484 Å was not observed by Reid, probably because of its low intensity.) The ethylene spectrum closely resembles the well known *V–N* absorption of ethylene at shorter wavelengths which has been discussed in detail by Wilkinson and Mulliken,[5] who give references to previous work. This absorption consists of a series of broad bands from 2069 (extremely weak) to 1752 Å, superimposed on an apparent continuum with a maximum at 1620 Å. The bands and continuum together have been assigned to an allowed $^1B_{1u}$–A$_{1g}$ transition There is little doubt that the bands given in Table 1 are due to the corresponding singlet–triplet transition *T–N* ($^3B_{1u}$–$^1A_{1g}$). Both transitions involve the excitation of an electron from the π-bonding orbital of the $>$C=C$<$ bond into the corresponding π-antibonding orbital. Presumably the bands observed by Reid for liquid ethylene represent the unperturbed singlet–triplet absorption although it is possible that traces of dissolved oxygen present as an impurity may have been responsible for their appearance.

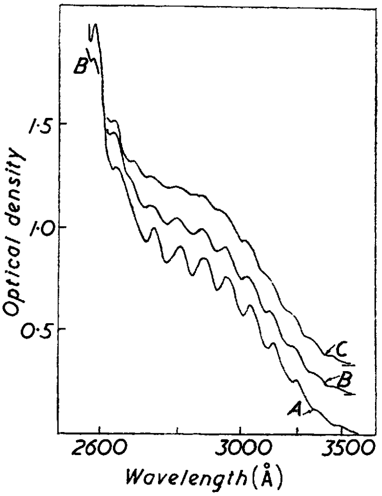

FIG. 1. *Light absorption of oxygen–ethylene (or deuteroethylene) mixtures* (5·2 *cm. cell*).

A, 50 *atm. ethylene, ca.* 25 *atm. oxygen. B, ca.* 50 *atm.* trans-*dideuteroethylene, ca.* 25 *atm. oxygen. C, ca.* 45 *atm. tetradeutero-ethylene, ca.* 30 *atm. oxygen. Optical density scale is shifted for B and C.*

TABLE 1. *Singlet–triplet absorption bands of ethylene,* trans-*dideuteroethylene and tetradeuteroethylene.*

C_2H_4				
O_2, high pressure	O_2, low pressure photographic	Reid [1] liquid ethylene	*trans*-$C_2H_2D_2$ O_2, high pressure	C_2D_4 O_2, high pressure
28,700			28,800	28,940
29,720		29,802	29,820	29,950
30,760	30,770	30,758	30,860	30,880
31,800	31,810	31,729	31,930	31,910
32,860	32,800	32,710	32,940	33,050
33,840	33,780	33,698	33,840	33,800
34,700	34,750	34,686	34,770	34,720
35,640	35,660	35,610	35,670	35,590
36,600	36,600	36,583	36,600	36,500
		37,540		
		38,476		

According to theory,[16] the triplet state *T* of ethylene, like the *V* state, will have minimum energy for a perpendicular configuration, in which the planes of the two CH_2 groups

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[16] Mulliken and Roothaan, *Chem. Rev.*, 1947, **41**, 219.

are at right angles to each other. Also, the equilibrium carbon–carbon distance will almost certainly be considerably greater than that in the ground state *N*. Both the C=C twisting vibration ν_4 and the C=C stretching vibration ν_2 of the triplet state should therefore be involved in the singlet–triplet transition. Reid[1] interpreted the ethylene triplet bands as due to transitions from a non-planar ground state with an angle of twist of about 20—30° to an upper state progression of the C=C twisting frequency. However, the close similarity between both the intensities and the positions of the singlet–triplet absorption bands of ethylene and the deuteroethylenes (Fig. 1 and Table 1) indicates that this assignment is not correct, and that the observed bands correspond to transitions from a planar or almost planar ground state to an upper state progression of the C=C stretching frequency. If anharmonicity is neglected, the calculated ratio $\nu_{C_2H_4}/\nu_{C_2D_4}$ is 1·069 for the stretching vibration, and 1·414 for the twisting vibration. The average value found experimentally is $\sim 1{\cdot}04_5$. (In the ground states of ethylene and tetradeuteroethylene, the frequencies[12] of the stretching vibration ν_2 are 1623 and 1515 cm.$^{-1}$ respectively, and those of the twisting vibration ν_4 are 1027 and 727 cm.$^{-1}$.) It is likely, nevertheless, that twisting vibrations of the triplet state will also occur during the electronic transition. The individual bands are not resolved, but are probably largely responsible for the diffuse nature of the absorption. Transitions involving large changes in the angle of twist will be strongly " Franck–Condon forbidden," and will lead to very weak absorption. The above interpretation is exactly analogous to that given by Wilkinson and Mulliken[5] for the *V–N* bands of ethylene. These authors observed fine structure in the *V–N* bands of tetradeuteroethylene which they tentatively attributed to individual quanta of the twisting frequency. No comparable fine structure was obtained in the singlet–triplet absorption of this compound, although there is some indication of complexity in the poorly resolved bands.

From the results given in Table 1, a value of ~1000 cm.$^{-1}$ can be derived for the C=C stretching frequency of the triplet state of ethylene. An accurate vibrational analysis including anharmonicity is precluded by the diffuse and (especially) the unsymmetrical nature of the bands. This value is much smaller than the corresponding frequency for the ground state (1623 cm.$^{-1}$) but rather greater than that for the *V* state (~852 cm.$^{-1}$).[5] By using the relationship $r_0^{2\cdot 88}\,\omega = \text{Constant}$ proposed by Wilkinson and Mulliken, the equilibrium carbon–carbon distance in the triplet state of ethylene is calculated to be ~1·58 Å, to be compared with 1·337 Å in the ground state and ~1·67 Å in the *V* state. An almost identical result is obtained from Badger's rule.[17] The gradual increase in intensity of the singlet–triplet bands of ethylene and the deuteroethylenes towards shorter wavelengths also indicates that the equilibrium carbon–carbon distance in the triplet state is considerably greater than that in the ground state. It is accordingly not certain whether the longest-wavelength band is the 0,0 band. The *V–N* bands of ethylene show a very large increase in intensity in going from the first, extremely weak, band at 2069 Å to the last band at 1752 Å. From a comparison of the spectra of ethylene and tetradeuteroethylene, Wilkinson and Mulliken estimated that the 0,0 *V–N* bands of these compounds, although too weak to be seen, probably lie near 2500 Å. A similar comparison of the singlet–triplet spectra of ethylene and tetradeuteroethylene suggests that if the longest-wavelength bands (at 3484 Å for ethylene and 3455 Å for tetradeuteroethylene) are not in fact the 0,0 bands, the actual 0,0 bands will not be very different in wavelength. The estimated absorption maxima at ~2700 Å for ethylene and the deuteroethylenes correspond, by the Franck–Condon principle, to transitions from a planar ground-state molecule to a planar triplet state of the same dimensions.

The present results are of interest in connection with the thermal *cis–trans*-isomerization of olefins. Harman and Eyring[18] originally suggested that those isomerizations having low activation emergies (~1 ev) proceed *via* the triplet level of the olefin. *trans*-Dideuteroethylene itself isomerizes to *cis*-dideuteroethylene by a high activation-energy

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[17] Badger, *J. Chem. Phys.*, 1934, **2**, 128.

[18] Harman and Eyring, *J. Chem. Phys.*, 1942, **10**, 557.

(singlet) route,[19] although in the presence of nitric oxide the activation energy drops from 2·82 to 1·20 ev.[20] In the absence of reliable numerical data as to the dependence of the ethylene triplet level on the angle of twist, it is not possible to test this theory quantitatively. However, it was observed that irradiation of a mixture of 1 atm. of *trans*-dideuteroethylene and 130 atm. of oxygen with radiation of wavelength 2900—3400 Å, or monochromatic radiation of wavelength 3130 Å, caused appreciable isomerization to *cis*-dideuteroethylene (detected by the strong infrared bands at 843 and 1344 cm.$^{-1}$).[12] After 36 hours' exposure to a filtered (2900—3400 Å) 250-w high-pressure mercury arc about 8% of *cis*-dideuteroethylene was found in the mixture. (Because of the low pressure of *trans*-dideuteroethylene only a few per cent of the incident radiation was absorbed.) No other volatile products could be detected from the infrared spectrum of the mixture, and no appreciable isomerization was obtained in the absence of oxygen under pressure. It seems very likely that the isomerization occurs by the radiative excitation of an ethylene molecule to the triplet state during a collision with an oxygen molecule. The excited molecule will then twist to the stable perpendicular configuration and, either spontaneously or in the presence of an oxygen molecule, will finally undergo a radiationless transition to a ground-state *cis*- or *trans*-molecule. A chemical reaction involving a triplet level produced photochemically in the presence of a paramagnetic perturber has been observed by Kemula and Grabowska [21] for benzene saturated with nitric oxide. In this case the triplet benzene molecule apparently reacts with the nitric oxide to give a nitroso-compound.

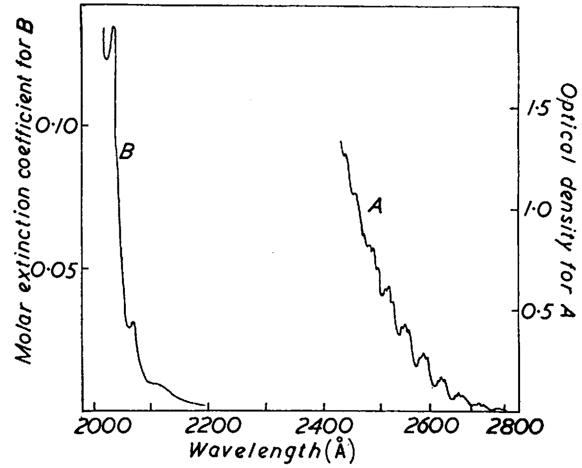

FIG. 2. *Light absorption of oxygen at* 100 *atm.* (*A*) *and ethylene* (*B*). *The positions of the oxygen bands are in good agreement with the more accurate photographs of Finkelnberg and Steiner.*[22]

The absorption spectrum of pure ethylene (50 atm.) down to 2002 Å was measured incidently and is shown in Fig. 2. The only previous results reported for wavelengths greater than 2050 Å are those of Snow and Allsopp.[6] The band at 2069 Å found by them is confirmed, but their extinction coefficients, especially at longer wavelengths, are much larger than the present ones, probably mainly owing to impurities (for 2200 Å Snow and Allsopp give $\varepsilon \sim 7 \times 10^{-2}$; we find $\varepsilon \sim 3 \times 10^{-3}$). The absorption of ethylene thus seems to fall in a normal manner with increasing wavelength to a very low value at about 2250 Å, and there is no evidence for any transition in this region other than the *V–N* transition. A shoulder is present at about 2110 Å, which is probably a further *V–N* band (the calculated wavelength from the formula derived by Wilkinson and Mulliken [5] is 2104 Å), although it is possible that a small amount of impurity is responsible.

The absorption bands in the region 2500—2100 Å observed by Potts [7] for alkyl-substituted ethylenes at low temperatures can hardly be due to the first singlet–triplet

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[19] Douglas, Rabinovitch, and Looney, *J. Chem. Phys.*, 1955, **23**, 315.
[20] Rabinovitch and Looney, *J. Chem. Phys.*, 1955, **23**, 2439.
[21] Kemula and Grabowska, *Bull. Acad. Polon.*, 1958, Vol. VI, **12**, 747.

transitions, on the basis of their position and also the vibrational interval of ~1400 cm.$^{-1}$. It is also rather unlikely that transitions to a higher triplet level are involved since the only higher triplet levels which arise from excitation of a π-electron are Rydberg-type levels. Rydberg bands are normally only observed in the gas phase.

The nature of the absorption below about 2700 Å in ethylene–oxygen mixtures remains to be discussed. It is convenient to consider first the absorption spectrum of pure compressed oxygen in the ultraviolet region above about 2200 Å, which has been extensively studied.[22-26] There are several weak bands in the region 6000—3289 Å whose intensities depend upon the square of the oxygen pressure but are independent of the presence of other added gases. These bands have been satisfactorily explained as arising from simultaneous electronic transitions involving two oxygen molecules.[23,25] The main absorption, however, comprises the " high-pressure " bands discovered by Wulf,[27] which are illustrated in Fig. 2. These consist of a progression of rather broad bands associated in groups of three in the region 2859—2440 Å, superimposed on a continuously rising background. The intensity of the absorption is approximately proportional to the square of the oxygen pressure, and is also increased by the addition of foreign gases (He, Ne, A, N_2, CO_2). Below about 10—20 atmospheres, another band system in the same region is also observed, the Herzberg bands, which are due to a forbidden $^3\Sigma_u^+$–$^3\Sigma_g^-$ transition of the isolated oxygen molecule.[28] The 0,0 band has never been observed in absorption because of its low intensity but is estimated [29] to lie at 2857 Å. The band origins of the Herzberg bands lie at wavelengths close to those of the centre bands of each triplet group of the high-pressure bands.

The relation between these two band systems is not certain. It has been suggested [24, 26] that the high-pressure bands are due to one oxygen molecule in an O_4 complex or " collision-pair " which undergoes a $^3\Sigma_u^+$–$^3\Sigma_g^-$ transition, although Herzberg [28] apparently considered that a different transition was involved. However, it may be noted that a possible explanation of the characteristic triplet structure of the bands can be given on the basis of the three possible states which arise from two oxygen molecules in contact, as a result of the coupling between the unpaired electrons of these molecules, namely singlet, triplet, and quintuplet. The statistical weights are in the ratio 1 : 3 : 5, respectively, and there is evidence that the singlet state lies lowest in energy.[30] The three bands in each group of the high-pressure bands can then be interpreted as arising from these three states. In each case one oxygen molecule is excited to a particular vibrational level of the $^3\Sigma_u^+$ state, the spin of which will be appropriately coupled with that of the other ground state ($^3\Sigma_g^-$) oxygen molecule, as a result of the selection rule $\Delta S = 0$. If the coupling energies between two oxygen molecules in the $^3\Sigma_g^-$ state are different from those between one oxygen molecule in a $^3\Sigma_g^+$ state and one in a $^3\Sigma_g^-$ state, then three separate bands would be expected.

As mentioned above, foreign gases (He, Ne, A, N_2, CO_2) increase the intensity of the high-pressure bands.[25] It is unlikely, however, that the bands below about 2800 Å in compressed ethylene (or deuteroethylene)–oxygen mixtures, and the similar bands starting at ~2850 Å in an acetylene–oxygen mixture at high pressure, are merely due to a similar effect. This was most clearly seen in the spectra obtained photographically at lower pressures. In an ethylene–oxygen mixture (2 atm. ethylene, 2 atm. oxygen), the more intense, broad singlet–triplet bands were observed (Table 1), but below about 2600 Å a

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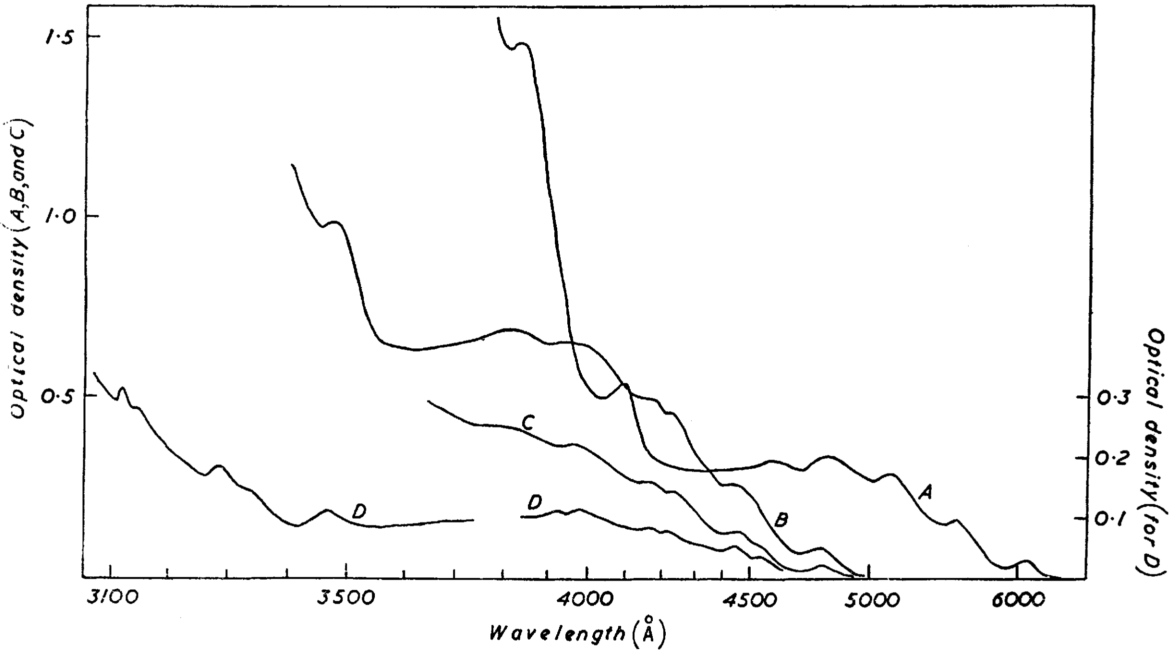
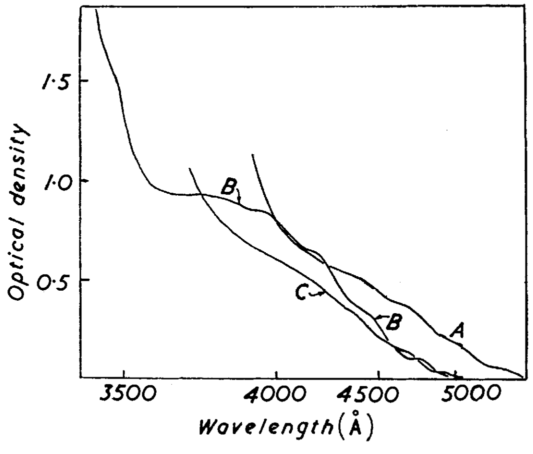
[22] Finkelnberg and Steiner, *Z. Physik*, 1932, **79**, 69.
[23] Ellis and Kneser, *Z. Physik*, 1933, **86**, 583.
[24] Steiner, *Trans. Faraday Soc.*, 1934, **30**, 34.
[25] Salow and Steiner, *Nature*, 1934, **134**, 463; *Z. Physik*, 1936, **99**, 137.
[26] Herman, *Ann. Phys.*, 1939, **11**, 548.
[27] Wulf, *Proc. Nat. Acad. Sci., U.S.A.*, 1928, **14**, 609.
[28] Herzberg, *Canad. J. Phys.*, 1952, **30**, 185.
[29] Broida and Gaydon, *Proc. Roy. Soc.*, 1954, *A*, **222**, 181.
[30] Buckingham and Pople, *Discuss. Faraday Soc.*, 1956, **22**, 17.

FIG. 3. *Perturbed singlet–triplet absorption of butadiene and hexa-*1,3,5-*triene* (5·2 *cm. cell unless otherwise stated*).



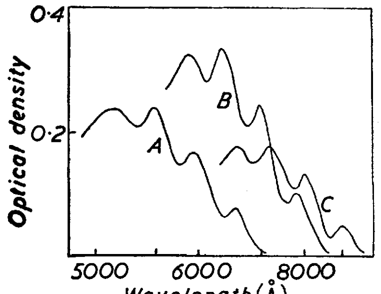
A, *oxygen at ca.* 130 *atm. dissolved in* 0·58M-*hexa*-1,3,5-*triene* (*chloroform solution*); *max.* 16,450, 17,920, *ca.* 19,170(i), 19,460, 20,770, 22,170, 24,310, 25,950 $cm.^{-1}$. *B*, *Oxygen at ca.* 130 *atm. dissolved in* 0·8M-*butadiene* (*chloroform solution*); *max.* 20,830, 22,390, *ca.* 23,600, 24,100, 25,190, 28,750 $cm.^{-1}$. *C*, *ca.* 3·2M-*Butadiene in ethyl iodide* (*reference cyclohexane in ethyl iodide*; *butadiene in chloroform showed no absorption*) (10 *cm. cell*). *D*, *ca.* 130 *atm. oxygen*, 2·5 *atm. butadiene. Max. at* 22,100(i), 22,470, *ca.* 23,700(i), 24,100, *ca.* 24,850(i), 25,200, 25,640, 28,770, *ca.* 29,900(i), 30,320, *ca.* 31,500(i), 31,900, *ca.* 33,100(i).

FIG. 4. *Light absorption of oxygen at ca.* 130 *atm. dissolved in chloroform solutions of conjugated systems.*



A, 0·5M-*Cyclohexa*-1,3-*diene*. *B*, 0·8M-*Isoprene*. *C*, 0·5M-*Cyclopentadiene*.

FIG. 5. *Light absorption of oxygen ca.* 130 *atm. dissolved in chloroform solutions of polyene-aldehydes* (5·2 *cm. cell*).



A, 0·44M-*Octa*-2,4,6-*trienal*; *max. at* 15,210, 16,700, 18,000 $cm.^{-1}$. *B*, 0·62M-*Deca*-2,4,6,8-*tetraenal*; *max.* 12,700, 14,160, 15,610, 16,970 $cm.^{1}$. *C*, 0·29M-*Dodeca*-2,4,6,8,10-*pentaenal*; *max. at* 11,050, 12,400, 13,700, 14,950 $cm.^{1}$.

sharper band system was present. These sharper bands were apparently the Herzberg bands, rendered more diffuse and also apparently considerably increased in intensity, when compared with spectra taken under similar conditions with 3 atmospheres of pure oxygen. A similar effect was also found with acetylene–oxygen mixtures (2 atm. acetylene, 2 atm. oxygen), although since no singlet–triplet bands were present the modified Herzberg bands extended up to ~2700 Å. They were also more diffuse than with ethylene–oxygen mixtures. No comparable effect was observed with an ethane–oxygen mixture (2 atm. ethane, 2 atm. oxygen). It therefore seems that ethylene and acetylene considerably perturb the Herzberg bands and increase their intensity, possibly by charge-transfer interaction during collisions between the organic molecule and an oxygen molecule. The bands below about 2800 Å in the high-pressure experiments can then be assigned as largely due to a similar effect, with the greater pressure leading to much broader bands. It may be noted that ethylene and acetylene are considerably more effective in perturbing the $^3\Sigma_u^+$–$^3\Sigma_g^-$ transition of an oxygen molecule than is oxygen itself. The Herzberg bands are extremely weak since a Σ^+–Σ^- transition is highly forbidden, and it is not surprising that they should be noticeably perturbed by even very weak interactions which slightly affect the symmetry of the electron distribution in the oxygen molecule.

Conjugated Olefins.—The spectra obtained are given in Figs. 3, 4, and 5. Well-defined singlet–triplet bands are normally observed. With butadiene and hexatriene two band systems seem to be present. The one at shorter wavelengths can be assigned as arising from a transition to the second triplet level of the olefin. Recent theoretical calculations discussed below do, in fact, suggest that two triplet levels should lie considerably lower in energy than the first excited singlet level.

It has been demonstrated by Kasha [31] that solvents containing heavy atoms (such as ethyl iodide) can induce the singlet–triplet absorption spectra of aromatic hydrocarbons (solvent perturbation technique). The absorption spectrum of butadiene dissolved in ethyl iodide (Fig. 3) shows bands in almost the same position as those obtained in the presence of oxygen. From the relative concentrations and cell lengths used, it is clear that ethyl iodide is a less efficient perturber than oxygen. (This is also found with aromatic hydrocarbons.)

The singlet–triplet spectra of the conjugated olefins have a main vibrational interval of ~1500 cm.$^{-1}$. This probably corresponds, as in the singlet–singlet spectra,[32] to an upper-state vibration which involves mainly the stretching of the C=C bonds. The intensity distribution of the bands indicates that a considerable change in molecular dimensions occurs during the transitions.

The 0,0 band of the first singlet–triplet transition was not observed for gaseous butadiene because of absorption by the oxygen. Nevertheless, it is apparent that there is very little shift of both the butadiene triplet levels in going from the gas phase to solution, in contrast with the normal (singlet–singlet) spectrum, where a red shift of ~1800 cm.$^{-1}$ is observed.

The frequencies both of the 0,0 bands and of the absorption maxima are given in Table 2 for all the olefins studied. Although the positions of the 0,0 bands can usually be obtained more precisely, theoretical calculations should generally be compared with experimental results for the absorption maxima. A further result of theoretical interest given in Table 2 is the difference in energy between the lowest triplet level and the first excited singlet level. These two levels will usually have the same electron configuration.

It can be seen from Table 2 that the lowest triplet levels of olefins are of comparatively low energy. The energy difference between the first excited singlet and the lowest triplet is quite large, and decreases only slowly with increase in the number of conjugated double bonds. There have been a large number of theoretical calculations of the energy levels of ethylene and butadiene, and no attempt will be made to give a detailed comparison

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[31] Kasha, *J. Chem. Phys.*, 1952, **20**, 71.

[32] Price and Walsh, *Proc. Roy. Soc.*, 1946, *A*, **185**, 182.

TABLE 2. *Singlet–triplet data for olefins (chloroform solutions unless otherwise stated).*

Molecule	0,0, Band (cm.$^{-1}$)	Absorption maximum (cm.$^{-1}$)	Absorption maximum ev	First excited singlet–lowest triplet separation (max.) (ev) †	Theor. absorption maximum (ev.) Pariser and Parr [a]	Theor. absorption maximum (ev.) Sidman [c]
$CH_2=CH_2$	$\leqslant$28,700 *	37,000	4·6	3·0	$^3B_{1u}$ 4·5, 5·7 [b]	$^3B_{1u}$ 4·2
$CH_2=CH-CH=CH_2$	(i) 20,830	(i) 26,000	3·2	2·8	^3B_u 3·9	^3B_u 3·4
	(ii) 28,750	(ii) ~31,000	~3·9		^3A_g 4·6	^3A_g 4·4
	28,770 *					
trans-	(i) 16,450	(i) 20,800	2·6	2·6		
$CH_2=CH-CH=CH-CH=CH_2$	(ii) 24,310	(ii) ~26,000	~3·2			
$CH_3\cdot[CH=CH]_3\cdot CHO$	15,210	18,000	2·2	2·0		
$CH_3\cdot[CH=CH]_4\cdot CHO$	12,700	15,600	1·9	1·9		
$CH_3\cdot[CH=CH]_5\cdot CHO$	11,050	13,700	1·7	1·8		
$CH_2=CMe-CH=CH_2$	21,000					
Cyclopentadiene	20,400	~25,000	3·1			
Cyclohexa-1,3-diene	18,700	~23,000	2·9			

* Gas phase. † Since the solvent shifts of the singlet–triplet transitions of olefins are much less than those of the singlet–singlet transitions, gas data for the olefin singlet–singlet bands are used where available. For the polyene aldehydes, 2000 cm.$^{-1}$ has been added to the observed frequencies [d] of the singlet–singlet bands in solution.

[a] Pariser and Parr, *J. Chem. Phys.*, 1953, **21**, 767. [b] Parr and Pariser, *ibid.*, 1955, **23**, 711. [c] Sidman, *ibid.*, 1957, **27**, 429. [d] Blout and Fields, *J. Amer. Chem. Soc.*, 1948, **70**, 189.

with the present results. It has been found [33-35] that the non-empirical molecular-orbital method (antisymmetrized product of molecular orbitals-LCAO approximation) does not give very accurate results for the energy levels of polyatomic molecules. In particular, the calculated separation between the first excited singlet and the lowest triplet levels is normally much too large. This is well illustrated with ethylene and butadiene, where the calculated values of this separation are 8·4 ev [33] and 5·1 ev [34] respectively, as compared with the experimental values of 3·0 and 2·8 ev. Recently, several modifications of the molecular-orbital approach involving the addition of empirical elements have been applied with considerable success to the calculation of the energy levels of hydrocarbons (especially aromatic hydrocarbons). The most widely used treatment is probably that due to Pariser and Parr.[35,36] The values calculated by these authors for the triplet levels of ethylene and butadiene are given in Table 2, together with those obtained by Sidman [37] who used a related method based on Pople's self-consistent field formulation.[38] Quite good agreement with the present experimental results is found. The first treatment of ethylene by Pariser and Parr,[35] which involved an empirical value for a certain two-centre integral based on a consideration of the spectrum of benzene, seems more satisfactory than their later calculation [36] in which the theoretical value for this integral was used.

It has been reported by Lewis and Kasha [3] that, while all-*trans*-lycopene does not phosphoresce, yet after it has been converted into *cis*-isomers by heat and iodine, phosphorescence emission in the visible region was obtained. Since lycopene contains 11 conjugated double bonds, from the results given above any phosphorescence from the lowest triplet level would almost certainly occur in the infrared region, and it seems most likely that the observed phosphorescence involved a higher triplet level or impurities formed during the iodine treatment.

Finally, a negative result for the " aromatic " hydrocarbon azulene may be mentioned. No phosphorescence in this compound could be detected by Beer and Longuet-Higgins,[39]

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[33] Parr and Crawford, *J. Chem. Phys.*, 1948, **16**, 526.
[34] Parr and Mulliken, *J. Chem. Phys.*, 1950, **18**, 1338.
[35] Pariser and Parr, *J. Chem. Phys.*, 1953, **21**, 767.
[36] Parr and Pariser, *J. Chem. Phys.*, 1955, **23**, 711.
[37] Sidman, *J. Chem. Phys.*, 1957, **27**, 429.
[38] Pople, *Proc. Phys. Soc.*, 1955, *A*, **68**, 81.
[39] Beer and Longuet-Higgins, *J. Chem. Phys.*, 1955, **23**, 1390.

or by Viswanath and Kasha.[40] Two very different explanations of this were given. Beer and Longuet-Higgins suggested that the triplet level lies *higher* in energy than the first excited singlet level at about 14,000 cm.$^{-1}$, while Viswanath and Kasha thought it more likely that the triplet level was of very *low* energy, so that any phosphorescence emission occurred in the infrared region above about 12,000 Å, and was thus not detected. In an attempt to locate the triplet level of azulene, the absorption spectrum of oxygen at 130 atmospheres dissolved in a 0·3M-solution of azulene in carbon tetrachloride was measured in the region 8000—25,000 Å (12,500—4000 cm.$^{-1}$). No induced singlet–triplet bands could be detected. Since, under similar conditions, both olefinic and aromatic hydrocarbons give quite strong singlet–triplet bands extending over several thousand wave numbers, it seems likely that the lowest triplet level of azulene does *not* lie below 12,500 cm.$^{-1}$ but is either of higher energy than the first excited singlet level, as suggested by Beer and Longuet-Higgins, or is only very slightly lower in energy than this level.

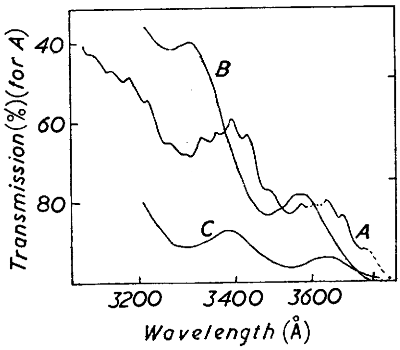

FIG. 6. *Perturbed singlet–triplet absorption spectra of diacetylenes* (5·2 *cm. cell*).

A, ca. 4 *atm. tetra*-1,3-*diyne, ca.* 130 *atm. oxygen*; *max.* 26,510, 27,020, 27,360, 27,970, 28,640, 29,060, 29,380, 29,660, 29,950, 30,380, 30,570, 30,990, 31,310, 31,650, 31,950 *cm.*$^{-1}$. *Slight background absorption due to an impurity. Broken lines indicate regions where absorption by oxygen interferes* (*this absorption was subtracted from the observed absorption*). *Two further singlet–triplet bands* (*at* 32,950 *and* 32,280 *cm.*$^{-1}$) *were present. B, Oxygen at ca.* 130 *atm. dissolved in* 0·5M-*hexa*-2,4-*diyne* (*chloroform solution*); *max.* 27,910, 30,090 *cm.*$^{-1}$. *C, Oxygen at ca.* 130 *atm. dissolved in* 0·15M-*hexa*-2,4-*diyne*-1,6-*diol* (*chloroform solution*); *max. at* 27,380, 29,440 *cm.*$^{-1}$.

Acetylenic Compounds.—The observed triplet levels are given in Table 3, and some of the spectra are illustrated in Fig. 6. The present result for the 0,0 band of octa-2,4,6-triyne (dimethyltriacetylene) (22,170 cm.$^{-1}$) is in quite good agreement with that obtained by Beer [8] from the phosphorescence spectrum (22,320 cm.$^{-1}$). This author also found a very weak absorption band at 28,100 cm.$^{-1}$ for hexa-2,4-triyne (dimethyldiacetylene) in hexane solution, which was tentatively assigned as arising from a transition to the lowest triplet level. The position of this band is close to that of the much stronger lowest-frequency band observed in the presence of oxygen under pressure (27,910 cm.$^{-1}$).

TABLE 3. *Triplet levels* (*cm.*$^{-1}$) *of acetylenes* (*chloroform solutions unless otherwise stated*).

	0,0 band		0,0 band		0,0 band
$HC\equiv C-C\equiv CH$	27,020 *	$CH_3\cdot[C\equiv C]_2\cdot CH_3$	27,910	$HO\cdot CH_2\cdot[C\equiv C]_2\cdot CH_2\cdot OH$	27,380
	27,300	$n\text{-}C_4H_9\cdot[C\equiv]_2\cdot H$	27,420	$CH_3\cdot[C\equiv C]_3\cdot CH_3$	22,170
		$n\text{-}C_4H_9\cdot[C\equiv C]_2\cdot C_4H_9\text{-}n$	27,820		
		$CH_2Cl\cdot[C\equiv C]_2\cdot CH_2Cl$	26,460		

* Gas phase; tentatively assigned 0,0 band.

The absorption spectrum of a gaseous diacetylene–oxygen mixture consists of four main groups of bands separated by an interval of ~2000 cm.$^{-1}$. This interval presumably corresponds to a triple-bond stretching frequency of the triplet state analogous to the Σ_g^+ frequency of the ground state which has a value of 2184 cm.$^{-1}$.[41] The first band in each of the first three groups is much weaker than the others, and is tentatively assigned as a " hot " band, due to transitions from those molecules which possess one quantum of the Π- ground-state bending frequency of 482 cm.$^{-1}$. In agreement with this interpretation, the average interval between this band and the next is ~450 cm.$^{-1}$. The spectrum

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[40] Viswanath and Kasha, *J. Chem. Phys.*, 1956, **24**, 574.

[41] Jones, *Proc. Roy. Soc.*, 1952, *A*, **211**, 285.

is thus consistent with Beer's assignment of the lowest triplet level as ${}^3\Sigma_v{}^+$, although as recognized by this author, it is possible that the triplet state is not linear.

It is noteworthy that alkyl substitution in diacetylene (and butadiene) causes shifts of the triplet level to higher frequencies (" blue shift "). Normally, for non-polar hydrocarbons, alkyl substitution causes red shifts of the observed bands, as found, for example, with the singlet–singlet spectra of acetylenes and olefins, and the singlet–triplet spectra of aromatic hydrocarbons. These red shifts are thought [42] to be due to two main effects: (i) the inductive effect of the alkyl group and (ii) hyperconjugation of the alkyl group with the unsaturated system. The inductive effect raises the energy both of the ground state and, to a smaller extent, of the excited state, while hyperconjugation raises the ground state and lowers the excited state. It is possible that the blue shifts observed for the singlet–triplet spectra of diacetylene and butadiene are due to an inductive effect which is greater in the triplet state than in the ground state. The relative contribution of the inductive effect as compared to that of hyperconjugation is expected to be greater in small molecules such as diacetylene than in larger molecules such as the aromatic hydrocarbons.

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[42] Crawford, *Quart. Rev.*, 1949, **3**, 226.