THE ABSORPTION SPECTROSCOPY OF SUBSTANCES OF SHORT LIFE

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The experimental methods available for the absorption spectroscopy of free radicals are critically discussed with special reference to flash photolysis and spectroscopy. Some free radical spectra which have been obtained in this way are described and values are given for the dissociation energies and vibration frequencies in the upper and lower states of the ClO, SH and SD radicals.

Most of our knowledge of the molecular structure of free radicals and similar short-lived substances is a result of the interpretation of emission spectra obtained from flames and electrical discharges. About 100 diatomic radicals have now been recognized in this way and many of their molecular constants determined, but there are very many other radicals whose emission spectra have not been observed and about whose structure virtually nothing is known. Chemical methods do not lend themselves readily to high-speed manipulation and other physical methods such as electron diffraction are not at present applicable. The method of absorption spectroscopy is almost alone in its suitability for investigations of this kind and has many advantages ; in particular it can be used to obtain spectra which cannot be observed in emission and it has the great advantage that it makes possible the determination of concentration. Furthermore, as more complex radicals are studied, it will be necessary to use other spectral regions such as the infra-red and far infra-red where absorption techniques become essential.

The difficulties associated with free radical absorption spectroscopy are almost entirely experimental ones and in the first part of this paper a brief account is given of the limitations of the existing methods with particular reference to the flash technique developed by the author. The second part deals with a few of the radical spectra which have been obtained by this method.

Experimental Methods

There are two problems associated with the kinetic absorption spectroscopy of short-lived substances in addition to those encountered with stable molecules. Firstly, the labile molecules must be produced rapidly in high concentration, and secondly, the spectrum must be recorded in a time which is short compared with their average life.

The Preparation of Free Radicals.—The partial pressure of radicals necessary for their observation in a path of 10 cm. varies from 10^{-5} mm. for a radical such as CN with high resolving power to 10 mm. or more under less favourable conditions. In many cases, and especially in the infra-red, a high relative concentration is also necessary if the spectrum is not to be masked by that of the parent molecule. There are four general methods available for free radical preparation and their uses for our purpose are summarized below.

THERMAL DECOMPOSITION.—This is only available when the dissociation of the radical does not occur much more readily than that of the parent molecule. It has not so far been possible to heat a gas rapidly enough to produce radicals instantaneously at high concentrations for kinetic studies and the method is limited to systems in thermodynamic equilibrium which have, however, one great advantage; if the thermochemical constants are known the radical concentration and hence its absorption coefficients can be determined.[1, 2, 3]

CHEMICAL REACTION.—Owing to the fact that diffusion is slow compared with the rate of most radical reactions it is difficult to produce mixing rapid enough to give a long absorption path and except in the special case of flames this method has been unsuccessful.[4] In flames also the reaction zone is narrow and sensitive methods, such as emission line reversal, are usually necessary.[5]

ELECTRICAL DISCHARGE.—By this means accurate synchronization and high percentage decomposition are readily attained and it was, until recently, the only successful method of instantaneous preparation.[6] Its main disadvantages are that it is limited to the low pressures, less than about 1 mm., at which the discharge can be passed, and the fact that the violence of the method results in the production of almost every possible molecular species making the interpretation of the kinetics a matter of great difficulty, except in the very simplest systems.

PHOTOCHEMICAL DISSOCIATION.—This method has many advantages; the system is relatively simple and well understood, a wide range of conditions may be used and almost all radicals can be produced photochemically. With ordinary light sources, however, the concentration of radicals which can be obtained is so low that it has been impossible to detect them by means of their absorption spectra. The use of high intensity flash sources has completely overcome this difficulty and partial pressures of atoms and radicals of the order of cm. Hg have been produced, making this the most powerful of all methods of preparation.[7]

The Rapid Recording of Absorption Spectra.—If the kinetics of the radical disappearance are to be studied the exposure time must be only a fraction of the radical lifetime which may mean 10^{-4} sec. or less. With continuous sources such as the hydrogen lamp the exposure time required is several seconds at least but three methods of high speed recording are available.

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[1] Bonhoeffer and Reichardt, *Z. physic. Chem.*, 1928, **139**, 75.
[2] Oldenberg, *J. Chem. Physics*, 1938, **6**, 439.
[3] White, *ibid.*, 1940, **8**, 439.
[4] Geib and Harteck, *Trans. Faraday Soc.*, 1934, **30**, 139.
[5] Kondratjew and Ziskin, *Acta Physicochim.*, 1937, **6**, 307.
[6] Oldenberg, *J. Chem. Physics*, 1934, **2**, 713.
[7] Porter, *Proc. Roy. Soc. A*, 1950, **200**, 284.

ELECTRONIC METHODS.—The response time of radiation detectors such as the photocell may be as low as 10^{-8} sec. but for high speed scanning a limit is set by the statistical fluctuations in the photocurrent. The relative fluctuations F_r are given by

$$F_r = 1/(nt)^{\frac{1}{2}},$$

where n = no. of electrons/sec. from the cathode $\simeq$ no. of photons/sec. and t = time interval resolved. For example, if the rate of scanning were 1000 Å/m. sec. and the s/n ratio were 50, the high output current of 100 μA from the 1P. 28 photomultiplier would only give a resolution of 1 Å. Only if resolution or scanning speed can be sacrificed is this method suitable with present sources, and similar considerations apply to infra-red detectors.

PHOTOGRAPHIC INTEGRATION.—If ordinary light sources are used the intensity may be increased by repeating the process many times, 60,000 such exposures being used by Oldenberg for each spectrum.[8] Maeder and Miescher have used a spinning mirror arrangement so that the decay of the radical is recorded at the same time.[9] Such methods are satisfactory if the interval between exposures is short but in flash photolysis the time required for lamp cooling, and for refilling and cleaning the reaction vessel owing to the high decomposition, makes a large number of exposures impracticable.

FLASH SPECTROGRAPHY.—The very high energy which can be dissipated in a single flash, the short duration and easy synchronization coupled with the fact that it gives a very good continuous spectrum makes the high-pressure rare gas filled flash-tube ideal for this purpose. A single flash from a 70 μF condenser at 4000 V across a 15 cm. tube, lasting 5×10^{-5} sec. gives a sufficient exposure on the plate of a Littrow (Hilger E.1) spectrograph down as far as the quartz absorption limit.[7]

Experimental Limitations of the Method of Flash Photolysis.—The construction and properties of flash tubes for photochemical and spectroscopic purposes have been described previously [7] and the present limitations of the method will now be given.

ENERGY DISSIPATION.—Energies of 10,000 J per flash have been dissipated in a 1 m. long tube, corresponding to a useful output of 2×10^{21} quanta in the quartz ultra-violet region. At the higher energies occasional refilling is necessary, for example, about every 100 flashes at 5000 J, and it has been found useful to have a separate pumping system for this purpose. It has also been found that xenon filling is the least troublesome in this respect. In most photochemical systems the pressure of intermediates produced by these energies is of the order of several mm. Hg.

FLASH DURATION.—It has become clear that the flash time of 1 msec. is longer than the lifetime of some of the radicals studied and it will be necessary to use the following methods of reducing its duration.

(*a*) DECREASE OF CAPACITY.—This reduces the duration of the flash without decreasing the intensity but the total output is thereby reduced.

(*b*) INCREASE OF VOLTAGE.—Up to the highest voltage used (8000 V) the energy dissipation of the tube does not appear to vary if CV^2 is kept constant by reducing the capacity, and as there is no consequent reduction in output this is the most useful method.

(*c*) DECREASE OF TUBE RESISTANCE.—This may be accomplished by increasing the diameter or decreasing the length of the tube, the latter being approximately proportional to flash duration. It has been found that the maximum energy dissipation of the lamp is also proportional to its length and again the total output must be reduced, but the output/unit length remains unchanged and, if the length of the reaction vessel can be reduced proportionately, the *percentage* decomposition is also unchanged.

The Determination of Radical Concentrations.—The approximate estimation of the lifetime of a radical by noting the disappearance of its absorption spectrum presents no difficulty and yields much interesting qualitative information about its chemical reactions, but there are many important data, such as rate constants and absorption coefficients, which cannot be obtained without a knowledge of absolute concentrations. At present such information is limited to the few radicals which can be obtained in thermodynamic equilibrium and it is important therefore that the relative simplicity of the photochemical system makes possible, in many cases, the estimation of radical concentration indirectly from the decrease in the absorption of the parent molecule

[8] Oldenberg, *J. Chem. Physics*, 1935, **3**, 266.

[9] Maeder and Miescher, *Helv. physic. Acta*, 1942, **15**, 511 ; 1943, **16**, 503.

and subsequently the appearance of the absorption by the stable products. A complication is introduced by the changing temperature, which is unavoidable in systems containing intermediate products at high concentrations, but the effect of temperature on the absorption spectrum of stable molecules can be determined and suitable corrections applied.

The flash technique was designed primarily for the study of the kinetics of radical reactions but much information is also obtained from the interpretation of the spectra themselves, and two such spectra, of the radicals ClO and SH, will now be considered.

The ClO Radical

A preliminary report and photograph of the spectrum attributed to this radical have been given elsewhere.[7] It appears whenever chlorine is photolyzed in the presence of oxygen and has a half-life of a few milliseconds. The simple vibrational structure strongly suggests a diatomic molecule and, under the circumstances, the only possibility is the ClO radical whose occurrence in chemical reactions has frequently been postulated. Very little is known about the diatomic compounds of Group 6 of the periodic table with Group 7 and the interpretation of this spectrum is therefore of some interest.

VIBRATIONAL STRUCTURE.—The main feature of the spectrum is a series of bands with fairly sharp heads degraded to the red which is clearly a $v'' = 0$ progression and the measurements of these heads with intensities on a scale of 10 are given in Table I. Most of the measurements are accurate to better than 10 cm.$^{-1}$ except for a few bands around $v' = 18$ where the overlapping rotational structure makes the heads difficult to locate.

TABLE I.—$v'' = 0$ PROGRESSION OF ClO

v'	Int.	λ Å	ν cm.$^{-1}$	v'	Int.	λ Å	ν cm.$^{-1}$
4	1	3034·5	32945	14	7	2729·4	36627
5	2	2993·0	33402	15	7	2711·1	36874
6	3	2954·3	33839	16	6	2695·0	37095
7	5	2918·0	34261	17	5	2682·5	37267
8	5	2884·0	34664	18	5	2671·2	37425
9	6	2851·8	35056	19	5	2661·0	37569
10	8	2822·4	35421	20	5	2652·5	37689
11	8	2796·0	35755	21	3	2645·8	37784
12	10	2771·6	36070	22	2	2640·6	37859
13	8	2749·5	36360	23	2	2636·3	37920

An assignment of vibrational quantum numbers in the upper state is not possible on this information alone but a band system attributed to ClO has been obtained in emission from flames containing chlorine or methyl chloride by Pannetier and Gaydon[10] and assuming their interpretation to be correct we may proceed as follows. The average value of the second difference of the wave numbers of the v' = constant progressions in the emission bands is 15 cm.$^{-1}$ and the corresponding value for the upper state, calculated from the absorption spectrum, is 22 cm.$^{-1}$. Starting with the last observed bands of the $v'' = 0$ and $v' = 0$ progressions the positions of further bands heads can be estimated, assuming linear convergence, to give the following values :

	Absorption, $v = 0$ progression cm.$^{-1}$		*Emission, $v' = 0$ progression* cm.$^{-1}$
Obs.	32945	Obs.	27598
Calc.	32466 31965 31442 30897	Calc.	28406 29227 30067 30920

The value for the last observed emission band has been adjusted slightly and the progression starts in effect from the previous band head which is

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[10] Pannetier and Gaydon, *Nature*, 1948, **161**, 242.

probably the more accurate measurement. It will be seen that there is a coincidence within the accuracy of the extrapolations between the last two figures given and a continuation in this way as far as the observed bands of the other system shows no other coincidence within 100 cm.$^{-1}$. The vibrational quantum numbers obtained in this way are given in Table I and the interpretation is supported by intensity considerations and the close agreement between the values for ω_e' obtained from the two spectra. The value of x in the Table of Pannetier and Gaydon is seen to be 4.

These data lead to the following values for the constants of the two states with a probable error in ω_e of 3 %. Account has been taken of a small cubic term in v' in the estimation of ω_e'.

Ground state. $\omega_e'' = 868$ cm.$^{-1}$ $x_e''\omega_e'' = 7·5$ cm.$^{-1}$.
Upper state $\omega_e' = 557$ cm.$^{-1}$ $x_e'\omega_e' = 11$ cm.$^{-1}$.
$\nu_e = 31{,}077$ cm.$^{-1}$.

FURTHER DETAILS OF BAND STRUCTURE.—Owing to the extended rotational structure the chlorine isotope effect is difficult to observe, the weaker isotope system being obscured by the stronger, and it has not been possible to confirm the above assignment of quantum numbers in this way.

In addition to the bands already discussed a second progression appears at about one-quarter of the intensity, the heads showing a fairly constant separation to higher frequencies from those of the main system. The bands appear to belong to a second multiplet component, the whole forming a doublet system and over the nine measured heads in Table II the doublet splitting decreases from 200 cm.$^{-1}$ to about 185 cm.$^{-1}$.

TABLE II.—SECOND SYSTEM OF ClO

v'	λ Å	ν cm.$^{-1}$	v'	λ Å	ν cm.$^{-1}$
5	2975·0	33603	10	2807·0	35615
6	2937·6	34032	11	2781·4	35943
7	2902·0	34449	12	2758·0	36248
8	2866·7	34874	13	2735·3	36548
9	2835·7	35255	—	—	—

A full analysis of the rotational structure has not yet been carried out, the resolution being rather too low. The P and R branches appear to be the most prominent feature of the bands and the structure suggests a $^2\Pi - {}^2\Pi$ or $^2\Delta - {}^2\Delta$ transition with near case (a) coupling. The former is supported by theoretical considerations which predict a $^2\Pi$ ground state for ClO.[11]

Determination of the Dissociation Energy.—The bands of the main system are observed almost to the convergence limit and a very good extrapolation can be made, the $\Delta\nu - v$ plot showing slight positive curvature. The value of the dissociation energy to products in the upper state obtained in this way is 37,930 cm.$^{-1}$ or 108·4 kcal./mole, ± about 0·1 %.

To obtain the dissociation energy to unexcited products the only low-lying levels of the atoms to be considered, ignoring multiplet splitting, are the ^2P ground state of chlorine and the ^3P ground and the ^1D and ^1S excited states of oxygen, the latter lying 15,868 and 33,793 cm.$^{-1}$ above the ground state. These lead to three possible values for D_0'' and the lower one is immediately eliminated by the fact that vibrational levels of the ground state are observed which lie above it. The upper one is confirmed by a linear extrapolation of the constants for the ground state which gives a value for D_0'' of 24,680 cm.$^{-1}$. It is clear therefore that the oxygen atom is liberated from the upper level in the ^1D state and the following values for the dissociation energies can now be given unambiguously.

Ground state. Dissociates to Cl ^2P and O ^3P.
$D_0'' = 22{,}062$ cm.$^{-1}$ = 63·04 kcal./mole ± 0·2 %.

Upper state. Dissociates to Cl ^2P and O ^1D.
$D_0' = 7{,}010$ cm.$^{-1}$ = 20·0 kcal./mole ± 1 %.

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[11] Perring (private discussion).

These values assume dissociation to the lowest atomic multiplet levels in each case as the actual levels are unknown. If the atoms are liberated in higher multiplet levels the value of D_0'' would need slight adjustment but the value of D_0' is unchanged. The normal dissociation energy of ClO to chlorine ${}^2P_{1\frac{1}{2}}$ and oxygen ${}^3P_2$ depends only on the multiplet level of the Cl atom liberated from the upper state, being the ground state value given above if Cl ${}^2P_{1\frac{1}{2}}$ is liberated and 881 cm.$^{-1}$ less if the product is Cl ${}^3P_{\frac{1}{2}}$.

Discussion.—The only existing information about the dissociation energy of ClO is obtained from the spectrum of the ClO_2 molecule.[12] The predissociation at 3750 Å, corresponding to an upper limit of 76 kcal./mole, is not inconsistent with the above value but much lower energies have been suggested from interpretations of the extrapolated convergence limit.

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It is interesting to compare the bond energy of ClO with the average bond energy in the other chlorine oxides calculated from the heats of dissociation as follows : [13]

Cl_2O	Cl_2O_7	ClO_3	ClO_2	ClO
47·0	50·3	55·6	59·5	63·0 kcal./mole.

The influence of the odd electron in strengthening the bond is clear and the last four molecules form a group of inorganic free radicals showing increasing chemical reactivity as the odd electron becomes localized.

The formation of ClO by the reaction of Cl atoms with O_2 suggests that a radical Cl—O—O· takes part as an intermediate, no trace of other chlorine oxides such as ClO_3 being found in the spectra. Subsequent reactions are then probably

$$\mathrm{Cl{-}O{-}O + Cl = (Cl_2O_2 =)\ 2ClO},$$

and at higher temperatures,

$$\mathrm{Cl{-}O{-}O + Cl_2 = (Cl_2O_2 + Cl =)\ 2ClO + Cl.}$$

Similar experiments with bromine indicate that the bromine atom does not react with O_2.

The SH and SD Radicals

The SH radical is the only diatomic hydride of the first two periods whose vibrational constants are completely unknown and one of the few common hydrides for which not even an approximate value of the dissociation energy is available. Its spectrum does not appear readily and only one band, the 0—0 band of the ${}^2\Sigma - {}^2\Pi$ transition, has ever been observed.[14] It is well known that hydrogen sulphide can be decomposed photochemically into its elements, and although other mechanisms have been proposed [15] it is probable that the primary decomposition is to H and SH.[16] For this reason the flash photolysis of H_2S was studied as a probable source of the SH radical.

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[12] Finkelnberg and Schumacher, *Z. physic. Chem.* (Bod. Fest.), 1931, 704.

[13] Goodeve and Marsh, *J. Chem. Soc.*, 1939, 1332.

[14] Lewis and White, *Physic. Rev.*, 1939, **55**, 894. Gaydon and Whittingham, *Proc. Roy. Soc. A*, 1947, **189**, 313.

[15] Goodeve and Stein, *Trans. Faraday Soc.*, 1931, **27**, 393.

[16] Herzberg, *ibid.*, 1931, **27**, 402.

Hydrogen sulphide was prepared from ferric sulphide and sulphuric acid and also by the action of water on an intimate mixture of calcium sulphide and phosphorous pentoxide. It was dried over $CaCl_2$ and P_2O_5 and fractionally distilled *in vacuo.* At pressures of 40 mm. of H_2S one flash produced a partial pressure of 9 mm. H_2, sulphur being deposited on the wall, and there was no overall pressure change. Spectra were taken of the products on a Littrow (Hilger E.I.) spectrograph at increasing time intervals, after the flash. Immediately after the flash the absorption spectrum showed, in addition to the continuum of H_2S and the $^3\Sigma - {}^3\Sigma$ system of S_2, the 0—0 band of SH at 3236·6 Å identical with that described by Lewis and White,[14] another similar band at 3060 Å, and a diffuse band system between 3168 and 3797 Å.

TABLE III.—SH 1—0 Band

ν (cm.$^{-1}$)	Int.	Branch (J)
32664·8	8	R_1 head
32634·4	6	$Q_1(1\frac{1}{2})$
32618·4	8	$Q_1(2\frac{1}{2})$. $P_1(1\frac{1}{2})$
32601·0	5	$Q_1(3\frac{1}{2})$
32587·9	3	$P_1(2\frac{1}{2})$
32580·2	4	$Q_1(4\frac{1}{2})$
32555·7	6	$Q_1(5\frac{1}{2})$. $P_1(3\frac{1}{2})$
32528·1	2	$Q_1(6\frac{1}{2})$
32518·4	2	$P_1(4\frac{1}{2})$
32498·1	2	$Q_1(7\frac{1}{2})$
32480·0	2	$P_1(5\frac{1}{2})$
32498·1	2	$Q_1(8\frac{1}{2})$
32469·6	1	$Q_1(9\frac{1}{2})$
32267·5	3	Q_2 head

SD 0—0 Band

ν (cm.$^{-1}$)	Int.	Branch (J)
30977·4	10	R_1 head
30959·6	3	$Q_1(1\frac{1}{2})$
30951·9	3	$Q_1(2\frac{1}{2})$
30943·6	3	$Q_1(3\frac{1}{2})$
30934·4	5	$Q_1(4\frac{1}{2})$
30923·6	2	$Q_1(5\frac{1}{2})$
30912·1	2	$Q_1(6\frac{1}{2})$
30899·6	3	$Q_1(7\frac{1}{2})$
30594·3	5	Q_2 head

SD 1—0 Band

ν (cm.$^{-1}$)	Int.	Branch (J)
32294·0	10	R_1 head
32277·0	4	$Q_1(1\frac{1}{2})$
32269·2	5	$Q_1(2\frac{1}{2})$
32260·7	3	$Q_1(3\frac{1}{2})$
32251·1	4	$Q_1(4\frac{1}{2})$
32238·8	8	$Q_1(5\frac{1}{2})$
32224·3	5	$Q_1(6\frac{1}{2})$
32211·4	5	$Q_1(7\frac{1}{2})$
32195·4	5	$Q_1(8\frac{1}{2})$
32174·8	5	$Q_1(9\frac{1}{2})$
32154·4	4	$Q_1(10\frac{1}{2})$
31907·1	3	Q_2 head

The 3060 Å Band.—The rotational lines of this band appeared with greater intensity than those the 0—0 band, the relative intensity of the two bands always being the same, and both bands had a half-life of about 1 msec. The resolving power of the spectrograph in this region was 1·5 cm.$^{-1}$ which was not sufficient to separate the satelite $^QP_{21}$ and $^RQ_{21}$ branches from the main Q_1 and R_1 branches nor in some cases the main branch lines from each other. For this reason some of the lines were very broad and the line measurements which are given in Table III are the observed maxima with the probable quantum number assignment for the main branch lines. It is found that, apart from the different spacing owing to the higher value of $B'' - B'$, this band is identical in structure with the

3236·6 Å band and it is fairly certain that it is the 1—0 band of the same system. This was confirmed by comparing the SH spectrum with the spectrum of the SD radical obtained from D_2S when it was found that there was a small isotope shift to shorter wavelengths with SD for the 3236·6 Å band and a greater one to longer wavelengths for the 3060 Å band, the order of magnitude leaving no doubt as to the correctness of the above interpretation. The measurements of the strongest lines of the 0—0 and 1—0 bands of SD are given in Table III.

There are two unusual features about the appearance of the 1—0 band of SH ; firstly, it has a greater intensity than the 0—0 band though a careful search for further bands of the progression shows that they are absent and secondly, Lewis and White observed the weaker 0—0 band only. Both these anomalies, as well as the difficulty experienced in obtaining the bands in emission, would be explained if there were a potential energy curve leading to a lower dissociation limit which crossed the $^2\Sigma$ curve at about the second vibrational level. In this case the 1—0 band might appear stronger at low resolution owing to the broadening of the lines even if the transition were of lower probability, whilst higher transitions might be completely diffuse.

Vibrational Constants and Dissociation Energy.—Apart from the upper limit of 93 kcal./mole set by the above-mentioned predissociation these constants cannot be obtained from the spectrum of SH alone as at least three vibrational bands are necessary for their derivation. By using the different zero point energy of the isotopic molecule, however, another relationship is introduced which makes the calculation possible. If we assume the same force constant for the two molecules it can be shown that

$$\Delta^2\nu = (\nu_{1-0} - \nu^i_{1-0}) - (\nu_{0-0} - \nu^i_{0-0}) = \omega_e'(1 - \rho) - 2x_e'\omega_e'(1 - \rho^2)$$

where $\rho = \sqrt{\mu/\mu^i}$, ν_{1-0} is the wave number of the 1—0 band, etc. and the superscript i refers to the SD molecule. We also have

$$\Delta\nu'_{1-0} = \nu_{1-0} - \nu_{0-0} = \omega_e' - 2x_e'\omega_e'$$

and therefore if the separations of the bands are known the values of ω_e' and $x_e'\omega_e'$ can be obtained. The values $\Delta^2\nu = 471$ cm.$^{-1}$ and $\Delta\nu'_{1-0} = 1787$ cm.$^{-1}$ are obtained from the origins of the $^2\Sigma - {}^2\Pi_{3/2}$ sub-bands estimated from the Q_1 branches, and substitution in the above equations gives for the $^2\Sigma$ state,

$$\omega_e' = 1950 \text{ cm.}^{-1} \quad \text{and} \quad x_e'\omega_e' = 81 \text{ cm.}^{-1}.$$

A linear extrapolation of these values gives the upper state dissociation energy $D_0' = 10{,}800$ cm.$^{-1}$ and in deriving a value for the normal dissociation energy two analogies with the $^2\Sigma$ state of OH, which might be expected to be very similar, will be made. The first is that the products in the upper state are H(^2S) and S(^1D) and this is fairly safe as the only alternative of S(^1S) would give a very low value for the normal dissociation energy.

The second analogy is that the linear extrapolation comes about 25 % too high and the final value obtained in this way will be assumed to have a possible error of 20 %. Applying this correction, subtracting the energy of promotion of S from the ^3P to the ^1D state and adding ν_{0-0} we get, for the normal dissociation energy, $D_0'' = 29{,}700$ cm.$^{-1}$ = 84·9 kcal./mole with an error probably less than 5 %.

From the relation

$$\nu_{v-0} - \nu^i_{v-0} = \omega_e'(v' + \tfrac{1}{2})(1 - \rho) - x_e'\omega_e'(v' + \tfrac{1}{2})^2(1 - \rho^2) - [\tfrac{1}{2}\omega_e''(1 - \rho) - \tfrac{1}{4}x_e''\omega_e''(1 - \rho^2)]$$

the quantity in square brackets is found to be 369·5 cm.$^{-1}$ and to find the value of ω_e'' a rough estimate of $x_e''\omega_e''$ may be made from the value of D_0'' + 10 % (as in OH) the term in $x_e''\omega_e''$ being small. Using the value $x_e''\omega_e'' = 52$ cm.$^{-1}$ obtained in this way we get $\omega_e'' = 2670$ cm.$^{-1}$. The corresponding values of the vibrational constants of the SD radical are $\omega_e' = 1400$ cm.$^{-1}$ and $\omega_e'' = 1910$ cm.$^{-1}$.

THE DIFFUSE BAND SYSTEM.—These bands form a regularly spaced system showing no fine structure, most of them being degraded to the red with fairly sharp heads, the measurements of which are given in Table IV. They appear and disappear with the SH bands and in all the spectra taken, using pressures of H_2S between 1 cm. and 10 cm. Hg their intensity was proportional to that of the SH bands. That they are not bands of sulphur is shown by the fact that they do not appear along with the S_2 bands in the photolysis of CS_2 or S_2Cl_2 and also that they show a shift when D_2S is used in place of H_2S. At first sight they might be another system of SH, their simple vibrational structure suggesting a diatomic molecule, but this is not supported by the isotope shift which occurs to shorter wavelengths with deuterium and is roughly the same, about 50 cm.$^{-1}$ throughout the system.

TABLE IV.—DIFFUSE BAND SYSTEM

λ Å	Int.	ν cm.$^{-1}$	λ Å	Int.	ν cm.$^{-1}$
3168·0	3	31557	3443·9	10	29028
3195·6	4	31284	2479·5	9	28732
3222·1	4	31027	3519·5	8	28405
3249·7	6	30764	3562·5	6	28062
3278·5	8	30493	3604·4	6	27736
3308·0	8	30222	3647·8	6	27406
3340·0	9	29932	3696·5	4	27045
3373·5	10	29634	3745·6	3	26691
3407·0	10	29343	3796·5	1	26332

These facts suggest that the system is that of a molecule, probably polyatomic, containing S and H atoms only. Of these the most likely are the HS_2 radical and the H_2S_2 molecule, the latter compound being quite stable but without a recorded spectrum. One might expect the spectrum of hydrogen persulphide to be entirely continuous by analogy with hydrogen peroxide and it also seems likely that some of it would survive the reaction and be detected in the products but it cannot be entirely ruled out on these grounds. The vibration frequency of something over 350 cm.$^{-1}$ is a reasonable value for the frequency of the —S—S— bond in either molecule, and the only other information which can be obtained from the spectrum is the dissociation energy which a fairly good linear extrapolation gives as 35,600 cm.$^{-1}$ or 102 kcal./mole. The energy of the —S—S— bond in S_8 is 52 kcal.[17] and if it is this bond which is broken dissociation of HS_2 to SH ($^2\Pi$) and S(^1S) gives fair agreement whereas dissociation of H_2S_2 to two SH radicals would not give this value unless there were another state of SH much lower than the $^2\Sigma$ state. Pending an investigation of the spectrum of H_2S_2 it seems more likely that the bands are those of the HS_2 radical which could be formed by the union of H atoms with the S_2 molecule.

Other Diatomic Hydrides of Group 6.—The absorption bands of the $^2\Sigma - {^2\Pi}$ systems of OH and OD have been obtained very strongly by the reaction of H or D atoms, prepared by photolysing a small amount of Cl_2 or Br_2, in the presence of H_2 or D_2, with oxygen. The first three bands of the $v'' = 0$ progression appeared at high intensity and this seems to be the first report of the OD bands in absorption. A very complex system of lines, which is the same in both cases and therefore attributable to oxygen

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[17] Siskin and Dyatkina, *Structure of Molecules* (Butterworth, 1950), p. 255.

alone, appears from 3000 Å to shorter wavelengths but no diffuse band system similar to that obtained with H_2S is present.

Attempts have been made to obtain the spectrum of the SeH radical in the photochemical decomposition of H_2Se but the only spectrum recorded on the plate was that of Se_2 despite the fact that the amount of decomposition was considerably greater than with H_2S. The absence of the spectrum of SeH may be explained if the predissociation occurs below the first vibrational level in this case, or if the SeH radical is chemically less stable, the latter explanation being probable in view of the decrease in stability from OH to SH, the former being observed for as long as 1/10th sec. after the flash.

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