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The Dissociation Spectra of Covalent Polyatomic Molecules

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I. INTRODUCTION

IN the following review an attempt is made to rationalize the continuous absorption spectra and some predissociation spectra of co-valent polyatomic molecules by correlating them to certain definite photo-dissociation processes. Only spectra taken in the vapor state have been considered, because in the liquid state or in solution a distinction between continua and banded structures in general is not possible. The molecules dealt with are those which are formed by a marked central atom, because for them resonance of the ground level with excited configurations apparently is negligible (1).* This excludes aromatic rings and molecules with conjugated double bonds for which rigorous energetic degeneracy of different structures causes a high degree of resonance. It leaves us with the inorganic and some simpler types of organic molecules. For these the review has been made as complete as possible for the author who has been away from his own library and notes. With the few exceptions mentioned below, all molecules of this type have been considered for which spectroscopical and thermochemical data are available.

It will be seen that the following list of molecules does not contain those very few molecules like N_2O which exhibit a complicated banded spectrum—and all hydrides are omitted. While the dissociation spectrum of every other molecule of this class fitted into the proposed theory with ease, not a single one of those of the hydrides could be accounted for. The energy of the long wave-length limit of the hydride spectra consistently leads to values much larger than any possible bond energy. On account of their much smaller internuclear distances, the transition from the low vibrational levels of the ground state apparently leads to those parts of the repulsive potential curves where their ascent and slope are already very steep.

For the other molecules we have to distinguish between two classes with entirely different mechanisms of photo-dissociation. The first are those in which the central atom is in a lower state of valency and therefore only its *p*-electrons are responsible for the chemical bonds. Here the primary photolytic process and therefore the position of selective absorption in the spectrum is simply governed by the bond energies. The other class is that of maximal valency of the central atom, in which also its *s*-electrons take part in the formation of the molecule. As these form a helium-like configuration in the unexcited state, they have to be activated by excitation to make maximal valency possible. In consequence, the primary photolytic process and the position of the selective absorption in the spectrum are determined not by the bond energies but by certain energies of reaction. Both the linkages due to the two *s*-electrons are broken simultaneously with an energy less than two, and often less than one, bond energy, while the energy of excitation of the central atom is

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* References in parentheses are given at the end of this article.

regained. Both types of mechanism will be discussed in detail below.

The spectra of the following molecules have been discussed:

A. Lower Valence State of Central Atom

(1) F_2O, Cl_2O, Br_2O, SCl_2, $TeCl_2$, $TeBr_2$;

(2) $SOCl_2$, $SOBr_2$, S_2Cl_2, $SeOCl_2$, Se_2Cl_2, Se_2Br_2, $SeCl_4$, $SeBr_4$, $TeCl_4$, $TeBr_4$;

(3) ICl_3, IBr_3, IBr_5;

(4) PCl_3, PBr_3, PI_3, $AsCl_3$, $AsBr_3$, AsI_3, $SbCl_3$, $SbBr_3$, SbI_3, $BiCl_3$, $BiBr_3$, BiI_3;

(5) $NOCl$, $SbOCl$;

(6) $SnCl_2$, $PbCl_2$, $PbBr_2$, PbI_2.

B. Maximal Valency of Central Atom

(1) SO_3, SO_2Cl_2, TeO_3, TeS_3;

(2) N_2O_5, P_2O_5, P_2S_5, P_2Se_5, PCl_5, PBr_5, $POCl_3$, $SbCl_5$;

(3) SnX_4, CX_4, CHX_3, CH_2X_2, CH_3X ($X=Cl$, Br, I);

(4) H_2CO, $H\cdot CO\cdot CH_3$, $H\cdot CO\cdot C_2H_5$, $CH_3\cdot CO\cdot CH_3$, $CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_3$;

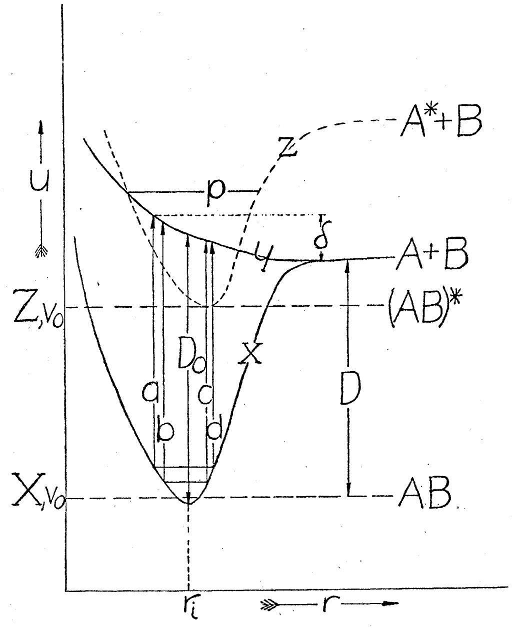

FIG. 1. Franck-Condon diagram of a covalent molecule AB.

(5) $H_3C\cdot OH$;

(6) $H\cdot CO\cdot OH$, $CH_3\cdot CO\cdot OH$, $CH_3\cdot CO\cdot OC_2H_5$, $CH_3CO\cdot SH$, $CH_3\cdot CS\cdot SH$, $NH_2\cdot CS\cdot NH_2$, $CH_3\cdot CO\cdot CO\cdot OH$, $CH_3\cdot CO\cdot CH_2\cdot CO\cdot OC_2H_5$, CO_2, COS, CS_2;

(7) Cl_2CO, Cl_2CS, $CH_3\cdot CO\cdot X$, $ClCH_2\cdot CO\cdot Cl$, $CCl_3\cdot CO\cdot Cl$, $CCl_3\cdot CO\cdot H$, $CBr_3\cdot CO\cdot H$.

II. EXPERIMENTAL CONDITIONS

The dissociation of a molecule produces two or more radicals or atoms possessing some kinetic energy relative to each other. Kinetic energy is never quantized, and therefore an absorption spectrum associated with a photo-dissociation process is not made up of discrete lines like an ordinary atomic line or molecular band spectrum. It is either a continuous absorption spectrum or a band spectrum with predissociation. The most frequent case is represented in Fig. 1 by means of a Franck-Condon diagram depicting the change of potential energy, U, of a system as a function of the internuclear distance r. On successive excitation of its vibrational levels, the ground state X of the molecule AB dissociates into the atoms or radicals A and B. Conversely, on the approach of A towards B, the molecule AB is formed in its unexcited electronic term, X, which possesses a stable minimum at the internuclear distance, r_0, and the dissociation energy D is liberated during this process. For a covalent molecule the necessary condition is that A and B possess free valencies, i.e., at least one free electron each in an incomplete quantum group or orbital (defined by particular values of the quantum numbers, 1 and λ). If two such electrons join in the same orbital of the molecule, a covalent bond obtains and the energy of dissociation D is identical with the bond energy. In most cases the two electrons will join the quantum group of the molecule with anti-parallel spin vectors, because the maximal number of electrons in the same quantum group is two for all orbitals of polyatomic and for many of the diatomic molecules. Hence according to Pauli's principle, the electrons will differ in the fourth quantum number, i.e., the spin, and the ground level X will be a $^1\Sigma$ term in most cases.

However, if on the approach of A towards B,

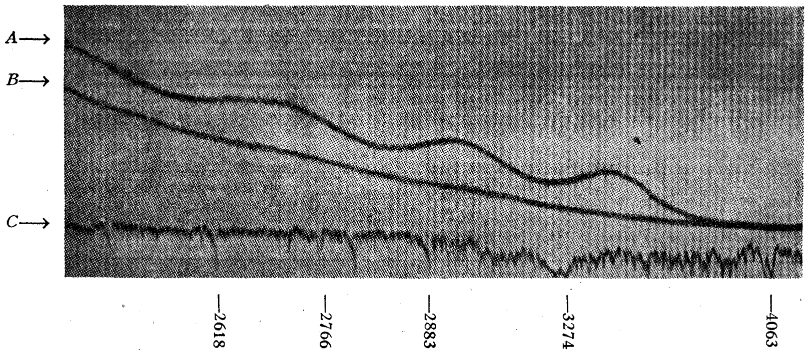

FIG. 2. Photogram of absorption spectra of CHI_3 (vapor). This was taken with a recording microphotometer from original plate. (*A*) Absorption spectrum of iodoform, (*B*) source of light (continuous hydrogen spectrum), (*C*) standard lines. Three different regions of selective absorption of CHI_3, their absorption maxima and long wave-length limit can be clearly distinguished.

the two electrons do not share in the same orbital of the molecule, no covalent bond is produced, no energy is liberated, and the resulting electronic level *Y* of the molecule AB is an unstable, repulsive, and non-bonding term. In most of such cases the electrons differ in the quantum number λ and therefore may have the same spin quantum number, the spin vectors may be parallel, and *Y* frequently will be a triplet term. But although the term *Y* does not possess a minimum of potential energy, it is as much an electronic level of the molecule as *X*. As a matter of fact, the corresponding $^3\Sigma$ term of H_2 is the lower one of that emission process during which the continuous hydrogen spectrum is emitted, now almost exclusively used as source of light for absorption spectroscopy in the ultraviolet. It is continuous because the term is unstable and permits the molecule to dissociate into two atoms with varying amounts of relative kinetic energy.

If *X* and *Y* are the only two energy levels of the molecule, the absorption process represents an excitation from the vibrational levels of *X* to various points of *Y*. According to the Franck-Condon principle—i.e., because the electron excitation is completed too quickly to permit the nuclei to change their position during this process—these transitions will lead to points on the potential curve of *Y* which are directly above those of the $U{:}r$ curve of *X* at which the molecule has been at that moment in which the light quantum is absorbed. The higher the vibrational level the greater the probability that this will be a moment in which the nuclei are just at rest against each other, represented by points on the $U{:}r$ curve itself. The arrows *a* and *b* show such excitations. They bring the molecule to points of the *Y* curve in which the molecule AB possesses an amount of potential energy, called δ, in excess of the system (A+B). Hence the molecule AB can dissociate spontaneously along the *Y* curve into the atoms A and B, converting the energy δ into the kinetic energy of the atoms relative to each other.

The spectrum which results, in this case in which *X* and *Y* are the only low terms of the molecule, is a strictly continuous absorption spectrum, such as is shown in Fig. 2. It forms one of the regions of selective and continuous absorption of this particular molecule. Any wavelength or frequency of this region is due to a transition from *X* to one of the points on the *Y* curve; the difference between any two wavelengths is due to the different values of the kinetic energy δ. One of them will be the most probable one and will give rise to the wavelength of the absorption maximum. Which it is, depends on the respective position of the two potential curves in the Franck-Condon diagram and on the population of the vibrational levels of *X*. The beginning of the absorption region, the so-called "long wave-length limit" (LWL), was thought to represent the dissociation of the molecule into two atoms with zero kinetic energy relative to each other; it should therefore be identical with the dissociation or bond energy D. We shall return to a discussion of this point below. Here it is sufficient to emphasize that such a region of continuous selective absorption is due to one and only one photo-dissociation process. On absorbing any of the quanta of any of the frequencies of this region, the molecule AB from its ground level X dissociates into the same atoms or radicals A and B (in the same electronic energy terms), and we obtain a broad region of selective absorption instead of a sharp line, only on account of the different vibrational levels of X and the different amounts of kinetic energy δ.

If X and Y are not the only low electronic levels, a third stable term, Z, may come sufficiently low to intersect Y (Fig. 1, broken line). In that case the spectrum has an entirely different appearance although the dissociation process remains the same. Absorption of light will excite the molecule from any of the vibrational levels of X to any vibrational level of Z, and after a short interval the absorbed energy will be reemitted as fluorescence spectrum or distributed over other molecules during collisions. The absorption spectrum will be a true band spectrum. However, if and when the absorption leads to one of those vibrational levels of Z, which (like p) intersect the potential curve at a point common both to Z and Y, the molecule, after reaching p by absorption, may now dissociate along the Y curve exactly as before.* The bands which involve such vibrational levels do not possess fine structure but are diffused; the phenomenon is known as predissociation. The dissociation process is the same as before, AB dissociates into two atoms, or radicals A and B, which possess a relative kinetic energy according to the energy difference δ between the point on the Y curve reached by absorption and the system A+B at infinite distance.

The dissociation energy D of an electronic term is also its bond energy D_B. By exciting the vibrational levels, v, of any term, one by one, until the level $v_{\max}$ is reached, we are tearing A from B, and that is the only energy which may rightly be considered to be the bond energy of the molecule AB in this particular electronic term or electron configuration. In the absorption spectrum we do not measure D_B itself but an energy of excitation of the non-dissociated molecule AB. We may denote this energy as the optical dissociation energy D_0, but we have to investigate under which conditions D_0 equals D_B or comes near to it.

It is clear from Fig. 1 that D_0 would equal D_B if (1) the potential curve of the repulsive term would run exactly parallel to the r axis and thus exclude all kinetic energy between the dissociation products, and (2) if the absorption process were confined to molecules in the lowest vibrational level of the ground term. Then the long wave-length limit of the continuous absorption would give us the correct value of D_B. This ideal case, of course, is never realized, and in any actual measurement allowances have to be made for these two factors. The first of these can be judged from the extension of the absorption region in the spectrum. The points a and d in Fig. 1 show transitions to the repulsive curve from the same vibrational level. The steeper the repulsive curve the greater will be the energy difference between a and d, i.e., the absorption region will be extended over more frequencies. In general it appears as if the slope of such levels is not very steep if these antibonding electronic levels themselves are low and therefore represent the approach towards each other of unexcited atoms or radicals. Even if no true bond is formed, the particles still interact with Van der Waals forces which to some extent neutralize the forces of repulsion and tend to keep the potential curve low.

The second factor makes it difficult to define that true value of the long wave-length limit, which belongs to the vibrationless molecule. Large shifts of the long wave-length limit occur, which are simply due to the absorption from higher vibrational levels of the normal state.

In $SnCl_4$, for instance, with an absorption cell of length 10 cm at room-temperature ($\sim$25°C) and a vapor pressure of about 1 mm of mercury it is at 2450A. With 9 mm of mercury and a cell of length 80 cm, it reaches 2570A; and with the temperature increased to 300°C and the pressure to 18 mm of mercury, with the same cell, the limit goes up to 2820A. The same, of course, is

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* Such conditions must not be maintained rigorously; according to wave mechanics, it is sufficient that p intersects the $U{:}r$ curve of Z close to that point at which it is itself intersected by the Y curve. However, it is difficult to give a definition of the meaning of "close."

true for predissociation spectra. In formaldehyde predissociation has been observed at 2670A at room temperature and at 2750A at 220°. The energy difference corresponds to 3.4 kcal./mole and according to the vibrational analysis of the accompanying band spectrum, at least two vibrational levels of the ground state are involved at the higher temperature. The higher the level the less it contributes to the selective absorption, and the contribution of higher levels beyond a particular one according to the particular conditions (length of absorbing layer, temperature, and vapor pressure) will fall below the last value indicated by the photographic plate on account of its threshold value. An increase of any of the above three parameters increases the number of molecules in higher levels, either by an increase of the population of the higher ones at the expense of the lowest or simply by an increase in the absolute number of molecules. A red shift of the first long wave-length limit results naturally, but this has no physical meaning for the vibrationless molecule, either as to its dissociation energy, or as to the shape of its potential curve, or as to the character of the bond. Since there appears to be some confusion on this point in the literature, attention may be drawn to two simple experimental facts which establish this interpretation. First, it can be seen from molecules exhibiting band spectra that the absorption is indeed by no means confined to the vibrationless molecule. For instance, bromine vapor in a layer of 10 cm and a pressure of about 1 cm exhibits the five lowest vibrational levels of the ground state of Br_2. Again in SO_2 in a 10-cm cell and pressure of the order of some tenths of a millimeter, the first three levels of the symmetric and antisymmetric valence vibration appear. These higher vibrational levels of the ground state are important, not only with regard to the actual energy difference between the higher and the lowest level, but even more on account of the change of relative position of two potential curves with decrease of internuclear distance. Secondly, in certain favorable cases we are able to estimate the beginning of absorption of a continuous spectrum independently of the experimental long wave-length limit. If, for instance, a molecule decomposes under the action of light in such a way that, in the first region of selective absorption, one of the dissociation products is an unexcited Br atom in its ground state $^2P_{3/2}$, and in the second absorption region an excited Br atom ($^2P_{\frac{1}{2}}$), the absorption spectrum will show two maxima whose energy difference is approximately equal to the term difference $^2P_{\frac{1}{2}}-{}^2P_{3/2}$ of Br, e.g. 3685 cm^{-1} or about 10.5 kcal./mole. The position of these two maxima will be influenced very much less by the experimental conditions; and the more nearly parallel the two repulsive curves concerned run, the better will the energy difference between the maxima agree with the energy of excitation of the Br atom.* The two maxima preserve their wave-lengths under different conditions, and the point of re-transmission between them also has a fairly constant wave-length. This latter point is near the beginning of the second absorption region, and hence the true long wave-length limit of the first absorption region of the vibrationless molecule should be found at a distance towards the red from the point of re-transmission which corresponds approximately to the excitation energy of Br ($^2P_{\frac{1}{2}}$) or the energy difference of the two maxima. Obviously, only for one of the many possible values of the first long wave-length limit is this necessary condition valid, and empirically this particular value lies rather more often than not in the vicinity of the maximum. As a rule the value of its extinction coefficient is of the order of one-tenth of that of the maximum. Such a value of the first long wave-length limit generally appears, e.g., in a 10-cm absorption tube at room temperature with a pressure of the order of 1 cm of mercury. Correlation of long wave-length

TABLE I. Energies of sublimation (and polymerization) of the elements in kcal./mole per g-atom.

Br	3.8	Sb	26.0
I	7.4	Bi	38.1
S	14.6	C	156.2
Se	14.7	Sn	77.0
Te	12.0	Pb	47.5
P	10.4		
As	12.8		

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* No reliance should be placed on spectra which simply show a blank and not the actual structure, maxima and minima, of the continuous absorption. It may be taken for granted that in such cases the number of absorbing molecules in high vibrational levels is much too great and that the last unabsorbed wave-length is far to the red of the true long wave-length limit of the vibrationless molecule.

limits to photolytic processes have been possible in such widely different cases as gases and vapors at room temperature and the experiments of Franck and his collaborators on alkali and silver salts of very high melting points. With a number of absorbing molecules roughly equal to that obtained under the conditions described above correlations of optical and thermochemical values have been possible, while measurements with absorbing layers of 10 or 30 meters(!) have not led to values related to thermochemically measured energies, and such observations do not concern the vibrationless molecule.

These difficulties which were involved in the determination of the true beginning of a continuous absorption spectrum may be minimized to some extent by taking the absorption spectrum of a vapor over a long range of varying pressures, and a comparison of different spectrograms of the same substance makes it easier to determine that long wave-length limit belonging to the molecule in its lowest state of vibration. However, it is never possible to overcome these obstacles entirely, and the measured value of D_0 will differ from the theoretical value of D_B sometimes by as much as 5 to 10 kcal./mole. But this is immaterial for our purpose. Such investigations are not undertaken to determine the bond energies. As will be seen in the next sections, the bond energies themselves can easily be calculated from thermochemical data. The total energy necessary to dissociate a polyatomic molecule into all its constituent atoms is known. The questions which absorption spectroscopy is able to answer are these:

(1) Which are the photolytic processes corresponding to the different regions of selective absorption, i.e., in which way is the molecule breaking up under the action of light?

(2) Do the bond energies remain approximately additive in the same molecule and constant from molecule to molecule?

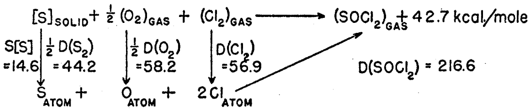
(3) Is it possible—as in the case of other additive molecular constants—to divide the dissociation energies into additive quantities according to entirely different theoretical concepts? In other words, do the individual bond energies really have a physical existence or are they only convenient arithmetical assumptions?

These questions can be answered even if the long wave-length limits can only be approximately determined in a continuous spectrum, and the answers, some of them surprising, will lead to some fundamental problems of the theory of valency.

III. THERMOCHEMICAL CALCULATIONS

In order to make use of the spectroscopical data, we have to calculate the heat of dissociation of a molecule into its *atoms* from the heat of formation from its *elements*. We shall call the former D and the latter Q. Then D has to be divided into the contributions of the various bonds, namely the mean bond energies D_B. For inorganic molecules Q is directly measured; for organic ones it can be calculated in the usual way from the heat of combustion.

As an example we take thionyl chloride. The heat of formation from the elements is 42.7 kcal./mole, when gaseous thionyl chloride is formed from solid sulphur, gaseous oxygen, and chlorine. Hence we have to add to this value the energy of sublimation S of sulphur into gaseous S_2 molecule, the energy of splitting these molecules into sulphur atoms, and similarly, the dissociation energies of O_2 and Cl_2. This leads us to Born's cycle in the following form:



The atomic heat of formation is the energy liberated when the gaseous atoms combine to form a gaseous molecule. It is for thionyl chloride 14.6+44.2+58.2+56.9+42.7 = 216.6 kcal./mole. From these energies of dissociation of the molecule into its constituent atoms, the bond energies of the individual linkages may be calculated.

Since this is the general scheme of calculation, some details have to be discussed at the outset. First of all, we mention that thermochemical data are by no means complete. It is surprising (at least, it was to the author) to see how many gaps still are left in the structure of thermochemistry after so many decades of investigations. For instance, we possess complete records of the absorption spectra of quite ordinary molecules like $BiBr_3$ which cannot be interpreted at all because the energies of formation of these molecules are not known. Most missing data, however, concern the heat of sublimation of inorganic compounds. In the above example, the elementary heat of formation Q directly concerns gaseous $SOCl_2$. Often, however, Q refers to liquid and solid compounds, and in such cases the heat of sublimation, i.e., the sum of latent heats of fusion and vaporization has to be deduced according to Born's cycle. While the heats of sublimation of the elements are determined, those of the inorganic compounds more often than not are unknown. The situation is somewhat eased by Kelley's (2) critical review of these data, and wherever possible his values have been taken in preference to others. But sufficient molecules remain for which these data have not been determined. In such cases we have to resort to one of the empirical formulae which permit the calculation of the latent heat of fusion (L) and of vaporization (V) from the melting and boiling points T_m and T_b in absolute temperature. For inorganic molecules Walden's rule (3*a*) and Forcrand's rule (3*b*) appear best suited, namely $L=13.5T_m$ and $V=30T_b$. Such values are marked by (∼), respectively. Fortunately these quantities are very small if compared with Q or D. In some cases like phosphorus, sublimation does not lead to diatomic molecules directly, but molecules such as P_4 are formed. The heats of sublimation in Table I stand for the entire energy necessary to convert 1 g-atom of the solid element into diatomic molecules, and in such cases include the heat of polymerization.

The energies of formation Q, if not otherwise mentioned, are taken from the work of Bichowsky and Rossini (4), and we have to thank Dr. Rossini for some additional data.

The basic spectroscopical values of the dissociation energies of the simple diatomic molecules are collected in Table II. They are taken from convergent points or predissociations, and most of them are beyond dispute. A few remarks are necessary about some of these molecules whose spectra permit different interpretations. First we consider the related molecules O_2, S_2, Se_2, Te_2, and SO. Herzberg determined the energy of dissociation for O_2 from the convergence point, and with a small correction (5) we have the very accurate value of

TABLE II. Dissociation energies of diatomic molecules in kcal./mole.

F_2	∼62	SO	116.5
Cl_2	56.9	N_2	169.0
Br_2	45.2	P_2	116.0
I_2	35.4	As_2	∼81.5
O_2	116.4	Sb_2	<85.0
S_2	88.4	Bi_2	∼39.0
Se_2	59.3	CO	241.4
Te_2	43.2	H_2	102.7

$$D(O_2)=5.05\text{ ev}=116.40\text{ kcal./mole.}$$

For all the other ones predissociation data are often used in literature. It is assumed that these values are fairly exact, because the repulsive curves appear to be rather flat. However, Rosen (6) has directly observed the convergence points in the spectra of S_2, Se_2, and Te_2, and it has been shown (7) that more accurate values may be deduced for these molecules in exactly the same way as for O_2. Indeed, it can be seen at once that the predissociation data are too high, in spite of the small slope of the repulsive curve. Thus predissociation gives $D(SO)=116.47$ kcal./mole (8), but as the field surrounding the core of sulphur is weaker than that of oxygen, it is impossible that $D(SO)$ should have the same (or even slightly higher) value than $D(O_2)$. This also disposes of the objection that the last discrete band observed by Rosen may not be the final one; even if true, it would affect the dissociation energy less than is indicated for the predissociation values by this comparison. Indeed for sulphur it has been shown that the predissociation value of D does not agree with that from the convergence point whatever dissociation products are assumed and therefore cannot be correct.

For some time indeed, it was not definitely known whether or not the bands observed for S_2, Se_2, and Te_2 constitute a transition to a $^3\Sigma$ term as in the case of O_2. However, no reasonable doubt is possible any longer. For S_2 the triplet character of the ground state is established by the rotational analysis of Christy and Naudé (9), and Bhatnagar, Lessheim, and Khanna (10) have shown that selenium vapor becomes more and more paramagnetic with higher temperature, i.e., the more Se_2 molecules are present in the

TABLE III. Atomic energies of formation (D).

Molecule	State	Q	S	D	Remarks
F_2O	*g*	-5.5		114.5	
Cl_2O	*g*	-21.7		83.4	
Br_2O	*g*	(~ -27)		~ 76	Estimate from absorption spectrum.
SCl_2	liq	~ 12	~ 10	~ 118	Dissolved in S_2Cl_2; S contains energy of solvation
SO_2	*g*	70.9		246.1	
$SOCl_2$	*g*	42.7		216.6	
S_2Cl_2	*g*	5.7		180.2	
S_2Br_2	liq	4.0	~ 6	168	
SO_3	*g*	93.9		327.3	
SO_2Cl_2	*g*	86.2		318.3	
$SeCl_2$	liq	-11	~ 5	85	
$SeCl_4$	*c*	46.1	~ 14	190	
SeO_2	*c*	56.4	~ 22	195	
Se_2Cl_2	liq	22.1	~ 12	156	
$TeCl_4$	*c*	77.4	~ 24	201	
$TeBr_4$	*c*	49.3	~ 21	168	
TeO_2	*c*	77.6	~ 30	198	
TeO_3	*c*	84	(~ 30)	262	Q from Mellor's Treatise
ICl	*g*			49.4	Conv. point, spectrum
IBr	*g*			41.6	Conv. point, spectrum
ICl_3	*c*	20.0	~ 8	122	
ClO_2	*g*	-23.5		121.7	
N_2O_3	*g*	-20.0		323.6	
NCl_3	in CCl_4	-55.0	~ 5	110	S indicates energy of solvation
$NOCl$	*g*	-12.8		158.4	
PCl_3	*g*	70.0		223.9	
PBr_3	liq	45.4	~ 3	190	
PI_3	*c*	10.9	~ 10	145	
$AsCl_3$	*g*	64.0		202.9	
$AsBr_3$	*g*	33		166	
AsI_3	*c*	13.6	~ 12	130	
$SbCl_3$	*g*	77.4		229	
$SbBr_3$	liq	56.5	~ 11	191	
SbI_3	*c*	22.8	~ 13	151	
$SbOCl$	*c*	89.2	~ 12	230	
$BiCl_3$	*c*	90.6	~ 18	206	
BiI_3	*c*	24	~ 14	133	
N_2O_5	*g*	-0.6		459.4	
PCl_5	*g*	91.0		302.0	
PBr_5	*c*	60	~ 11	250	
P_2O_5	*c*	367.0	37	758	
$POCl_3$	*c*	138.4		350.5	
$P(OH)_3$	liq	22.6	4	619	
$\frac{1}{2}P_2O_3$		——		<255	$D(P(OH)_3)-3D_B(O-H)$, difference between double and 2 single bonds neglected
$SbCl_5$	*g*	93.7		302.2	
$SnCl_2$	*c*	81.1	26.7	188.3	
$SnBr_2$	*c*	61.4	27	164	
SnI_2	*c*	38.9	37	127	
$PbCl_2$	*g*	49.4		153.8	
$PbBr_2$	*g*	5		101	
PbI_2	*g*	-10		88	
$SnCl_4$	*g*	118.4		309.2	
$SnBr_4$	*c*	94.8	14	263	
SnI_4				~ 210	Estimate from SnI_2
CH_4	*g*	18.2		379.8	
CH_3Cl	*g*	20.1		358.8	
CH_2Cl_2	*g*	21.7		337.5	
$CHCl_3$	*g*	23.6		316.6	
CCl_4	*g*	25.9		295.9	
CH_3Br	*g*	8.5		345.3	

TABLE III—*Continued.*

Molecule	State	*Q*	*S*	*D*	Remarks
CH_2Br_2	*g*	1		313	
$CHBr_3$	*g*	−6		281	
CBr_4		——		249	Estimate from difference CH_4-CHBr_3
CH_3I	*g*	−4.5		331.0	
CH_2I_2	*g*	−25		284	
CHI_3	*g*	−44		239	
CI_4		——		184	Estimate from difference CH_4-CH_3I
$H_3C\cdot OH$	*g*	48.4		468.2	
H_2CO	*g*	28.6		345.6	
$CH_3\cdot CO\cdot H$	liq	46.8	6	617	
$C_2H_5\cdot CO\cdot H$	*g*	47.7		882.8	
$(CH_3)_2CO$	*g*	50.8		885.7	
$CH_3\cdot CO\cdot CO\cdot CH_3$	liq	78.8	10	1118	
$CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_3$		——		1401	Calculated from $CH_3\cdot CO\cdot CH(CH_3)\cdot CO\cdot CH_3$
$H\cdot CO\cdot OH$	liq	99.8	5.5	469.6	
$CH_3\cdot CO\cdot OH$	gas	111.1		745.3	
$CH_3\cdot CO\cdot OC_2H_5$	liq	113.9	5	1261	
$CH_3\cdot CO\cdot SH$		——		700	Extrapolated from acetic acid, cf. Section VI.
$CH_3\cdot CS\cdot SH$		——		640	
$(NH_2)_2CS$	*c*	20	14	596	*Q* is the latest value, according to Landolt Bornstein, III Supplement
$CH_3\cdot CO\cdot CH_2\cdot CO\cdot OC_2H_5$	liq	153.7	9	1770	
$CH_3\cdot CO\cdot CO\cdot OH$	liq	140.3	13	976	
Cl_2CO	*g*	53.5		324.8	
Cl_2CS	*g*	——		265	Estimate from Cl_2CO
$CH_3\cdot CO\cdot Cl$	*g*	60.9		614.0	
$CH_3\cdot CO\cdot Br$	liq	54.9	4	602	
$CH_3\cdot CO\cdot I$	liq	41.5	5	587	
$ClCH_2\cdot CO\cdot Cl$	liq	68.4	5	593	
$CCl_3\cdot CO\cdot Cl$	liq	79	6	557	
$CCl_3\cdot CO\cdot H$	*g*	45.5		552.7	
$CBr_3\cdot CO\cdot H$				511	Estimate from $CCl_3\cdot CO\cdot H$
CO_2	*g*	94.5		367.1	
COS	*g*	35		308	
CS_2	*g*	−26		248	

mixture with Se_8 and possibly Se_6 molecules. Hence S_2 and Se_2 are entirely analogous to O_2, and exactly as in this case the correct value of D will be obtained by deducting from the energy of the convergence point that of the atomic ^1D level. The convergence points are observed by Rosen at 4.94, 3.81, and 3.22 ev for S_2, Se_2, and Te_2, respectively, the term values of ^1D are 1.14, 1.18, 1.30 ev in the same order, and the energies, therefore, are $D(S_2)=3.80$ ev $=88.4$ kcal./mole, $D(Se_2)=2.63$ ev $=59.3$ kcal./mole, $D(Te_2)=1.92$ ev $=43.2$ kcal./mole. These values differ from those obtained from predissociation data by a few kcal./mole only, and for the purpose of comparison with the long wave-length limits of a continuous spectrum, this difference does not matter too much. The results of such a comparison as obtained below are hardly affected by this change of values. However, to our mind they are the much better values, and in some cases they also match better with the spectroscopical data obtained for polyatomic molecules. For $D(SO)$ no other value but 116.5 kcal./mole from predissociation is available, but we have to use it, bearing in mind that it is most probably about 3 to 5 kcal./mole too high.*

The dissociation energy of CO, on the other hand, is not yet definitely known. While vibrational predissociation gives 10.45 ev $=241.4$ kcal./mole, rotational predissociation should give a more accurate value. But here a number of questions arise, such as which of the observed predissociations are real, which are the dissociation products, and what is the amount of excess kinetic energy. While Herzberg favors the value of 210 kcal./mole, we are inclined to use the value of 241.4 kcal./mole leading to a value of the sublimation energy of carbon of 156.2

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* Another value deduced from the same predissociation under the assumption of excited $S(^1D)$ as product is $D(SO)=92.4$. This value is too near to $D(S_2)=88.4$ and too far from $1/2D(SO_2)=123.0$, as discussed below.

kcal./mole. The reasons for this choice, discussed earlier (11), are partly of a spectroscopical nature, partly of general thermochemical considerations such as the rapid reaction of CH_3 radicals with H_2. However, it will be seen that for the purpose of comparing bond energies and absorption spectra of all those organic molecules which possess a $C=O$ bond, the value of $D(CO)$ enters twice into the calculation of the photolytic processes, once directly and once in the form of the sublimation energy of C derived therefrom and used for the calculation of the energy of formation from the heat of combustion. Hence it cancels out in all such cases, and its actual value becomes immaterial.

Using the fundamental data of Tables I and II, it is now possible to calculate the atomic energies of dissociation. The data are listed in Table III, which is self-explanatory.

IV. BOND ENERGIES

On the basis of the atomic energies of formation it is now possible to determine the energies of the individual bonds. This section is concerned exclusively with molecules *formed by a marked central atom in one of its lower but not in its maximal state of valency*. For example, the bond energies of molecules such as SCl_2, SO_2, $SOCl_2$, etc., will be discussed here, but the molecules SO_2Cl_2 or SO_3 will be separately dealt with below (Section VI), as they exhibit an entirely different behavior.

For these molecules of lower valence state we assume *additivity* of the bond energies *in first approximation*. It will be seen that the dissociation spectra bear out this assumption entirely. Indeed it is for this very reason that these spectra permit some knowledge of the term systems of polyatomic molecules to be obtained. But in some favorable cases it is possible to establish the first-approximation additivity directly. Thus, for $D(ICl)$ the value of 49.4 kcal./mole has been determined spectroscopically, and as in this case the convergence point of a band system has been observed, this value is very accurate. For $D(ICl_3)$ the value of 122 has been obtained, and one-third of it gives 40.7, which figure includes an estimate of the heat of sublimation of ICl_3 by means of Forcrand's rule. It is sufficiently close to $D(ICl)$ not to consider this as a coincidence.

The latter value being uncertain by several kcal./mole, it is difficult to say how much the deviation from $D(ICl)$ really is; most probably the difference is of the order of 10 to 15 percent. That, of course, cannot be called rigorous additivity. But, anything even approaching strict additivity cannot be expected. The atomic energy of dissociation is not the sum of the bond energies only, but includes also contributions due to the forces acting between those atoms which are not linked together by chemical bonds (e.g., the three Cl atoms of ICl_3 or the two oxygen atoms in SO_2). These mostly repulsive forces depend on the geometrical structure of the molecules, which is profoundly influenced, for instance, by the number of constituent atoms. The repulsive forces acting upon the oxygen atom of SO_2 must undergo a change if in the planar SO_2 one of them is replaced by two Cl atoms, leading to the pyramidal $SOCl_2$; again in $SOBr_2$ the repulsive forces will be weaker on account of smaller polarity and larger distance. With these forces the valence angle varies, and this may be considered as an indicator of the changes of the repulsive forces. Thus the valence angle of oxygen varies from $100\pm3°$ in F_2O to $115\pm4°$ in Cl_2O. The lower amines possess a pyramidal structure similar to NH_3, but this changes gradually and finally the triphenylamine is planar and does not possess an electric moment any longer.

Since this is the situation, a rigorous additivity cannot be expected, and in fact does not exist for any of the additive molecular constants, like molecular volume (parachor), refractivity, bond-moments, bond distances, or bond energies. If the percentage deviation appears to be somewhat smaller in any one of them, it only goes to show that this particular constant is less sensitive, and it is quite characteristic that in the amines the most anomalous behavior is found.

These are the true conditions confronting us, and that this is so is finally shown by a highly significant fact. The most favorable case for any molecular constant would be the isomeres of organic substances. Here the bonds and even the tetrahedral valence angles remain identical, and only the geometrical structure changes and with it the distance between some of those atoms not linked by a bond.

But as Fajans (12) has pointed out three decades ago, the atomic energies of dissociation vary for such isomeres by several kcal./mole. For butane, for instance, we now have accurate figures, measured directly and not as the difference of two heats of combustion (13). The heat of combustion is smaller and, therefore, the atomic energy of dissociation is 2.3 kcal./mole larger for the iso-form. In the iso-compounds certain carbon and hydrogen atoms approach nearer to each other than in the straight chains. Since they are the negative and positive ends, respectively, of the $C-H$ moment, they attract each other more in the former than in the latter. This effect is sufficient to bring about a positive contribution to the atomic heat of formation, which incidentally is of the same order as many of those often taken as "ionic resonance" energies.

However, a rough first approximation additivity really exists, as the comparison of ICl and ICl_3 has shown. This is sufficient for our purpose and will permit us to interpret spectra and photo-dissociation processes and to draw some conclusions on the term systems of polyatomic molecules.

For the calculation of the bond energies the usual procedure is adopted. The value of $\frac{1}{3}D(ICl_3)$, for instance, is considered here as the *mean* bond energy of the $I-Cl$ linkage in that molecule and denoted by $D_B(I-Cl)$. These mean bond energies are calculated here for covalent molecules (of Werner's first order) formed by a marked central atom, which is *not* in its maximal state of valency. In other words, we confine our considerations at first to atoms of the fourth to seventh groups and to those molecules which they form by means of their p-electrons. These bond energies are then compared with the corresponding dissociation spectra in the next section. Molecules formed by the same atoms in their *maximal* state of valency, when the inner s-electrons are chemically active in addition to the p-electrons, are dealt with in Section VI, as their behavior and optical properties are entirely different.

In reality, a further distinction should be made. In ICl and in ICl_3, the bonding effect is due to p-electrons as well of I as of Cl. But these $p-p$ bonds cannot possess exactly the same dissociation energies. In ICl the bonding pair is in the field of the core of the iodine atom while it is screened by six electrons. Thus, in ICl_3 only four electrons remain chemically inactive. The screening effect is much reduced as shown by the dipole moments of such bonds in many instances. It would be more consistent to distinguish $D_B(I^{III}-Cl)$ in ICl_3 from $D_B(I^{I}-Cl)$ in ICl, or $D_B(S^{II}-Cl)$ in SCl_2 from $D_B(S^{IV}-Cl)$ in $SOCl_2$. However, as long as the s-electrons are not activated and p-electrons only are considered (SO, SO_2 but not SO_3; ICl, ICl_3, IF_5, but not IF_7), these differences amount to a few kcal./mole only and, therefore, are inside the experimental accuracy of the determination of a long wavelength limit of a continuous spectrum. Hence, in such an early attempt to rationalize such spectra, it is sufficient to work with the same mean bond energy of the $I-Cl$, $S-Cl$, or $S=O$ bond, as long as the maximal state of valency alone of the central atom is excluded.

We begin with molecules formed by S, Se, and Te as central atoms, because among them some of the bonds are met more than once and permit one to check the value of the bond energy.

The mean energy of the $S-Cl$ bond could be calculated as one-half of the atomic heat of formation of SCl_2 to 59 kcal./mole. Unfortunately the heat of formation from the elements refers to sulphur dichloride dissolved in sulphur monochloride, and the energy of solvation is not known. Hence $D_B(S-Cl)=59$ kcal./mole is only an upper limit. As the dissociation energy of S_2 is accurately known from a convergence point, another way would be to calculate the energy of the $S-Cl$ linkage by means of: $2D_B(S-Cl)=D(S_2Cl_2)-D(S_2)=180.2-88.4=91.8$; $D_B(S-Cl)=46$. In the same way, deducting $D(SO)=116.5$ from $D(SOCl_2)=216.4$ we obtain $D_B(S-Cl)=50$.

The disagreement between these three values, in part at least, is due to a further difficulty, encountered just for molecules like S_2 or SO, which possess a paramagnetic ground level. For diatomic molecules Lessheim and Samuel (14) have shown that the presence of unshared electrons always disturbs the linkage and weakens the bond energy. The latter increases immediately if the odd electron is torn off by ionization, or partly removed by excitation, or converted into a shared electron by the formation of an additional covalent bond. Although the theo-

TABLE IV. Mean bond energies D_B.

Bond	Calculated from	D_B kcal./mole	Remarks
$S^{II}-Cl$	$\frac{1}{2}D(SCl_2)$	<59	Upper limit
$S^{IV}=O$	$\frac{1}{2}D(SO_2)$	123	Accepted value
$S^{II}=O$	$D(SO)$	116.5	Predissociation, upper limit
$S^{IV}-Cl$	$D(SOCl_2)-D_B(S^{IV}=O)=93.6$	47	Accepted value
$S^{IV}=S$	$D(S_2Cl_2)-2D_B(S^{IV}-Cl)=87$, or $D(S_2)$	88	
$S^{IV}-Br$	$D(S_2Br_2)-D(S_2)=80$	40	
$F-O$	$\frac{1}{2}D(F_2O)$	58	
$Cl-O$	$\frac{1}{2}D(Cl_2O)$	42	
$Se^{II}-Cl$	$\frac{1}{2}D(SeCl_2)$	42.5	Accepted value = 44
$Se^{IV}-Cl$	$\frac{1}{4}D(SeCl_4)$	47.5	
$Se^{IV}=O$	$\frac{1}{2}D(SeO_2)$	98	
$Se^{II}=Se$	$D(Se_2)$	59	
$Se^{IV}=Se$	$D(Se_2Cl_2)-2D_B(Se^{IV}-Cl)$	68	$D(Se_2)=59$
$Se^{IV}-Br$		~ 38	Estimate
$Te^{IV}-Cl$	$\frac{1}{4}D(TeCl_4)$	50	
$Te^{IV}-Br$	$\frac{1}{4}D(TeBr_4)$	42	
$I-Cl$	$D(ICl)$	49.4	Converg. point, band spectrum
$I^{III}-Cl$	$\frac{1}{3}D(ICl_3)$	41	
$I-Br$	$D(IBr)$	42	
$N^{III}=O$	$D(NO)$	121	Different value for radical NO and saturated molecules, cf. Section V
$-N^{III}=O$	$D(N_2O_3)$, $D(C_2H_5\cdot O\cdot N:O)$	138	
$N^{III}-Cl$	$\frac{1}{3}D(NCl_3)$	37	
$P^{III}-Cl$	$\frac{1}{3}D(PCl_3)$	75	
$P^{III}-Br$	$\frac{1}{3}D(PBr_3)$	63	
$P^{III}-I$	$\frac{1}{3}D(PI_3)$	48	
$As^{III}-Cl$	$\frac{1}{3}D(AsCl_3)$	68	
$As^{III}-Br$	$\frac{1}{3}D(AsBr_3)$	55	
$As^{III}-I$	$\frac{1}{3}D(AsI_3)$	43	
$Sb^{III}-Cl$	$\frac{1}{3}D(SbCl_3)$	76	
$Sb^{III}-Br$	$\frac{1}{3}D(SbBr_3)$	64	
$Sb^{III}-I$	$\frac{1}{3}D(SbI_3)$	50	
$Sb=O$	$D(SbO)$	122	Band spectrum, cf. reference (14*b*)
$Bi^{III}-Cl$	$\frac{1}{3}D(BiCl_3)$	69	
$Bi^{III}-Br$		54	Estimate
$Bi^{III}-I$	$\frac{1}{3}D(BiI_3)$	44	
$Sn^{II}-Cl$	$\frac{1}{2}D(SnCl_2)$	94	
$Sn^{II}-Br$	$\frac{1}{2}D(SnBr_2)$	82	
$Sn^{II}-I$	$\frac{1}{2}D(SnI_2)$	64	
$Pb^{II}-Cl$	$\frac{1}{2}D(PbCl_2)$	77	
$Pb^{II}-Br$	$\frac{1}{2}D(PbBr_2)$	51	
$Pb^{II}-I$	$\frac{1}{2}D(PbI_2)$	44	

retical reasons are not yet entirely understood, no exception is known to this rule and the wealth of experimental data in its support is overwhelming.

For polyatomic molecules it is sufficient to draw attention to the molecules H_2O and OH. For the latter Dwyer and Oldenberg (15) have recently determined a dissociation energy of 100 kcal./mole, while $D(H_2O)$ is 218. The fissure of the $O-H$ bond, therefore, requires considerably more energy when it takes place in the saturated molecule H_2O, and considerably less, if the same process concerns the OH radical with its free valency and an odd number of electrons.

The molecules SO and S_2 have an even number of electrons but as shown by their $^3\Sigma$ ground state, two of them are uncoupled and therefore represent free valencies. A similar behavior has to be expected, and this is immediately borne out by the atomic energy of formation of SO_2, which is 246.2 kcal./mole. If we accept for $D(SO)$ the predissociation value of 116.5, then the first fissure of the same $S=O$ bond in the saturated molecule SO_2 requires 129.7 kcal./mole, about 15 percent more than in the diatomic molecule SO. Consequently, if for instance in the dissociation of a molecule such as $SOCl_2$, the two $S-Cl$ bonds are broken first and the SO molecule such as $SOCl_2$, the two $S-Cl$ bonds are broken first and the SO molecule dissociates afterwards, this latter process will require 116.5 kcal./mole or less. But if the $S=O$ bond is broken first and the $S-Cl$ bonds afterwards, we may expect the dissociation process $SOCl_2+h\nu=SCl_2+O$ to be associated with a spectrum whose long wavelength limit lies at higher energy values, perhaps at 130 kcal./mole. The other dissociation product then would be a paramagnetic $SCl_2(^3\Sigma)$ with reduced energy of the $S-Cl$ bond. Similar considerations are valid for the bonds $S=S$ and $Se=Se$.

Under such circumstances, and in order to avoid such difficulties, for the time being, it seems better to use a mean value. We, therefore, adopt as the energy of the $S=O$ bond in polyatomic-molecules, as distinct from the dissociation energy of the diatomic SO, the value $D_B(S^{IV}=O)=\frac{1}{2}D(SO_2)=123.0$. Deducting this value from $D(SOCl_2)$ as before, we obtain $D_B(S-Cl)=47$.

The first values being established, it is now simple to determine the others. This is done in Table IV, which is almost self-explanatory. A few doubtful values are these: for $D_B(Se-Cl)$ two values are obtained, *viz.*, 42.5 from $SeCl_2$ and 47.5 from $SeCl_4$. Expecting this bond to be weaker than $S-Cl$, we accept 44 for $D_B(Se-Cl)$.

Arranging these mean bond energies according to the periodic table, we obtain

	S	Se	Te
Cl	47	44	50
Br	40	(~38)	42

TABLE V. Continuous absorption spectra of halides and oxyhalides of VI group atoms. (First line in A, second line in kcal./mole).

Absorption region:	*A*		*B*		*C*		*D*		*E*		Reference
	LWL	Max	LWL	Max	LWL	Max	LWL	Max	LWL	Max	
F_2O	5400 51	(4210)			2640 107	——					(19)
Cl_2O	6670 43	(?)			~3750 ~87	——					(18)
Br_2O	7500 38	——	5300 53	——							(20)
SCl_2	5825 48.5	3860			2770 104	2610			2350 122.4	2280	(17)
Bond energies: (F—O) =58, (Cl—O) =42, (S—Cl) =47.											
S_2Cl_2					2770 104	2580					(17)
$SOCl_2$					2900 97	2450			2380 119	——	(17)
$SOBr_2$					3780 75	3270	2810 101	2650	2450 116	——	(21)
Bond energies: 2(S—Cl) =94, 2(S—Br) =80, with excited Br 2(S—Br) =101, (S≡O) =123.											
$SeCl_4$	LWL not determined (>4150) (<68)	3250			3010 94	2750	one further maximum not determined				(21)
$SeOCl_2$					3150 90	2660	2500 114	?			(21)
Se_2Cl_2			4100 69	3500	3200 89	2950			2490 114	2370	(21)
Bond Energies: (Se—Cl) =44, (Se=Se) =68, 2(Se—Cl) =88, (Se=O) =98, (Se=Se) with excited Se =95.											
$SeBr_4$	5800 47	4900	5300 55	4270	3500 81	2620	~2500 ~114	——			(21)
Se_2Br_2			4650 61	3840	3500 81	3220	2880 98	2570			(21)
Bond energies: (Se—Br) =38, with excited Br =48.5, 2(Se—Br) =76, with one or two excited Br =86.5 and 97, (Se=Se) =68, with excited Se =95.											
$TeCl_2$	4800 59	3170			2900 98	2510	(?)				(21)
$TeCl_4$	4800 59	3240			2720 105	2470					(21)
$TeBr_2$	5350 53	4730	4200 67	3800	3400 84	3140	(2930) 97	(2280)			(21)
$TeBr_4$	5250 54	(?)	(?)	(~4000)	2960 96	2650	(2490) (114)				(21)
Bond energies: (Te—Cl) =50, 2(Te—Cl) =100, (Te—Br) =42, with excited Br =53, 2(Te—Br) =84.											

It can be seen that the energy decreases from S to Se as expected, but increases again towards Te. This anomalous course appears to be quite real. It has been found again for the heats of formation of the trioxides (16), and the energies of atomic excitation (and probably also of ionization) increase again from Se to Te. Sb and Bi behave similarly. The rapidly increasing polarity of the bonds may be a contributing factor. Incidentally, this little chart also permits us to estimate the energy of the Se—Br bond with some accuracy.

Again, as no thermochemical data are available for $BiBr_3$, we estimate its bond energy from the comparison of the following chart:

	As	Sb	Bi
Cl	68	76	69
Br	55	64	(∼54)
I	43	50	44

The estimated value of $D_B(\mathrm{Bi^{III}-Br}) \sim 54$ would lead to $D(\mathrm{BiBr_3}) = 162$.

Attention may also be drawn to the low value of $D_B(\mathrm{N^{III}-Cl}) = 37$, which has to be compared with $D_B(\mathrm{P^{III}-Cl}) = 75$. However, confirmation is offered by the experimental value of $D(\mathrm{NOCl}) = 158.4$, which agrees well with

$$D(\mathrm{NO}) + D_B(\mathrm{N^{III}-Cl}) = 121 + 37 = 158.$$

V. SPECTRA AND DISSOCIATION PROCESSES OF MOLECULES OF LOWER VALENCY

We begin the discussion with the spectra of halides and oxyhalides formed by the sixth group elements S, Se, and Te (17), (21) because here a good number of measurements are available. They all exhibit continuous spectra, the experimental results are listed in Table V. Each of the various regions of selective absorption, representing a photolytic process, is due to the transition of the molecule to one or the other nonbonding term. As all the various regions of absorption are fairly extensive, these terms will possess medium steepness, and the dissociation energies thus determined by the spectroscopical long wave-length limit in general should be slightly in excess of the thermochemical value. The first absorption region (counted from the red) of $SOBr_2$, $TeBr_2$ and $TeBr_4$, and all three of $SeBr_4$, are more narrow than those of the others. The repulsive curves should be slightly less steep, and the agreement of optical and thermochemical figures should be better in these cases.

The absorption spectra of some of the triatomic molecules exhibit some quite unusual features. For $SeCl_2$, $TeCl_2$, and $TeBr_2$ discrete absorption bands have been observed on the long wave side of continuous absorption, sometimes overlapping it. Cl_2O shows three subsidiary maxima ($\lambda = 6250$, 5300, and 4100) inside the first absorption region which have an entirely unusual appearance. They are extremely narrow, and the absorption coefficient decreases only slightly between maximum and re-transmission point. It appears that they are due to the overlap of a corresponding undeveloped band system or else that they are fluctuations of intensity due to the vibrational levels of the ground state similar to those observed for some of the alkali halides. Asundi and Samuel (17) also describe a similar subsidiary maximum of SCl_2 at $\lambda = 5165$ and make the doublet ground level of the radical SCl responsible for the splitting of the first absorption region. As the definite band spectra of the heavier homologues have been discovered in the meantime, we now prefer the present interpretation. These secondary maxima are of no interest for the mechanism of photo-dissociation.

Certain regularities are immediately apparent. Thus, for example, the bromides always possess more maxima of selective absorption than the corresponding chlorides, and the oxyhalides less than the di- and tetrahalides. Molecules possessing other double bonds like S=S and Se=Se, corresponding to the S=O double bond of the oxyhalides, behave as the latter. We shall now discuss this series of molecules in detail.

We begin with the molecule SCl_2 in which only the (S—Cl) linkage exists, for which a mean bond energy of 47 kcal./mole has been calculated. SCl_2 exhibits two regions of selective absorption, which we have called *A* and *C* (in order to conform with the bromides which show a "*B*" maximum in between). The long wavelength limits of these two regions lie at 48.5 and 104 kcal./mole and are due to the fission of one and two bonds, respectively. The second region also could be ascribed to a process in which an unexcited Cl atom and an excited SCl radical is produced, as nothing is known about the term system of the latter. But the same maximum C occurs in all molecules possessing two (S—Cl) bonds and with corresponding values in all the molecules under discussion (with the exception of Br_2O, of which the spectrum of shorter waves is not yet known). Hence only the above interpretation is possible. The third region *D* (LWL = 122.4) may involve an excited SCl radical, but again the lack of knowledge of its energy levels would make any identification impossible at this time. Another possibility would be the production of an excited $S(^1D)$ atom with 26 kcal./mole of excitation energy.

We can therefore write safely:

$SCl_2 + h\nu(A) = SCl + Cl$; 48.5 obs., 47 calc.;

$SCl_2 + h\nu(C) = S(^3P) + 2Cl$; 104 obs., 94 calc.,

and possibly:

$SCl_2 + h\nu(D) = S(^1D) + 2Cl$; 122.4 obs., 120 calc.

In Fig. 3 an attempt is made to represent graphically these conditions. In order to draw it in one plane, we shall frequently resort to such schemes of the terms of polyatomic molecules, which may be considered as simplified Franck-Condon diagrams.

We begin with the level of the unexcited atoms $S(^3P) + 2Cl(^2P)$. On the approach of one Cl towards S, the radical SCl is produced, and its ground term, *viz.* the term SCl+Cl lies 47 kcal./mole below that of the separated unexcited atoms. But a repulsive term (*b*) is produced at the same time, which shows that not every collision between S and Cl leads to a SCl molecule, but that an elastic collision may take the place of molecular formation.

In exactly the same way another stable term, *viz.* SCl_2 and another non-bonding term (*viz. a*) are produced on the approach of a second Cl atom towards SCl. The former is the ground level of unexcited SCl_2, $2 \times 47 = 94$ kcal./mole below that of the three separated unexcited atoms. If however sulphur is in the excited state ^1D, 26 kcal./mole above normal $S(^3P)$, a repulsive level (*c*) is produced; there is no evidence that excited S and unexcited Cl can form a molecule. The transitions from the ground level of SCl_2 to these three excited repulsive energy terms account for the three regions of continuous absorption of SCl_2 in the visible and near ultraviolet, which we have called the *A*, *C*, and *E* regions.

The molecule Cl_2O presents a complete confirmation of these conclusions. Its atomic energy of formation is 83.4 kcal./mole, and therefore $D(Cl-O) = 41.7$. Its absorption spectrum possesses two main regions of absorption (18), the first of which is subdivided into a number of secondary maxima, mentioned above. We have a region *A* with a long wave-length limit of about 43 kcal./mole,* and a point of re-transmission at about 76 kcal./mole. The second region of absorption (*B*) ($\lambda_{max} = 2650$) is exceptionally broad, and the point of re-transmission of the logarithmic absorption curve in all probability is not the long wave line referring to the vibrationless molecule. If, according to our empirical rule, the point of the curve is taken, where the absorption coefficient has about one tenth the value as at maximum *B*, the resulting energy of the long wave-length limit is about 87 kcal./mole. The true value will be between these limits, and, as the figures show, the same conditions obtain as in SCl_2. The two regions of selective absorption can be represented by

	Obs.	Calc.
$Cl_2O + h\nu(A) = ClO + Cl(^2P)$;	43 to 46	41.7,
$Cl_2O + h\nu(B) = O + 2Cl(^2P)$;	76 to 87	83.4.

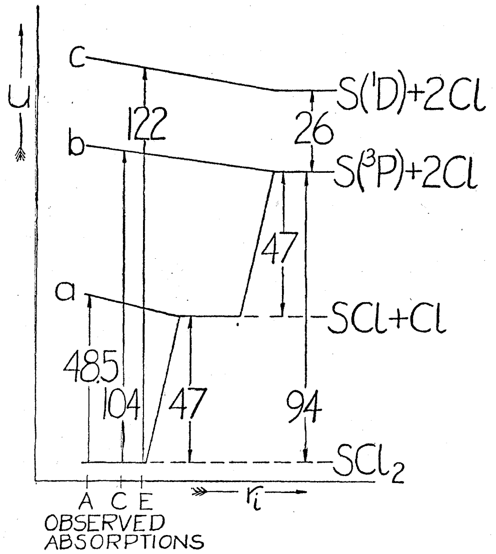

FIG. 3. Energy terms of SCl_2 in the system S+2Cl.

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* Slightly higher, ~46 kcal./mole, in reference (18*b*), but reference (18*a*) shows more details.

It is quite remarkable, that the main maxima of Cl_2O present a perfect confirmation of the interpretation of the spectrum of SCl_2 because both differ by a complete change of polarity. The O atom is the negative end of the dipole in Cl_2O, but S the positive one of SCl_2. *Its polarity appears to be of little influence on the position of the energy levels of the undisturbed molecule.*

Again the molecule F_2O shows (19) two long wave-length limits at the energy values necessary for the splitting off of one and two fluorine atoms, and in between two additional maxima which may indicate fluctuations and bands, or dissociation into F and excited FO radicals. Accordingly we obtain (in kcal./mole):

$F_2O+h\nu(A)=FO+F(^2P)$; 51 obs., 57 calc.,
$F_2O+h\nu(C)=O+2F(^2P)$; 107 obs., 114 calc.

No thermochemical values are known for Br_2O, and of its spectrum only the long wave part is measured (20). The first long wave-length limit lies at 7500A = 38 kcal./mole. As the spectrum appears to be similar to those of SCl_2, F_2O, and Cl_2O, this will be the approximate value of the energy of the Br–O bond, leading to about 76 kcal./mole for the atomic heat of formation of this molecule.

The absorption spectrum is very similar for $TeCl_2$ and $TeBr_2$ and also for the tetrahalides $SeCl_4$, $SeBr_4$, $TeCl_4$, and $TeBr_4$. They all possess a first absorption region whose long wave-length limit agrees with the energy of the halide bond, and this is followed by another one with about double this energy. Indeed it is gratifying to see how regularly the long wave-length limits shift towards the red, if Cl is replaced by Br, e.g., $SeCl_4$ $\lambda(A)=4150$, $\lambda(C)=3010$ as against $SeBr_4$ $\lambda(A)=5800$, $\lambda(C)=3500$; or $TeCl_2$ $\lambda(A)=4800$, $\lambda(C)=2900$ as against $TeBr_2$ $\lambda(A)=5330$, $\lambda(C)=3400$. These two processes explain all the absorption regions marked (A) and (C) of these molecules, and we get (in kcal./mole):

	Obs.	Calc.
$SeCl_4+h\nu(A)=SeCl_3+Cl(^2P_{3/2})$	<68	44
$SeBr_4+h\nu(A)=SeBr_3+Br(^2P_{3/2})$	47	~ 38
$TeCl_2+h\nu(A)=TeCl+Cl(^2P_{3/2})$	59	50
$TeCl_4+h\nu(A)=TeCl_3+Cl(^2P_{3/2})$	59	50
$TeBr_2+h\nu(A)=TeBr+Br(^2P_{3/2})$	53	42
$TeBr_4+h\nu(A)=TeBr_3+Br(^2P_{3/2})$	54	42

For the C region of absorption we obtain:

	Obs.	Calc.
$SeCl_4+h\nu(C)=SeCl_2+2Cl(^2P_{3/2})$	94	88
$SeBr_4+h\nu(C)=SeBr_2+2Br(^2P_{3/2})$	81	76
$TeCl_2+h\nu(C)=Te+2Cl(^2P_{3/2})$	98	100
$TeCl_4+h\nu(C)=TeCl_2+2Cl(^2P_{3/2})$	105	100
$TeBr_2+h\nu(C)=Te+2Br(^2P_{3/2})$	84	84
$TeBr_4+h\nu(C)=TeBr_2+2Br(^2P_{3/2})$	96	84

The determination of the second long wave-length limit appears to be more accurate as expected, because the point of re-transmission between two absorption regions is less influenced by experimental conditions. This interpretation is further confirmed by the other selective absorptions of these substances. The halogen atoms possess a first excited term immediately above the ground level, namely its second component $^2P_{1/2}$. For Cl the energy difference $^2P_{1/2}-{}^2P_{3/2}$ is only 881 cm^{-1} (~ 2 kcal./mole) and two regions of continuous absorption so close together cannot be separated. But for Br the same difference in 3685 $cm^{-1}=0.45$ ev $=10.5$ kcal./mole. Indeed, in all bromides the region associated with the liberation of unexcited Br atoms is followed by a second region (missing in the chloride spectra) at this approximate energy difference. In $TeBr_4$ this second maximum was only indicated and its long wave-length limit could not be accurately measured. But for the others we obtain:

	Obs.	Calc.
$SeBr_4+h\nu(B)=SeBr_3+Br(^2P_{1/2})$	55	~ 48.5
$SeBr_4+h\nu(D)=SeBr_2+2Br(^2P_{1/2})$	114	~ 97
$TeBr_2+h\nu(B)=TeBr+Br(^2P_{1/2})$	67	52.5
$TeBr_2+h\nu(D)=Te+2Br(^2P_{1/2})$	97	105
$TeBr_4+h\nu(D)=TeBr_2+2Br(^2P_{1/2})$	114	105

This method of identifying the dissociation products by means of the term difference $^2P_{1/2}-{}^2P_{3/2}$ of Br and I was first used by Franck and his collaborators when investigating the spectra of silver and alkali halides. They have pointed out that the absorption maxima frequently are less subject to changes by experimental conditions than the long wave-length limits, and therefore their difference should agree even better with that of the two components of the P term. In those cases where this comparison can be made, we find the following values (in ev):

Difference of maxima A and B
$SeBr_4$: 0.4; $TeBr_2$: 0.6.
Difference of maxima C and D
$SOBr_2$: $0.8=2\times0.4$; Se_2Br_2: $1.0=2\times0.5$;
$TeBr_2$: $1.3=2\times0.65$.

There remain the molecules possessing a double bond, viz. $SOCl_2$, $SOBr_2$, S_2Cl_2, $SeOCl_2$, Se_2Cl_2 and Se_2Br_2. Their absorption spectrum is similar to that of the di- and tetrahalides at shorter waves, but quite different at longer waves. Exactly as these halides, these molecules all possess a region of selective absorption, (*viz. C*), in which two halogen atoms are liberated simultaneously, namely:

	Obs.	Calc.
$SOCl_2+h\nu(C)=SO+2Cl(^2P_{3/2})$;	97	94
$S_2Cl_2+h\nu(C)=S_2+2Cl(^2P_{3/2})$;	104	94
$SOBr_2+h\nu(C)=SO+2Br(^2P_{3/2})$;	75	80
$SeOCl_2+h\nu(C)=SeO+2Cl(^2P_{3/2})$;	90	88
$Se_2Cl_2+h\nu(C)=Se_2+2Cl(^2P_{3/2})$;	89	88
$Se_2Br_2+h\nu(C)=Se_2+2Br(^2P_{3/2})$;	81	76

The agreement is extremely good, or in other words the repulsive curves are very flat for this type of molecule.

Again this interpretation is supported in the case of the bromides by the shift of the long wave-length limits toward red and by the appearance of additional absorption maxima indicating excited bromine atoms as dissociation products:

	Obs.	Calc.
$SOBr_2+h\nu(D)=SO+2Br(^2P_{1/2})$;	101	91
$Se_2Br_2+h\nu(D)=Se_2+2Br(^2P_{1/2})$;	98	87

The maximum D of selenium monobromide possible is overlapped by one indicating an excited $Se(^1D)$ atom as product. The calculated value of such a limit is 86.

Furthermore, the double bond $Se=Se$ is not only weaker than the $S=O$, $S=S$, and $Se=O$ bonds, but also weaker than two $Se-Cl$ or $Se-Br$ bonds. Hence in the so-called monohalides of selenium a new region of selective absorption is promptly exhibited on the *long* wave side of the C-maximum which stands for the fission of two $Se-Cl$ or $Se-Br$ linkages. Accordingly we find:

	Obs.	Calc.
$Se_2Cl_2+h\nu(B)=SeCl_2+Se(^3P)$;	69	68
$Se_2Br_2+h\nu(B)=SeBr_2+Se(^3P)$;	61	68

According to the considerations dealt with in Section IV, we expect for the dissociation of doubly linked Se from a saturated molecule an energy value 10 percent to 15 percent larger than $D(Se_2\,^3\Sigma)$, or 65 to 68 kcal./mole. This agrees excellently with the long wave-length limit of Se_2Cl_2, slightly less well with that of Se_2Br_2. Two facts make this interpretation very certain, namely that this absorption region is identical for these two molecules with different halide bonds, and the other, that a similar one in this region of the spectrum is missing for $SOCl_2$, $SOBr_2$, and S_2Cl_2, where the tearing off of an O or S atom requires considerably more energy.

However these molecules of $SOCl_2$-type, possessing a double bond, differ from the simple di- and tetrahalides in one respect. None of them shows a region of selective absorption in which a *single* atom-halogen bond is fissured. The A-maximum is missing for all of them, and consequently they are much less colored. The reason for this different behavior is obscure at this time, but a simple and possible explanation may be offered. We have to bear in mind that the electronic terms, drawn for the sake of convenience as lines in one plane, in reality are surfaces in space. The simplest possibility to account for this surprising difference in optical properties may therefore be the difference of geometrical structures. The dihalides of course are planar, and the tetrahalides probably form trigonal bipyramids with the "lone pair" of the tetravalent central atom occupying one of the equatorial positions (22). The oxyhalides and the so-called monohalides, however, possess a pyramidal structure with the central atom at the apex. For $SOCl_2$ this structure has been directly observed; for others it is born out by the dipole moments. It may well be that the surface of the repulsive electronic term (radical+1X atom) lies perpendicular above that of the ground level and can be reached from it in one geometrical structure, but not in the other.

Finally, there are three regions of selective absorption to be accounted for, which have been called "E" in Table V. Here, where the maxima are hardly known, an interpretation is much more difficult, and tentatively we suggest the following correlations:

	Obs.	Calc.
$SCl_2+h\nu(E)=S(^1D)+2Cl$;	122.4	118
$SOCl_2+h\nu(E)=SCl_2+O$;	119	123
$SOBr_2+h\nu(E)=SBr_2+O$;	116	123

For Se_2Cl_2 the corresponding dissociation into an excited atom $Se(^1D)$ plus $SeCl_2$ leads to an energy of 95 kcal./mole. Such an absorption region would be overlapped by maximum C which shows a long wave-length limit of 89 kcal./mole. Hence the E maximum should be due to the next excited term of Se, which would be the ^1P term with approximately 39 kcal./mole. If this amount is added to the bond energy ($Se=Se$) of 68, 107 kcal./mole is obtained, while the long wave-length limit of the maximum E of Se_2Cl_2 lies at 114.

It is now possible to construct schemes of energy levels of these molecules, $SeBr_4$ (Fig. 4) and Se_2Br_2 (Fig. 5) are taken as examples. In the diagram of selenium tetrabromide we again find the separated atoms on the right-hand side. In four steps of about equal energy value the radicals SeBr, $SeBr_2$, $SeBr_3$, and finally the molecule $SeBr_4$, are built up. However, the approach of a Br atom towards $SeBr_3$ does not only lead to the stable ground level of $SeBr_4$, but also produces the unstable term (a). If an excited Br atom in its $^2P_{1/2}$ level approaches a similar non-bonding term (b) of the system $SeBr_4$ is created, which lies 10.5 kcal./mole higher than (a). But no stable term has been found for this combination of $SeBr_3$ with an excited Br atom; the repulsive one appears to be the only electronic term produced. Also for the combination $SeBr_2+2Br$, an unstable term (c) is produced besides the stable ground level of the radical $SeBr_3$. For the latter this non-bonding level might be the first excited term and probably could be found in its absorption spectrum. Absorption spectra of radicals, particularly in the gaseous phase are hardly known for obvious reasons. But this term (c) is also an electronic level of the system $SeBr_4$ and may be reached from the ground level of this molecule in the absorption region C. Then two of the four Br atoms are liberated simultaneously. The recombination of $SeBr_2$ with two excited atoms Br ($^2P_{1/2}$) does not lead to a stable state; only the unstable term (d) has been found, lying $2\times 10.5=21$ kcal./mole above (c). Higher terms are omitted, as they would be outside the range of the quartz spectrograph. In general a comparison of observed and calculated figures gives the impression that the estimated value of 38 kcal./mole of the energy of the $Se-Br$ bond is a few kcal./mole too low.

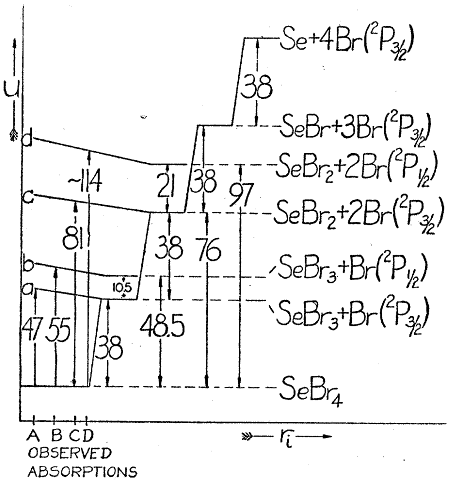

FIG. 4. Energy terms of $SeBr_4$ in the system $Se+4Br$.

The scheme of electronic levels of Se_2Br_2 is slightly more complicated because such a molecule can be formed and can dissociate in two different ways. From the energy level of the totally separated atoms $2Se+2Br$ it may be built up in the steps $Se_2(^3\Sigma)+2Br\rightarrow Se_2Br+Br\rightarrow Se_2Br_2$, and the corresponding energy levels are shown on the right-hand side. Or it may be formed in another three-step reaction, $SeBr+Br+Se\rightarrow SeBr_2(^3\Sigma)+Se\rightarrow Se_2Br_2$, the energy terms being shown on the left-hand side. On the strength of the discussion in Section IV and the empirical evidence of molecules like H_2O or SO_2, we have assumed that the splitting off of a Se atom from the diamagnetic, saturated molecule Se_2Br_2 requires about 10 percent more energy than in the paramagnetic "radical" Se_2, and the same concept applies to the $Se-Br$ bond.

On the right-hand side, the molecule Se_2 in its spectroscopically known ground state $^3\Sigma$ is formed first. The approach of unexcited $Br(^2P_{3/2})$ atoms

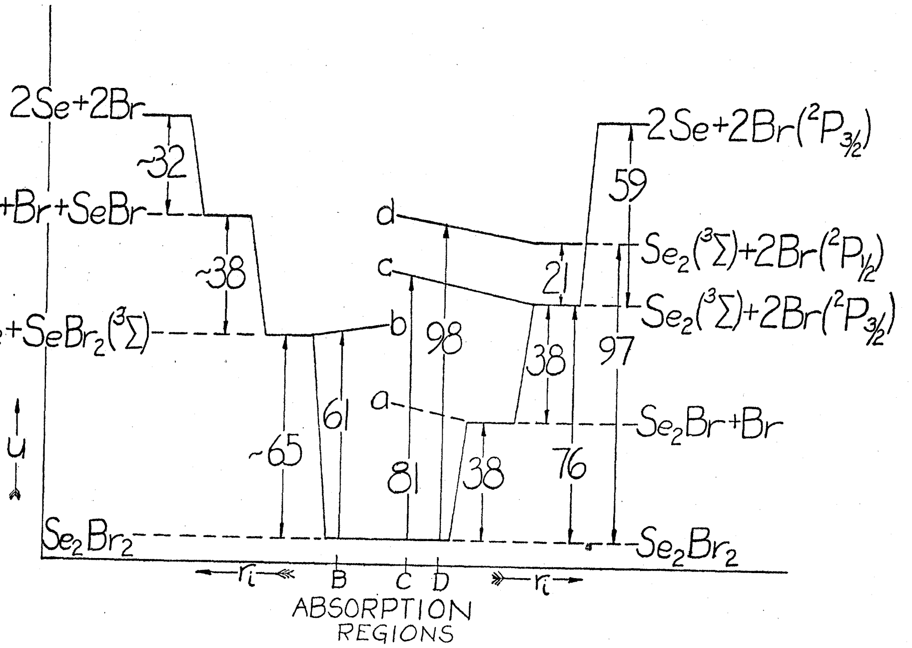

FIG. 5. Energy terms of Se_2Br_2 in the system 2Se+2Br.

to this molecule leads to the ground levels of Se_2Br and finally of Se_2Br_2. Simultaneously the repulsive term (*c*) is formed in the system $Se_2+2Br(^2P_{3/2})$ while a non-bonding term of Se_2Br+Br, similar to the term (*a*) of $SeBr_4$ or SCl_2 has not been found in the absorption spectrum of any molecule of this type. The approach of excited Br atoms in $^2P_{\frac{1}{2}}$ produces only a repulsive level (*d*), 21 kcal./mole higher, but no bonding term. Thus, on the right-hand side, the molecule dissociates by the action of light into $Se_2(^3\Sigma)+2Br(^2P_{3/2})$ or $Se_2(^3\Sigma)+2Br(^2P_{\frac{1}{2}})$. On the left-hand side, however, the approach of an Se atom to the paramagnetic radical $SeBr_2$, possessing two unshared electrons, produces both an unstable term (*b*) and the same stable ground level of the molecule. The transition from the latter to the former, absorption region *B*, corresponds to the photolytic process $Se_2Br_2 \rightarrow SeBr_2(^3\Sigma)+Se(^3P)$. The great wealth of detailed experimental confirmation, such as the regular shift of the absorption spectra towards the red from chlorides to bromides or from sulphur compounds to the corresponding ones of selenium and tellurium, the appearance of the secondary maxima for the bromine compounds, the generally good agreement of thermochemical and spectroscopical values, etc.—leave little doubt but that this interpretation is correct.

The molecules formed by the atom of the sixth group have been discussed at some length in order to give a detailed description of the method in which the experimental data of the absorption spectra of vapors may be utilized. It is now possible to deal with the other families of the periodic table in a shorter manner.

For the halides of the seventh group no absorption spectra of vapors of those polyatomic molecules for which thermochemical data are available could be found in literature. For that reason a few unpublished results of the present author and his collaborators for ICl_3, IBr_3, and IBr_5 are given here. However as this work was interrupted by the outbreak of the war, they are only of preliminary nature, especially since these substances decompose easily. On heating, the bands of the corresponding diatomic molecules appear, the vapor pressure increases rapidly, and the absorption spectrum changes simultaneously. The spectra for which numerical values are given in Table VI have been taken at low temperatures of 30–40°C, without any bands being observable on the plates. But they comprise only some of the maxima; others are indicated on the plates but could not yet be resolved and measured by variation of the experimental conditions. They are, however, sufficient to show that the bond energies again are constant to a first approximation. If the dissociation energy of the diatomic molecules IX is considered as the mean bond energy of IX_3 and IX_5, the long wave-length limits of the regions A and C of ICl_3 clearly indicate the dissociation processes:

$$ICl_3+h\nu(A)=ICl_2+Cl,\quad 59\ \text{(obs.)}\quad 49\ \text{(calc.)}$$
$$ICl_3+h\nu(C)=ICl+2Cl,\quad 98\quad 98$$

and, therefore, in the selective region (B) an excited ICl_2 radical should be one of the dissociation products. The same correlation appears to hold for IBr_3 and IBr_5 too. For both the first long wave-length limit is near to D_0(IBr), the second of IBr_3 near twice that value.

Turning to the trihalides of the fifth group of the type PCl_3, we find in general and particularly in some cases the agreement between thermochemical and optical data much less satisfactory than for similar molecules of group six. This is partly due to experimental conditions. A number of these substances begin to dissociate when heated in vacuum and it is not always easy to obtain sufficient vapor pressure. Hence for some of them only a rather uncertain value of the first long wave-length limit has been measured. Furthermore some of the regions of selective absorption are extremely extensive. This indicates a very steep slope of the repulsive curve, i.e., photo-dissociation takes place with a great surplus of kinetic energy of the products. The first absorption region of PBr_3 for instance covers about 5500 cm^{-1} in the spectrum and a comparison of its long wave-length limit with the bond energy reveals indeed about 30 kcal./mole of kinetic energy. Apparently only the steeper ascent of the repulsive curve can be reached from the low vibrational levels of the ground state, and the pyramidal structure of these molecules may be the reason for it.

TABLE VI. Absorption spectra of halides of VII group atoms. (First line in Å; second line in kcal./mole).

Absorption region	A		B		C	
	LWL	Max	LWL	Max	LWL	Max
ICl_3:	5410	4684	3850	3200	2890	2580
	52		74		98	
IBr_3:	>5330	4630			3110	2605
	<53				91	
IBr_5:	5730	4215				
	49					
	$D_B(I-Cl)=49$				$2D_B(I-Cl)=98$	
	$D_B(I-Br)=42$				$2D_B(I-Br)=84$	

Fortunately the more metallic character of the heavier atoms makes some of the heavier molecules easier to vaporize, and their spectra are well investigated. Here the correlation of long wave-length limits and bond energies, although far from ideal, is clear and convincing and lends conviction also to those cases, where the agreement is much less good. The larger internuclear distances may make it easier to reach the lower part of the repulsive curve.

We begin our consideration with the tri-iodides of Bi and Sb, because the great excitation energy $^2P_{3/2}-{}^2P_{\frac{1}{2}}$ of the iodine atom (21.5 kcal./mole) produces a wide and easily found separation of the regions of selective absorption. Data are listed in Table VII.

For BiI_3 we have calculated a mean bond energy of 44 kcal./mole. The absorption of this amount of energy should break the first bond and cause dissociation into unexcited BiI_2 and $I(^2P_{3/2})$. With 21.5 kcal./mole more, the second repulsive curve could be reached, and the absorption of 65.5 kcal./mole could produce $BiI_2+I^*(^2P_{\frac{1}{2}})$. Two iodine atoms could be separated with 88 kcal./mole, resulting in unexcited $BiI+2I(^2P_{3/2})$, and with 21.5 kcal./mole more, i.e., with 109.5, the molecule would break up in a similar way, but with one excited iodine atom: $BiI+I^*(^2P_{\frac{1}{2}})+I(^2P_{3/2})$. A photolytic process with two excited iodine atoms, i.e., $BiI+2I^*(^2P_{\frac{1}{2}})$ needs $88+(2\times21.5)=131$ kcal./mole. This corresponds to about 2160A and lies already beyond the usual limit of the quartz spectrograph. The same is true for a process producing $Bi+3I$ with 132 kcal./mole. Hence, disregarding the possibility of additional maxima leading to processes with excited radicals, we expect long wave-length limits at 44, 65.5, 88, and 109.5 kcal./mole for the first four regions of selective absorption. We find four regions with 57, 78, 90, and 104 kcal./mole. Of these experimental data, the two first are considerably in excess of the expected ones. This is due to the slope of the repulsive

TABLE VII. Trihalides of V group.

Molecule	D_B	Abs. region	Observed long wave-length limit A	Observed long wave-length limit kcal./mole	Calculated	Dissociation products	Distance of maxima	Ref.
BiI_3	44	*A*	4980[1]	57	44	BiI_2+I	15.5	(23)
		B		78	65.5	BiI_2+I^*	17.1	
		C		90	88	$BiI+2I$		
		D		104	109.5	$BiI+I+I^*$		
$BiBr_3$	~54	*A*	4120[1]	69	54	$BiBr_2+Br$	18	(23)
		B		92	65.5	$BiBr_2+Br^*$		
		C		113	108	$BiBr+2Br$		
$BiCl_3$	69	*A*	3656	77	69	$BiCl_2+Cl$		(24)
			−3350	−84				(25)
		B	2660	107[2]		$BiCl_2^*+Cl$		
SbI_3	50	*A*	4160[1]	68	50	SbI_2+I	20	(23)
		B	3210	88.5	71.5	SbI_2+I^*		
		C	2545	111.5	100	$SbI+2I$		
		D	2225[3]	127.5	121.5	$SbI+I+I^*$		
$SbBr_3$	64	*A*	<5450[4]	>52.2	64	$SbBr_2+Br$		(25)
$SbCl_3$	76	*A*	3256	87	76	$SbCl_2+Cl$	8	(24)
			−2837	−100				
		B	2694[3]	105		$SbCl_2^*+Cl$		
		C	2475	115[2]		$SbCl_2^*+Cl$		
AsI_3	43	*A*	5616	51	43	AsI_2+I		(25)
$AsBr_3$	55	*A*	3248[4]	87	55	$AsBr_2+Br$		(25)
$AsCl_3$	68	*A*	3466	82	68	$AsCl_2+Cl$		(24)
			−2687	−106				
		B	2475	115		$AsCl_2^*+Cl$		
PI_3	48	*A*	3147[4]	90	48	PI_2+I(?)		(25)
PBr_3	63	*A*	3082	92	63	PBr_2+Br	9	(24)
		B	2635	108	74	PBr_2+Br^*		
		C	2440	116	126	$PBr+2Br$		
PCl_3	75	*A*	2957	96	75	PCl_2+Cl		(24)
			−2816	−101				

[1] Butkow gives in his text values for the maxima and the first long wave-length limit only. The subsequent limits are taken from his curves.

[2] Rather low for $BiCl+2Cl$ and $SbCl+2\ Cl$, hence excited radical assumed.

[3] This fourth long wave-length limit has not been dealt with in literature but is clearly indicated in Butkow's curve. A spectrum at higher temperature should show the corresponding maximum in the region of 2400A.

[4] Spectra observed by Trivedi show no structure. Apparently vapor pressure too high, values only very provisional.

curve; as the first two regions of absorption cover about 7500 cm^{-1}, the third about 4800 cm^{-1}, it is clear that the first two repulsive curves are rather steep, resulting in a larger amount of kinetic energy, while the third is much more flat. Furthermore, 44 kcal./mole represents the *mean* bond energy, but we have seen above, that the fission of the same bond requires more energy in a saturated molecule like BiI_3, than in a radical like BiI_2; as far as the first photolytic process is concerned, this value represents the lower limit only.

The conditions are exactly similar for SbI_3, and as a matter of fact for all the molecules of this type. For all of them the first long wave-length limit, or in the case of bromides and iodides, the two first ones, are considerably in excess of the bond energy. But whenever the structure of the absorption spectrum is observed, the subsequent limits come closer to the thermochemical value and the required number of absorption regions is found at approximately the expected energy value. Only for PI_3 this excess energy is very great; but this is one of the spectra which are not yet sufficiently investigated and whose maxima are not yet determined.

This correlation is also supported by the position of the maxima themselves. While the excitation energy is 10.5 and 21.5 kcal./mole for Br and I atoms, respectively, we find the energy difference of the two first maxima to be 15.5 and 20 kcal./mole for BiI_3 and SbI_3, and 9 for PBr_3. This agreement seems to rule out any correlation of the first long wave-length limit to processes involving excited halogen atoms.

The dissociation processes of NOCl and SbOCl present some particularly interesting features because in these cases we have some knowledge about the energy terms of the radicals NO and SbO. The visible and ultraviolet spectrum of NOCl has been investigated several times, by Goodeve and Katz (26) as well as by Natanson (27), and the results of these independent investigations, although different from previous ones, agree excellently among themselves. In addition Price and Simpson (28) have measured the Schumann spectrum. Beginning from the red, NOCl exhibits first a set of predissociated bands beginning at about 6450A = 44 kcal./mole, which ought to be due to a stable excited state of the molecule, which already from its lowest vibrational level onwards is intersected by one or more repulsive terms. These bands become entirely continuous at about 4350A, but according to the absorption curve, no special photolytic significance is attached to this value; the repulsive curve now is above the stable vibrational levels of the excited bonding state. The next long wave-length limit of a second continuous spectrum lies at 2980 to 2900A (according to different measurements) corresponding to 95 to 97 kcal./mole. Two further sets of predissociation bands begin at 2200 and 1700A or 129 and 166 kcal./mole, respectively, and a final continuum has its limit at 1350A = 210 kcal./mole. Altogether five photo-dissociation processes have to be accounted for.

The correlation with thermochemical figures is shown in Table VIII and Fig. 6. The stable terms of NOCl have been left out of Fig. 6 for the sake of simplification, as their origin is unknown at this time. As $D(\text{NOCl})$ is 158 and $D(\text{NO}) = 121$ kcal./mole this leaves 37 for the N−Cl bond, which is the same value as $\frac{1}{3}D(\text{NCl}_3)$. Hence the beginning of predissociation at 44 kcal./mole is due to the breaking of this bond. Predissociation (D) at 166 may be due either to the process $\text{NOCl} \rightarrow \text{N}+\text{O}+\text{Cl} = 158$, or $\text{NOCl} \rightarrow \text{NO}(A^2\Sigma)+\text{Cl}$. As the $A^2\Sigma$ term of NO has an energy of excitation of 125 kcal./mole above the ground level $\text{NO}(X^2\Pi)$, it lies $125+37=162$ kcal./mole above the ground level of NOCl. This term is the lowest excited term yet found experimentally in the NO spectrum. However, we do not only know theoretically that a combination $\text{N}(^4S)+\text{O}(^3P)$ should give rise to a number of other terms, but some of the missing terms indeed are known from the related spectrum, e.g., of $\text{SbO}\cdot\text{NO}(A^2\Sigma)$ does not originate from unexcited N and O atoms and lies in close vicinity to $B^2\Pi$, characterized by its increased dissociation energy and decreased internuclear distance. This term is represented (29) by the b-level of the SbO spectrum and in its vicinity lies the term a, corresponding to $A^2\Sigma$ of NO. But below it lies the so-called d level of SbO, for which no corresponding term is yet known in the NO spectrum. Similarly low lying terms are known in BiO, and a low $^2\Sigma$ term dissociating into unexcited atoms must exist in the NO molecule too. We assume the existence of such a term $Y^2\Sigma$. Estimating from SbO and BiO, we find that its excitation energy most probably will be between 65 and 75 kcal./mole, i.e., about 102 to 107 kcal./mole above the ground level of NOCl. An excited radical $\text{NO}(Y^2\Sigma)$ as product

TABLE VIII. NOCl and SbOCl.

Molecule	Abs. region	Observed predissociation or LWL		Calculated	Dissociation products	
		A	kcal./mole			
NOCl	A	6450	44	37	$\text{NO}(X^2\Pi)+\text{Cl}(^2P)$	
	B	2980–2900	95–97	about 105	$\text{NO}(Y^2\Sigma)+\text{Cl}(^2P)$	$Y^2\Sigma$ estimated to about 70
	C	~2200	~129	130	$\text{O}+{>}\text{NCl}$	
	D	~1700	~166	158	N+O+Cl and/or	
				162	$\text{NO}(A^2\Sigma)+\text{Cl}$	
	E	1350	210		NO (highly excited)+Cl or $(\text{NOCl})^+ + e$	
SbOCl	A	2460	115	>108	SbO+Cl	

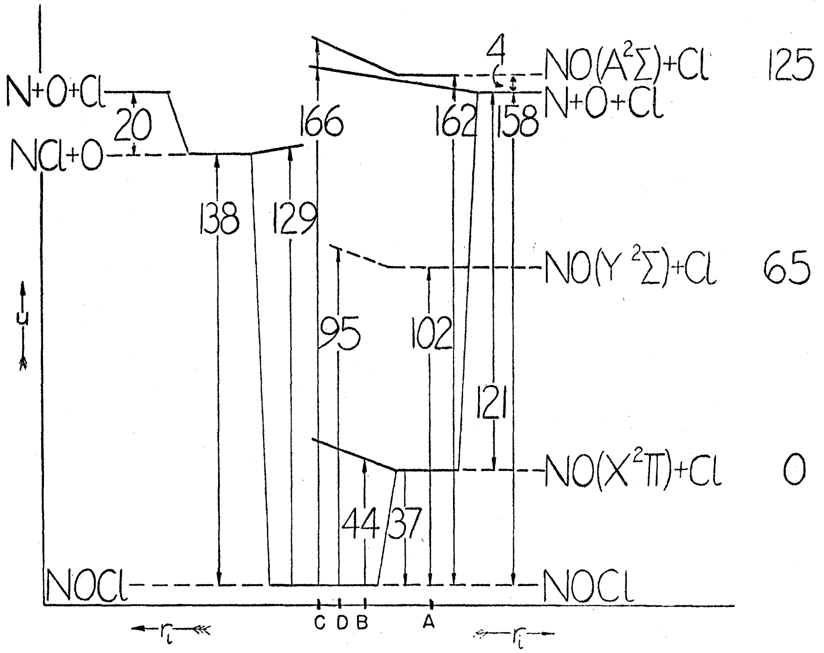

FIG. 6. Energy levels of NOCl in the system N+O+Cl.

then accounts for the long wave-length limit (*B*) at 95 to 97 kcal./mole.

These repulsive terms are marked on the right-hand side of the diagram of Fig. 6. They represent the formation of NOCl by means of the two-step reaction $N+O+Cl \rightarrow NO(X^2\Pi)+Cl \rightarrow NOCl$. As dissociation is the converse of molecule formation, this right-hand side shows the processes involved, if the $N-Cl$ bond is broken first, and the $N=O$ bond later.

The left-hand side of the same diagram pictures the processes which are involved if the $N=O$ bond is broken first and the $N-Cl$ bond later, or, in terms of formation, if NOCl is formed by the two-step $N+O+Cl \rightarrow NCl+O \rightarrow NOCl$. Here again a slight difficulty as to the energy values has to be faced. Formerly first the actual molecule NO was formed, as we know it chemically and spectroscopically. During this second process of formation or dissociation, the molecule NO never exists. Instead the $N=O$ bond is broken not in the free NO radical but in the saturated molecule NOCl. Here the energy of this bond will be different from the dissociation energy of $NO(X^2\Pi)$. Nitric oxide belongs to those diatomic molecules with an odd number of electrons, which are really radicals with free valencies. It could be shown (14) that an excitation of this odd electron increases the dissociation energy of the molecule—e.g., in the term $B^2\Pi$—and the same is true for PO, AsO, and SbO. As "sharing" is also a partial removal of the odd electron, the energy of the $N^{III}=O$ bond is expected to be larger in a completed molecule than in the unexcited radical NO, as has been seen in the example of HO and H_2O discussed above (Section IV). This increase may be 15 percent. Indeed the atomic energy of formation of the grouping $-O-N=O$ is 171 kcal./mole,* the energy of the single bond $N^{III}-O$ is 33 kcal./mole,** leaving approximately 138 kcal./mole for the energy of the double bond $N^{III}=O$ in a molecule with saturated valencies, just about 15 percent more than $D(NO, X^2\Pi)$. This value has been used in the left-hand side of the diagram of Fig. 6. The repulsive term arising from the level NCl+O, 138 kcal./mole above the ground level of NOCl,

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* $\frac{1}{2}D(N_2O_3)=171$, same value in ethylnitrite.

** From hydroxyl amine, and 32 from acetaldoxim; both are calculated with a value $D_B(O-H)=117$, derived from alcohols, while the real bond energy in H_2O is 118, as discussed in Section IV. With a mean value $D_B(O-H) = 109$, that for $D_B(N^{III}-O)$ becomes 41, $D_B(N^{III}=O)$ 130 kcal./mole.

will be responsible for the predissociation bands beginning at 2200A = 128 kcal./mole. Incidentally, the dissociation energy of the radical NCl then is 20 kcal./mole, or about 17 less than the bond energy N – Cl in a saturated molecule. If we do not make this assumption about the N = O bond, the predissociation at 129 kcal./mole is also in agreement with the value of $D(\mathrm{NO}, X^2\Pi) = 121$ for the same photolytic process. This would explain better why $D(\mathrm{NOCl})$ equals the sum of $D(\mathrm{NO})$ plus $\frac{1}{3}D(\mathrm{NCl_3})$, but leaves unexplained the higher value of the N = O bond in N_2O_3 and in organic molecules. As $D(\mathrm{NCl_3})$ seems to be the less certain value, the former figures have been used in Fig. 6.

The atomic energy of formation of SbOCl is 230 kcal./mole. The spectroscopic value (14) of $D(\mathrm{SbO})$ is 122, but this figure is derived by linear extrapolation and therefore is an upper limit only. The dissociation of SbOCl into Cl atoms and actual SbO radicals therefore needs $230 - (<122) = (>108)$ kcal./mole. The one long wave-length limit observed up till now lies at 2475A = 115 kcal./mole, in good agreement.

Molecules formed by atoms of group IV in their lower state of valency are represented by the dihalides of tin and lead, and the absorption spectra of $SnCl_2$, $PbCl_2$, $PbBr_2$, and PbI_2 are well investigated by Butkow (30). Data are listed in Table IX and it is only necessary to discuss one of them in detail. We choose PbI_2, because the small bond energy shifts the spectrum more to longer waves and the large energy difference of the two components of the ground level of the iodine atom causes a better separation of the different absorption regions of the molecule. The dihalides of Pb in the liquid state, it is true, show all the characteristics of electrovalent linkage, such as high boiling point and high conductivity. But as the halides of silver (31) and even such typical salts as potassium and lead nitrate (32) have been shown to be covalent in the vapor state, the same will be true to the dihalides of the lead and tin *a fortiori*. The ionization potential of silver is 173 kcal./mole, the sum of the first two of Pb is 514, so that 257 kcal./mole act against each halogen atom, and we are on safe grounds by assuming a covalent bond as far as the vapor state is concerned.

The absorption spectrum of PbI_2 exhibits four maxima with their long wave-length limits, and the beginning of a fifth is clearly indicated in the ascent of the absorption curve towards the Schumann region. The position of the maxima in A is 5185, 4005, 2878, 2380, i.e., in kcal./mole 55, 70, 99, and 119. The difference of the first and third agrees exactly with the bond energy $D_B(\mathrm{Pb^{II}} - \mathrm{I}) = 44$, those of the first and second and third and fourth, 15 and 20 kcal./mole, respectively, agree quite well with the excitation energy of $\mathrm{I}(^2P_{\frac{1}{2}}) = 21.5$ kcal./mole. The long wave-length limit of the first maximum lies at 5775A = 49 kcal./mole, in excellent agreement with the bond energy. The exact values of the other limits are not given by Butkow, but from his absorption curve it can be seen that these values roughly are (in A) 4760, 3330, 2630, and 2250, i.e., in kcal./mole 60, 85, 108, 126. These figures do not leave any doubt about the primary photolytic processes. On irradiation with light representing one bond energy, the molecule breaks up into PbI + I. With light representing 21.5 kcal./mole more, the iodine is removed in its excited state. With twice the bond energy PbI_2 dissociates into Pb + 2I; but now either one or both the iodine atoms can be excited and hence two more regions of absorption are exhibited 21.5 and 43 kcal./mole higher. For $PbBr_2$ atomic lines of Pb and bands of Br_2 have been observed as fluorescence on irridation with light of absorption region *D*. This is in entire agreement with our interpretation, as it establishes the existence of Pb and one excited Br atom among the products (30*a*).

Similar relations exist for the other molecules. $SnCl_2$ may be mentioned specifically because it possesses two maxima at longer waves which do not fit into the above simple scheme. Its vapor consists largely of dimerized molecules $(SnCl_2)_2$. Butkow makes the energy of polymerization responsible for both of them; the energy of 63.5 kcal./mole however appears to be much too large to be explained this way. In the meantime a band spectrum of $SnCl_2$ has been observed in emission (34) showing an excited term of this molecule precisely 63 kcal./mole above the ground level. A dissociation of $(SnCl_2)_2$ into a normal and excited $SnCl_2$ molecule appears much

TABLE IX. Dihalides of Group IV.

Molecule	D_B	Abs. region	Observed long wave-length limit A	kcal./mole	Calculated	Dissociation products	Distance of maxima kcal./mole	Ref.	Remarks
PbI_2	44	*A*	5775	49	44	$PbI+I$		(30)	
		B	4760	60	65.5	$PbI+I^*$	$B-A=15$		
		C	3330	85	88	$Pb+2I$	$C-A=44$		
		D	2630	108	109.5	$Pb+I+I^*$	$D-C=20$		
		E	2250	126	131	$Pb+2I^*$			
$PbBr_2$	51	*A*	4600	61.5	51	$PbBr+Br$		(30), (30a)	
		B	3700	77	62.5	$PbBr+Br^*$	$B-A=23.5$		
		C	2890	98	102	$Pb+2Br$	$C-A=46.5$		
		D	2270	125	112.5	$Pb+Br+Br$			
$PbCl_2$	77	*A*	3900	72.5	77	$PbCl+Cl$		(30)	
		B	3475	—	—	—			Typical Cl_2-absorption
		C	2950	96		$(PbCl)^*+Cl$			
		D	2530	112					
$SnCl_2$	94	*A*	4480	63.5	~63	$(SnCl_2)_2\rightarrow SnCl_2+SnCl_2^*$		(30), (33), (34)	
		B	3712	—	—	—			Typical Cl_2-absorption
		C	2858	100	94	$SnCl(^2\Pi_{1/2})+Cl$			
		D	2380	119	101	$SnCl(^2\Pi_{3/2})+Cl$			

more plausible, leaving for the energy of polymerization a few kcal./mole only.

The second of these two maxima is in the exact position of the Cl_2 absorption; chlorine gas exhibits a continuous absorption only on account of the position of the potential curve of the excited term. Again the second maximum of PbCl, although not so marked, has the wavelength of the Cl_2 maximum, and we have disregarded these two maxima in Table IX.

Sometimes absorption maxima have been measured at such wave-length as to indicate that an excited radical is one of the dissociation products. In general such excited terms are not yet known. Again the beginning of a fourth absorption region is clearly marked in the absorption curve of $SnCl_2$, but in this case the band spectrum of the radical SnCl has been observed and it is known that it really possesses an excited term close to its ground level. The latter is a $^2\Pi$ term and hence has two components $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. The excitation energy of the latter is 2360 cm^{-1} or about 7 kcal./mole. This does not agree too well with the difference of 19 kcal./mole of the long wave-length limits *C* and *D* of $SnCl_2$, but as their determination is uncertain, and the repulsive curves may vary in slope, it is still sufficiently close. Also a continuous emission spectrum of $SnCl_2$ has been observed (34), besides the band spectrum mentioned above. It shows two regions of emission with maxima of roughly 4500 and 3100A, corresponding to 63 and 92 kcal./mole, almost identical with the long wave-length limits of absorption region *A* and *C*. There are reasons to believe that for continuous spectra observed in *emission* the maxima and not the long wave-length limits correspond to the energy difference of the electronic states. At this time, however, it is impossible to say whether this agreement is accidental or not.

Stable polyatomic molecules formed by atoms of groups II and III are not known for lower valence states of the central atom. In those of the types BeX_2 and BX_3, the maximal valency of the central atom comes into play. Attention therefore may now be drawn to this second large class of molecules, in which the central atom is in its maximal valence state, and in which not only its *p*-electrons but also its *s*-electrons are chemically active.

VI. SPECTRA AND DISSOCIATION PROCESSES OF MOLECULES OF MAXIMAL VALENCY

When turning to molecules formed by a central atom in its maximal state of valency, we find conditions very much changed. First of all, the atomic energy of formation of such molecules cannot be calculated from the bond energies as determined for the corresponding molecules of lower valence states.

Thus, for example, $D_B(S^{IV}=0)=\frac{1}{2}D(SO_2)$ is 123 kcal./mole; however $D(SO_3)$ is not three times this value, namely 369, but 327 kcal./mole only. On the other hand it is possible to divide these energies for such molecules into new additive contributions, as is well known for organic molecules. Such values as $\frac{1}{4}D(CH_4)=94.9$ kcal./mole remain almost rigorously constant throughout and similar values can also be derived for inorganic molecules of maximal valency.

This is not surprising, as the energies appear to fall in line with other additive molecular constants. For all of them different sets of values have to be derived according to the state of valency of the central atom. Thus the contribution to the molecular volume in terms of the parachor is 49.8, 29.5, 13.9, respectively, for di-, tetra-, and hexavalent sulphur, while the electric moment is 1.6 for the $S^{IV}=O$, and 3.9 for the $S^{VI}=O$ bond (1). In its lower state of valency only the p-electrons of sulphur are employed for chemical binding, while in the hexavalent state the electrons of the closed groups $3s^2$ are made use of in addition to the p-electrons. This fact accounts for the different behavior and properties as far as additive molecular constants are concerned. For the interpretation of the spectra, however, further difficulties arise. Sulphur trioxides (35, 36) for instance, possesses a region of selective absorption between 3300 and 2600A, and on irradiation with light of such wave-lengths, an oxygen atom is liberated. The beginning at 3300A corresponds to 86.7 kcal./mole, which figure does not in the least agree with $\frac{1}{3}D(SO_3)=109$. But it does agree nevertheless with $D(SO_3)-D(SO_2)=327.3-246.1=81.2$ kcal./mole, indicating that for this type of molecule the photo-dissociation often does not consist in the breaking of a bond but the reconversion of the molecule into one of lower valency. As a matter of fact, it will be seen below that neither of the two figures 81.2 and 109 represents the true energy of the $S^{VI}=O$ bond, as measured by adiabatic dissociation, and a different type of mechanism has to be looked for in order to understand the photolytic process and the absorption spectrum corresponding to it.

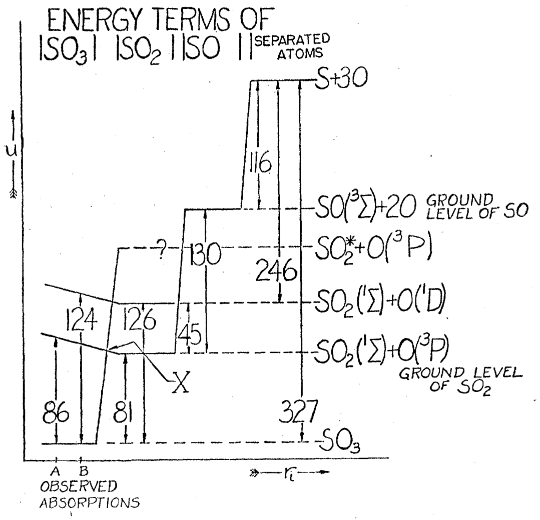

FIG. 7. Energy terms of SO_3 in the system S+3O.

This mechanism becomes clear, if we consider the successive formation of SO_3 in the system S+3O at various internuclear distances (37). The ground level of SO_3 is only one of the many electronic terms of this system and it is possible to show in which way it is related to some of them. In the simplified Franck-Condon diagram of Fig. 7 various electronic levels of the same system are given, beginning with S+3O at the right, followed by SO+2O, SO_2+O, and finally by SO_3. In this system, the approach of unexcited $S(3s^23p^4-{}^3P)$ and one of the unexcited atoms $O(^3P)$ leads to the formation of $SO(^3\Sigma)$, whose ground level is 116.5 kcal./mole lower than that of the separated atoms. The approach of the second unexcited O atom leads to the formation of SO_2, with a ground level $^1\Sigma$ which is 246.1 kcal./mole lower than S+3O, and 129.4 lower than $SO(^3\Sigma)+2O(^3P)$.

But the formation of SO_3—and this is the crucial point—does not follow the same scheme, because it cannot be brought about by the combination of unexcited SO_2 in its ground state $^1\Sigma$ plus unexcited oxygen atoms in the ^3P term. The electronic configuration of the sulphur atom is $3s^23p^4$ and its di- and tetravalent state involve unexcited sulphur atoms. To make sulphur hexavalent an excitation to a $3s3p^5$ term is indispensable because the completed group $3s^2$ does not possess bonding power, but acts repulsively only, according to the Heitler-London pair bond theory of valency.* The ground level of SO_3 therefore does not belong to the same series as those of the SO and SO_2 molecules. The normal states of these latter compounds are formed by combination of unexcited atoms and molecules, whereas the adiabatic dissociation of unexcited SO_3 involves *excited* products. Experimentally this is quite certain, as both molecules SO_2 and SO_3 are diamagnetic, which a molecule formed by the combination of $SO_2({}^1\Sigma)$ plus $O({}^3P)$ could not be. All vectors being counterbalanced already in the singlet level of SO_2, there are no free vectors left to neutralize those of the triplet term of oxygen to yield a singlet term of SO_3.

Hence on the approach of unexcited O atoms towards unexcited SO_2 no chemical union but an elastic collision takes place. This is represented in the diagram by a repulsive curve without a stable minimum. The products of *adiabatic* dissociation of SO_3 most certainly are either $SO_2({}^1\Sigma)+O^*$ or SO_2^* plus $O({}^3P)$ and no direct experimental evidence exists at present which permits us to decide between these two possibilities. But another low term of the system can be identified as belonging to unexcited SO_2 and excited $O({}^1D)$. Theoretically, indeed, chemical union is not possible unless the original s^2 group of sulphur is split previously. Therefore in the diagram the ground level of SO_3 is connected with a level involving an excited SO_2 molecule. The adiabatic dissociation of this state finally involves a sulphur atom in the $3s3p^5$ configuration. The known state $3s3p^5-{}^3P$ appears to be identical with the lowest term of this configuration. It has an energy of excitation of 8.9 ev = 205 kcal./mole which added to $D(SO_3)$ yields a value of 532 kcal./mole for the adiabatic energy of dissociation of SO_3 into $S(3s^3p^5-{}^3P)+3O({}^3P)$. For the mean bond energy $D_B(S^{VI}=O)$ one-third of this figure (177 kcal./mole) is taken. This term of excited SO_2, therefore, lies approximately 177 kcal./mole above the ground level of SO_3 or 96 kcal./mole above that of SO_2.

The existence of the repulsive potential curve $SO_2({}^1\Sigma)+O({}^3P)$ is indicated by the absorption spectrum. The long wave-length limit of continuous absorption has been measured by various authors and lies at an energy value of about 80 to 85 kcal./mole, slight differences being accounted for by the experimental difficulty of determining the value associated with the lowest state of vibration. This result, therefore, agrees very well with the energy difference $D(SO_3)-D(SO_2)=81.2$ kcal./mole. Kornfeld directly used the SO_2 absorption bands as an indicator of the photo-dissociation of SO_3. Moreover, Dutta found the beginning of the second region of selective absorption at 124 kcal./mole. The difference between the two long wave-length limits agrees with the excitation energy of the ${}^1D$ term of O, which is 1.95 ev or 45.1 kcal./mole. Similarly, the long wave-length limit of the continuous absorption spectrum of TeO_3 lies at 62.1 kcal./mole and agrees with the thermochemical energy difference $D(TeO_3)-D(TeO_2)=64$ kcal./mole. Again that of SO_2Cl_2 at 108.6 kcal./mole agrees with the value of $D(SO_2Cl_2)-D(SOCl_2)=101.7$ and pyrosulphuryl chloride $S_2O_5Cl_2$ shows a long wave-length limit of a similar value, i.e., 113 kcal./mole. For all of them the long wave-length limits of the subsequent maxima agree well with the excitation energies of $O({}^1D)$, showing that indeed an unexcited O atom is liberated in the long wave-length region. For TeS_3 no thermochemical data are known, but again the energy differences of the three observed long wave-length limits agree with the excitation energies of $S({}^1D)$ and $S({}^1P)$, its two lowest terms. (Table X.)

The new mechanism, which distinguishes molecules of maximal valency from those of lower valence state, may be described as follows:

On the approach of an atom towards a saturated molecule of lower valency (i.e., SO_2) in its ${}^1\Sigma$ state, no molecular formation takes place and no stable electronic level is created. The resulting electronic term is a repulsive one of the higher molecule (i.e., SO_3). The energy difference (i.e., 81.2 kcal./mole) between the ground levels of the molecule of higher valency (i.e., SO_3) and the corresponding one of lower valency (SO_2) is less than the bond energy of the latter, 123, and much less than the true bond energy of the former, 177. Therefore the new unstable electronic term will often be the lowest excited term of the higher molecule (SO_3) and will often be the first one to be reached by absorption of light energy. If so, the molecule will

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* Cf. the discussion in reference 37 and literature mentioned there.

Table X. Sixth group molecules.

Molecules	Absorption region	Observed long wave-length limit A	Observed long wave-length limit kcal./mole	Calculated	Dissociation products	Ref.	Remarks
SO_3	*A*	3300	86.7	81.2	$SO_2(^1\Sigma)+O(^3P)$	(35), (36)	SO_2 and O observed as photolytic products
	B	2300	123.5	126.3	$SO_2(^1\Sigma)+O(^1D)$		
SO_2Cl_3	*A*	2600	109	101.7	$SOCl_2(^1\Sigma)+O(^3P)$	(17)	
TeO_3	*A*	4600	62	64	$TeO_2(^1\Sigma)+O(^3P)$	(38)	
	B	3000	94.5	109	$TeO_2(^1\Sigma)+O(^1D)$		
TeS_3	*A*	4900	58	X	$TeS_2(^1\Sigma)+S(^3P)$	(39)	
	B	3260	87	$X+26.2$	$TeS_2(^1\Sigma)+S(^1D)$		
	C	2300	123.5	$X+41$	$TeS_2(^1\Sigma)+S(^1P)$		(?)

dissociate and the two bonds formed by the original two *s*-electrons of the central atom, will be fissured. The energy necessary for this process will often be less than one bond energy, while that energy will be regained, originally needed to split the original non-bonding s^2 group of the central atom.

Hence in such cases the photolytic process and the absorption spectrum are governed not by a bond energy D_B, but by an energy difference such as $D(SO_3)-D(SO_2)$. This is an energy of reaction, and as a dissociation takes place after all, we shall denote such energy differences by the symbol D_R.

The reverse process, namely the formation e.g., of SO_3 will follow the same lines, and the SO_2 molecule must not be fully excited to its triplet term. The oxidation of SO_2 may be described as follows, provided the process takes place with sufficient kinetic energy of the particles: On the approach of an unexcited O atom to unexcited SO_2, the system will follow the repulsive curve until the point of intersection (X in the diagram) with the potential curve of the ground level of SO_3 is gained. The energy difference between X and the term SO_2+O (i.e., the ground level of SO_2) will form part of the energy of activation, together with $D(O_2)$ and other contributions.

Of the molecules formed by the fifth group atoms, the spectra of the two halides PCl_5 and PBr_5, of the two oxides N_2O_5 and P_2O_5, and of $POCl_3$, have been investigated. Furthermore, the spectra of P_2S_5 and P_2Se_5 are known, but no thermochemical data are available, and a rough value of the first long wave-length limit of $SbCl_5$ also has been determined. The latter has been observed at too high vapor pressure and the energy value therefore is too low for the vibrationless molecule. In the following Table XI, the first long wave-length limits are compared with two sets of thermochemical data. First the energies of reaction are calculated according to $D_R=D(PCl_5)-D(PCl_3)$, etc. Secondly, the energy to fissure the s^2 group of the atoms, i.e., the excitation energy $s^2p^3\rightarrow sp^4$ is added to the energy of dissociation and the same divided into equal parts, considered to be the mean bond energies. The excitation energies (E) are about 250, 170, and 135 kcal./mole, respectively, for N, P, and Sb. Hence we obtain $\frac{1}{5}[D(N_2O_5)+2E(N)]=\frac{1}{5}(459\div 250)=192=D_B(N^V=O)$. The difference between the double and two single bonds is neglected in this procedure,* but it is sufficient to obtain the order of magnitude.

If the photolytic reaction follows this course, and is governed by a true bond energy D_B (i.e., defined by adiabatic dissociation along the vibrational levels of the ground term), the products will be an unexcited atom, like O or Cl, and a radical like $-OCl_4$ or $=N_2O_4$. The latter will be in an excited state and in a doublet or triplet term, respectively. This has been indicated in Table XI by an asterisk for excitation and symbols ^2X and ^3X, respectively. If, however, the photo-dissociation consists in the reconversion of the molecule into one of lower valency, it is governed by the energy of reaction D_R, for example $D(N_2O_5)-D(N_2O_3)=459.4-323.6=135.8$,

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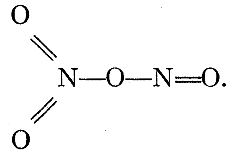
* The same is true for the value of $\frac{1}{2}D(P_2O_3)$; no reliable thermochemical data being available, $D(P(OH_3))$ minus $3D_B(O-H)$ has been used. D_R therefore is a lower limit in this case.

TABLE XI. Fifth group molecules.

		Observed LWL		Possible dissociation processes (calculated):					
Molecule	Abs. region	A	kcal./mole	D_R	Dissociation products	D_B	Dissociation products	Remarks	Reference
N_2O_5	*A*	3800	74	68	$N_2O_4(^1\Sigma)+O(^3P)$	192	$N_2O_4^*(^3X)+O(^3P)$	(*a*)	(40), (38)
P_2O_5	*A*	2530–2270	112–125	~124	$P_2O_4(^1\Sigma)+O(^3P)$	225	$P_2O_4^*(^3X)+O(^3P)$		(24)
P_2S_5	*A*	3180	89.5	*X*	$P_2S_4(^1\Sigma)+S(^3P)$			(*b*)	(24)
	B	2300	123.5	*X*+26	$P_2S_4(^1\Sigma)+S(^1D)$			(*c*)	
P_2Se_5	*A*	3420	82.5	*X*	$P_2Se_4(^1\Sigma)+Se(^3P)$			(*b*)	(41)
	B	2534	112	*X*+27	$P_2Se_4(^1\Sigma)+Se(^1D)$				
PCl_5	*A*	2625	108	78	$PCl_3(^1\Sigma)+2Cl(^2P)$	95	$PCl_4^*(^2X)+Cl(^2P)$		(24)
PBr_5	*A*	3146	99	60	$PBr_3(^1\Sigma)+2Br(^2P_{3/2})$	84	$PBr_4^*(^2X)+Br(^2P_{3/2})$		(24)
$SbCl_5$	*A*	≪4130	≪69	73	$SbCl_3(^1\Sigma)+2Cl(^2P)$	88	$SbCl_4^*(^2X)+Cl(^2P)$		(25)
$POCl_3$	*A*	2250	126	127	$PCl_3(^1\Sigma)+O(^3P)$	95	$POCl_2^*(^2X)+Cl(^2P)$		(24)

(*a*) The long wave absorption recorded in (38) is due to N_2O bands under high pressure; cf. reference (24).
(*b*) The fair agreement of the difference between the two long wave-length limits with the excitation energy of S and Se, respectively, can be correlated to either process. But the low value of the first limit can be in agreement only with D_R, but not with D_B.
(*c*) The long wave-length limit at 4900A recorded in reference (24) is doubtful, cf. reference (41).

and one-half of it gives $D_R=68$. The products are an O or two halogen atoms and a molecule such as



The latter is unexcited and in its $^1\Sigma$ ground state.

As far as the two oxides and phosphorous oxichloride are concerned, this comparison clearly shows the same mechanism acting as in SO_3. The dissociation does not take place according to any bond energy but by excitation to the repulsive curve produced by the approach of oxygen atoms to a molecule of lower valency in its $^1\Sigma$ state with saturated valencies. For the pentahalides the result is not quite certain. The recorded value of the beginning of absorption of $SbCl_5$ is extremely doubtful. PCl_5 and particularly PBr_5 make it probable that here rupture of one single linkage takes place, according to its bond energy. This is the more probable since for PBr_5 a second region of absorption has been found, indicating one excited Br atom as one of the dissociation products, but no trace of a third maximum, produced by two excited Br atoms has been discovered. This, however, is not quite conclusive and an investigation of the near Schumann spectrum of such molecules could decide the question definitely. For the time being we shall assume that oxides and halides of this group dissociate according to different mechanisms.

This difference of behavior resembles the other one already observed e.g., for $SeOCl_2$ and $SeCl_4$, and, if true, most probably will be due to the geometrical structure of these molecules. They form trigonal bipyramids and such as e.g., P_3AsCl_2 do not possess a dipole moment. Hence the chlorine atoms form the apices, and a reaction such as $P_3As+2Cl$, and also PCl_3+2Cl probably only takes place when the two Cl atoms approach the parent molecule from different sides. Hence the surfaces of the energy levels in space will have such a position that the level PCl_3+2Cl cannot be reached from that of PCl_5 without structural rearrangement and change of internuclear distances.

The most interesting application of the second type of photolytic process will be among molecules formed by atoms of group IV, because almost all organic molecules contain *C* in its maximal state of valency. However, those of tetravalent tin will be considered first, because here thermochemical data are more complete.

If the so-called "lone pair" of electrons of a molecule SnX_2 is chemically inert, because it represents the s^2 group of electrons which are paired among themselves and do not possess bonding power in the Heitler-London theory, we may expect conditions as described in the diagram of Fig. 8 for $SnBr_4$. The lowest excited energy level of SnX_4 is the repulsive curve $SnX_2(^1\Sigma)+2X$, formed on the approach of two X atoms towards SnX_2 in its diamagnetic ground level. Absorption of light will rupture two of the four bonds and the first long wave-

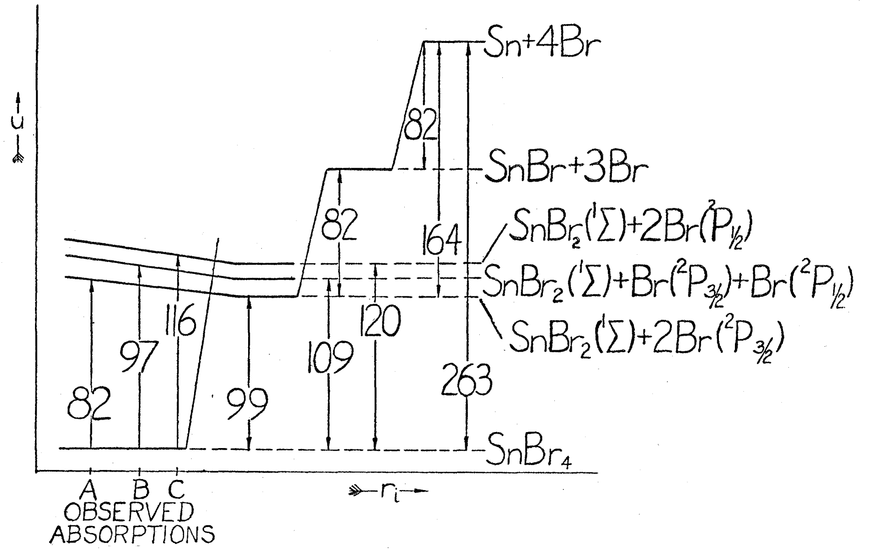


FIG. 8. Energy terms of $SnBr_4$ in the system $Sn+4Br$.

length limit should be near the value of the energy of reaction $D_R = D(SnX_4) - D(SnX_2)$. Furthermore, for the bromides and iodides we expect two additional regions of absorption, i.e., three maximal in all due to the three processes producing two unexcited, one unexcited, and one excited, and finally two excited halogen atoms, respectively. The differences of the three limits and the three maxima ought to be of the order of 10.5 and 21 kcal./mole, respectively, for Br and I.

We find indeed (cf. Table XII) that $SnCl_4$ possesses only one, $SnBr_4$ and SnI_4 three maxima each. The absolute values of the long wave-length limits agree best for $SnCl_4$, where all thermochemical data both of $SnCl_4$ and of $SnCl_2$ are available, slightly less well for the others, where certain data, particularly the heat of vaporization, had to be computed. The spectrum of SnI_4 has been taken with a very long cell (1.5m) and for that reason the recorded value of the first beginning is too low for the vibrationless molecule. The heat of formation of this molecule had to be computed, as it is not known at all. This was done on the basis of

$$D(SnX_4) : D(SnX_2) = 5:3,$$

according to the precedence of the tin chloride. At the time when the spectrum of $SnBr_4$ was investigated, also $Q(SnBr_4)$ was not known and $D(SnBr_4)$ was extrapolated in the same way to ~ 265 kcal./mole. The value now calculated from Bichowsky and Rossini's $Q = 94.8$ is 263. We mention this to show that this and a similar extrapolation necessary for carbon halides can be undertaken with some confidence.

In general, i.e., considering uncertainties connected with measurements of continuous spectra, the agreement with thermochemical data and the differences of the maxima among themselves is quite good. The mere fact that three such regions of absorption are observed makes it certain that two halogen bonds are ruptured simultaneously, and no other explanation is possible for such energy values. Furthermore, Terenin (46) observed the iodine bands in fluorescence on irradiating SnI_4 with light of region *B* or *C*, but not with wave-lengths of region *A*. This shows excited iodine atoms as products for these two regions, but not for region *A*, in exact agreement with the above prediction.

The system of electronic terms of an organic molecule like CH_4 should be essentially similar to those of SnX_4. Carbon as a fourth group atom is divalent only as long as it is in its unexcited configuration ($2s^2 2p^2 - {}^2P$). On the approach of two hydrogen atoms it will form a molecule CH_2 in a ${}^1\Sigma$ state and the approach of two further hydrogen atoms towards this unexcited molecule will not lead to the formation of a molecule CH_3 or CH_4; only a repulsive term is produced during this process. The formation of a molecule CH_4 is only possible in those terms, which originate in the excited atom C (sp^3). This is a definite conclusion from the Heitler-London concept, which not only is *also* correct but furnishes the best description of the molecule precisely at those large interatomic distances where the reactions begin.

The atomic energy of formation of CH_4 is 379.8 kcal./mole. If we assume that the energy levels are still similar to those of $SnCl_4$ and again apply the extrapolation

$$D(SnX_4):D(SnX_2)=D(CH_4):D(CH_2)=5:3,$$

we obtain for the atomic energy of CH_2 the value of 228 kcal./mole. It is true that CH_2 is not known as a molecule which is stable in the sense of the chemist. This, however, is not due to any intrinsic difference between Sn and C, but simply to the enormous energy of sublimation of carbon. The above value of $D(CH_2)$ leads to an energy of formation, which is vastly negative: $Q(CH_2)=-41$ kcal./mole. In other words: because the crystal lattice of carbon is formed by covalent interatomic forces, its energy cannot be overcome by the energy liberated in the formation of two C–H bonds, but only when four of them are formed. That is the reason why so few molecules of divalent carbon are known, but it is of purely thermodynamical nature and has no bearing on the relative position of the energy levels of the molecules CH_4 and CH_2. As such a level exists for $SnCl_4$, $SnBr_4$, and SnI_4, a repulsive level $CH_2(^1\Sigma)+2H$ also should exist for CH_4. Its position will be $D(CH_4)-D(CH_2)=380-228=152$ kcal./mole above the ground level of CH_4.

Hardly anything is known about the continuous absorption spectrum of CH_4, which lies far in the Schumann region. We, therefore, begin our considerations with that molecule whose spectrum is shifted most to longer waves on account of its low bond energies, namely CI_4.

From $D(CI_4)=184$ kcal./mole, exactly the same extrapolation leads to $D(CI_2)=111$. By absorbing the difference, namely 73 kcal./mole the molecules CI_4 should be able to dissociate into $CI_2(^1\Sigma)$ plus two unexcited $I(^2P_{3/2})$ atoms. If the products of dissociation are one or two excited atoms $I(^2P_{\frac{1}{2}})$, the minimum energy is increased by 21.5 and 43 kcal./mole, respectively. Hence, on account of a strict application of the Heitler-London theory we expect *three* regions of selective absorption, with long wave-length limits corresponding to 73, 94.5, and 116 kcal./mole, respectively. The molecule CI_4 exhibits *three* regions of selective absorption at 3930A = 72 kcal./mole, 3177A = 89.5 kcal./mole, and 2795A = 102 kcal./mole. As our calculation was based on the rather long extrapolation from $SnCl_2$, as it further includes some thermochemical values of not too high accuracy, and as the long wave-length limit is never very accurately defined, the agreement may be called very good indeed. As a matter of fact, the mere existence of three regions of absorption with differences of long wave-length limits and maxima approximately corresponding to the

TABLE XII. Tin tetrahalides.

Molecule	Abs. region	Observed maxima A	Difference of maxima in kcal./mole	Observed LWL A	Observed LWL kcal./mole	Calculated D_R	Dissociation products	Reference
$SnCl_4$	*A*			~2450	116	121	$SnCl_2(^1\Sigma)+2Cl$	(42), (43), (44)
$SnBr_4$	*A*	3063	11	3471	82	99	$SnBr_2(^1\Sigma)+2Br(^2P_{3/2})$	(42)
	B	2728		2915	97	109.5	$SnBr_2(^1\Sigma)+Br(^2P_{3/2})+Br^*(^2P_{1/2})$	(44)
	C			2442	116	120	$SnBr_2(^1\Sigma)+2Br^*(^2P_{1/2})$	
SnI_4	*A*	3570	21	4700	60	87	$SnI_2(^1\Sigma)+2I(^2P_{3/2})$	(45)
	B	2800	15	~3000	~94	105	$SnI_2(^1\Sigma)+I(^2P_{3/2})+I^*(^2P_{1/2})$	
	C	2450		~2350	~124	129	$SnI_2(^1\Sigma)+2I^*(^2P_{1/2})$	

Additional first long wave-length limits have been recorded for molecules like $SiCl_4$, $SiBr_4$, and others, with such long absorbing layers and high pressures that they cannot be taken into account for the vibrationless molecules.

The long wave-length limit at 3400A recorded for $SnCl_4$ in (42) is due to Cl_2 gas, cf. reference (44).

The long wave-length limits *B* and *C* of SnI_4 have been roughly estimated from the reproduction of the plate in reference (45).

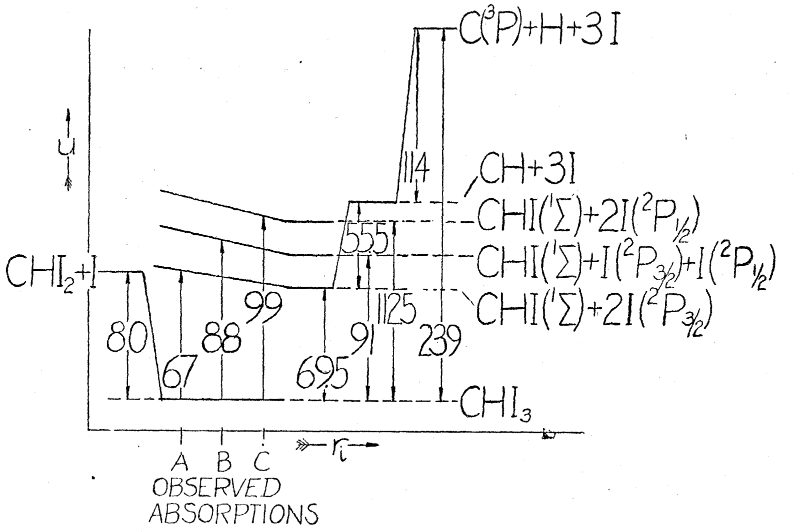


FIG. 9. Energy terms of CHI_3 in the system $C+H+3I$.

excitation energy of iodine, the mere existence of *three* such maxima makes it perfectly clear that *two* such atoms are liberated simultaneously and no other interpretation of the spectrum is therefore at all possible.

The photolytic process of iodoform is similar to that of carbon tetra-iodide. There are two possibilities for the same mechanism, the products may be $CHI(^1\Sigma)+2I$ or $CI_2(^1\Sigma)+H+I$. The repulsive curve however, which corresponds to the former must be the lower one. In order to obtain its position, we take as the bond energies of the molecules formed by divalent carbon one-half of the corresponding energies of formation:

$$D_B(C^{II}-H)=\tfrac{1}{2}D(CH_2)=114$$

and

$$D_B(C^{II}-I)=\tfrac{1}{2}D(CI_2)=55.5.$$

The repulsive curve in question then lies as shown in Fig. 9 approximately at

$$D(CHI_3)-[D_B(C^{II}-H)+D_B(C^{II}-I)]$$
$$=239-(114+55.5)=69.5.$$

Three regions of absorption are expected with long wave-length limits corresponding to 69.5, 69.5+21.5=91 and 69.5+2×21.5=112 kcal./mole. Observed are three long wave-length limits at 3780, 3229, and 2872A, i.e., 67, 88, and 99 kcal./mole, respectively. The agreement again is excellent. It is not necessary to discuss the spectra of the other carbon halides. The data are all collected in Table XIII. From the atomic energies of formation of the CX_4 molecules those of CBr_2 and CCl_2 have been extrapolated to 149 and 177 kcal./mole, respectively, by means of the same ratio between $D(SnCl_4)$ and $D(SnCl_2)$. Half of these values have been used as bond energies $D_B(C^{II}-X)$, and all calculations carried out exactly as discussed for CI_4 and CHI_3.

Attention may be drawn first of all to the fact that those molecules containing only *one* halogen atom, like CH_3I, exhibit only two maxima. They correspond to the products $CH_2(^1\Sigma)+H+I$ and $CH_2(^1\Sigma)+H+I^*$. A third maximum cannot be expected. It would involve an excited hydrogen atom, but the energy of the first line of the Lyman series is about 233 kcal./mole and places such an absorption far into the Schumann region. For the chlorides the excitation energy of $^2P_{\frac{1}{2}}$ of Cl is so small that the maxima must overlap and cannot be separated. At the same time the higher energies shift this combined maximum into the Schumann region and only the beginning of the absorption can be measured with the quartz spectrograph. As always when the structure of the continuous spectrum cannot be observed, the determination of the long wave-length limit then becomes more difficult and the data of different observers vary according to vapor pressure and length of absorbing layer. In such cases we have given in Table XIII—first the value which appears to be the best one according to experimental conditions and the other ones only in kcal./mole in parenthesis. These "best" values are mostly those of Henrici (47), but that of Hukumoto (43) for CH_3I, because he observed both absorption regions.

The agreement with calculated data in general is quite good and becomes the better the more the spectrum is shifted towards the more accessible long waves. Only the methylene halides CH_2X_2 are an exception. The position of their energy levels may of course be different from those of the other molecules, for some reason. It is, however, more probable that this discrepancy is due to the thermochemical values as they apparently are by far less accurate than those of most of the other molecules of this series.

Before discussing other organic molecules, attention may be drawn to the relation of their atomic energies of dissociation to their bond energies.

The heat of formation of a substance, e.g., formaldehyde, from the atoms (D) is obtained by calculating the heat of formation from the elements (24.5 kcal./mole) from the heat of combustion and applying Born's cycle. All the D values used have been obtained by this method. In the classical way, these D values may be divided into contributions (d) of individual bonds. Starting from methane, a quarter of the total D is ascribed to each of the $C-H$ bonds. According to Rossini's most recent measurements, $D(CH_4)$ amounts to 379.9 kcal./mole, hence $d(C-H)=95$ kcal./mole. These d values are fundamentally different from the bond energies. In the system $C+4H$, only the energy differences between the ground level of the molecule CH_4, and the level of the separated unexcited atoms (carbon bivalent!) is repre-

TABLE XIII. Carbon halides.

Molecule	Abs. region	Observed long wave-length limit		Calculated	Dissociation products	Ref.
		A	kcal./mole			
CI_4	*A*	3930	72	73	$CI_2(^1\Sigma)+2I$	(44)
	B	3177	89.5	94.5	$CI_2(^1\Sigma)+I+I^*$	
	C	2795	102	116	$CI_2(^1\Sigma)+2I^*$	
CHI_3	*A*	3780	67	69.5	$CHI(^1\Sigma)+2I$	(44)
	B	3229	88	91	$CHI(^1\Sigma)+I+I^*$	
	C	2872	99	112.5	$CHI(^1\Sigma)+2I^*$	
CH_2I_2	*A*	3499	81	56	$CH_2(^1\Sigma)+2I$	(43), (44), (47), (49)
	B	2640	107	78.5	$CH_2(^1\Sigma)+I+I^*$	
	C	2365	120	100	$CH_2(^1\Sigma)+2I^*$	
CH_3I	*A*	2952	96(102, 90)	103	$CH_2(^1\Sigma)+H+I$	(43), (42), (48)
	B	2110	134	124.5	$CH_2(^1\Sigma)+H+I^*$	
CBr_4	*A*	2932	97	100	$CBr_2(^1\Sigma)+2Br$	(44)
	B	2453	116	110.5	$CBr_2(^1\Sigma)+Br+Br^*$	(47)
$CHBr_3$	*A*	2750	103	92.5	$CHBr(^1\Sigma)+2Br$	(43), (44), (47)
	B	2497	114	104	$CHBr(^1\Sigma)+Br+Br^*$	
	C	2195(?)	129	114.5	$CHBr(^1\Sigma)+2Br^*$	
CH_2Br_2	*A*	2507	113	85 125	$CH_2(^1\Sigma)+2Br$, or $CHBr(^1\Sigma)+H+Br$	(47)
CH_3Br	*A*	2415	117(123, 96)	117	$CH_2(^1\Sigma)+H+Br$	(43), (47), (48)
CCl_4	*A*	2300	124(117, 121)	119	$CCl_2(^1\Sigma)+2Cl$	(43), (44), (47)
$CHCl_3$	*A*	2126	134(121, 128)	115	$CHCl(^1\Sigma)+2Cl$	(43), (44), (47)
CH_2Cl_2	*A*	2090	136(123)	110 140	$CH_2(^1\Sigma)+2Cl$, or $CHCl(^1\Sigma)+H+Cl$	(43), (47)
CH_3Cl	*A*	1995	143(151, 125)	131	$CH_2(^1\Sigma)+H+Cl$	(43), (47), (48)

sented by D, but adiabatic dissociation of methane, which according to the terminology used here measures the bond energies, leads to a level in which the carbon atoms are excited and therefore tetravalent.

The energy of excitation of the C atom to the term $sp^3-{}^5S$ is 4.3 ev = 100 kcal./mole. Of the configuration sp^3 this is the lowest term, and the others will not be much higher. For each C−H bond, 100/4 = 25 kcal./mole have to be added to the d value, giving 120 kcal./mole for the true bond energy of $C^{IV}-H$. It should be understood that this is a rough mean value for the single bond energy of C−H, and the energy of any bond will vary somewhat in different molecules and radicals. In a similar way, two other fundamental values, *viz.* for the C−C and the C−O bond, may be obtained from ethane and ether, respectively:* $d(C-C)=75$, $d(C-O)=76$, hence the true bond energies for $C^{IV}-C^{IV}$ and $C^{IV}-O$ become 125 and 101 kcal./mole, as in the latter case the excitation of one, in the former that of two carbon atoms must be taken into account. Analogously the energy of the bond $C^{II}-C^{IV}$ is 100 kcal./mole. For $D_B(C^{II}-H)$ we have already calculated 114 kcal./mole. This value is 6 kcal./mole less than $D_B(C^{IV}-H)$ and, although such an extrapolation cannot be expected to give accurate results, it shows nevertheless that the $C^{II}-H$ bond will be slightly weaker than the $C^{IV}-H$ linkage.

In the following the dissociation spectra and dissociation processes of a number of organic molecules are examined, whose structure is slightly more complex. In order to give an example, we will apply the considerations developed so far to the much discussed case of formaldehyde. This molecule makes a good example because all thermochemical data are well known, the dissociation energy is measured with rather high accuracy by a point of predissociation, and as only one C atom is involved, no complicating thermochemical extrapolation or reductions are necessary. The excellent agreement between calculated and observed values is therefore highly significant. We follow the discussion of Bergmann and Samuel (55).

Formaldehyde possesses a band spectrum (50), therefore, a non-repulsive, bonding excited term above the ground state. The energy difference between these two electronic levels is about 80 kcal./mole for the vibrationless molecule. The band spectrum shows a point of predissociation between 2670 and 2750A (107.0–103.6 kcal./mole). The final products of photolysis are hydrogen and carbon monoxide (51).

The following scheme of the electronic energy levels of the system, Fig. 10, shows the possibilities of building up formaldehyde from the single atoms and the ways of its decomposition. The molecule may be built up either from $CO+2H$ or from CH_2+O, which possibilities are indicated by the right and the left side of the diagram, respectively. From the system $C+2H+O$ on the left side, CH_2+O is formed in two steps (*via* $CH+H+O$). The heat of combustion, measured thermochemically, being 134 kcal./mole, 345.6 kcal./mole obtains for the atomic energy of formation D. The term $CH_2(^1\Sigma)+O$ is placed at

$$D(CH_2O)-2D_B(C^{II}-H)=346-2\times 114 = 118 \text{ kcal./mole}$$

above the ground level of formaldehyde. When the oxygen atom approaches the molecule $CH_2(^1\Sigma)$, no combination takes place, and a repulsive curve arises. The molecule $CH_2(^1\Sigma)$ has to be excited and the original s^2 group to be split in order to bring about the formation of CH_2O in this way. We have placed this level rather arbitrarily at 217 kcal./mole above the ground level, i.e., $d(CO)$ plus half the excitation energy of ^5S.

From the system C+O another two-step reaction leads on the right-hand side of the diagram to the formaldehyde molecule. The first involves formation of carbon monoxide in its unexcited ($^1\Sigma$) state, in which it does not possess free valencies. As discussed in Section III, we take 241.4 kcal./mole as the spectroscopic value for the energy of formation of CO. The approach of two H atoms of $CO(^1\Sigma)$ does not induce molecule formation, but this becomes possible after the CO is excited to a higher term. Therefore,

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* The following values have been used in this paper as contributions (d) of the various bonds to the energy of formation of an organic molecule (in kcal./mole): $d(C-H)=95$, from CH_4; $d(C-C)=75$, from C_2H_6; $d(C-O)=76$, from CH_3-O-CH_3; $d(C=O)=167$, from aldehydes; $d(C=O)=184$, from carboxyl groups; $d(O-H)=109$, from H_2O and CH_3-OH; $d(S-H)=83$, from H_2S.

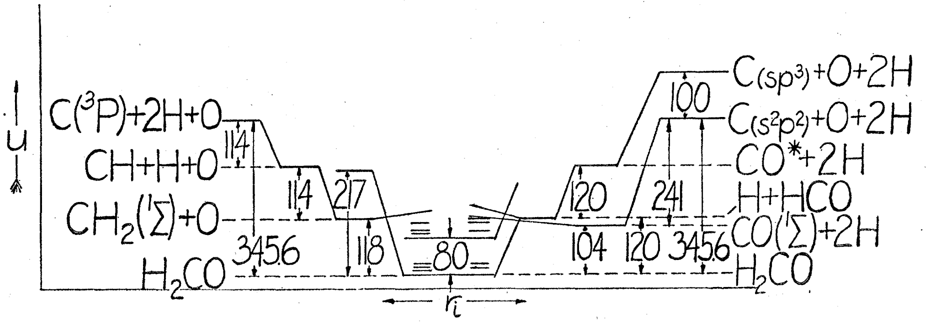

FIG. 10. Energy terms of H_2CO in the system C+O+2H.

we have again a repulsive curve, $D(CH_2O)-D(CO)=345.6-241.4=104.2$ kcal./mole above the ground level of the formaldehyde molecule. On the basis of a true single bond energy of 120 kcal./mole per each $C^{IV}-H$ bond, the position of the bonding triplet term of CO would be $240-104=136$ kcal./mole ($=5.9$ ev) above its ground state $(X)^1\Sigma$.

The band spectrum indicates another term 80 kcal./mole higher, exhibiting vibrational levels, which accordingly is not a repulsive, but a stable term. Such spectra, and, therefore, such terms, are characteristic of molecules containing the carbonyl group. Mulliken (52) ascribed this stable level to the excitation of a certain $\pi(p)$ electron in this group. This is, however, immaterial for our purpose; the level is an excited level of the whole system, and the products of photo-dissociation are not determined by the stable, but by the intersecting repulsive curve.

By light absorption the formaldehyde molecule is at first excited to this lowest level at 80 kcal./mole. The "origin" of the corresponding band spectrum lies at 80 kcal./mole but it extends to shorter and longer waves on account of the various transitions between the higher vibrational levels of the two electronic states. If the absorbing molecule is already in some excited vibrational state of the ground term, less energy than 80 kcal./mole may be required, and if excitation leads from the ground level to a higher vibrational level of the excited electronic term such a transition needs more than 80 kcal./mole. The 104 kcal./mole calculated above as difference between $D(H_2CO)$ and $D(CO)$ are in agreement with the observed value of 107.0 to 103.6 kcal./mole for the point of predissociation. Predissociation, therefore, appears to occur at the intersection of the lowest repulsive curve $CO(^1\Sigma)+2H$ with the vibrational levels of the higher, stable electronic term. Predissociation always indicates the existence of such an intersection, while continuous absorption corresponds to the existence of an unstable state only. Formaldehyde is decomposed into CO+2H, by absorbing light of 103 kcal./mole or more, (2750A or less).

This mechanism of photo-dissociation is closely related to that proposed earlier by Norrish (51). The main difference appears to be that we picture the dissociation as a single elementary process, i.e., a simple transition to the repulsive curve produced by the non-bonding s^2 group of electrons. Therefore the dissociation energy is not related to the bond energies, and the two H atoms are indeed split off simultaneously. It is obvious that formally the process can be represented by the scheme: $CH_2O\rightarrow CO+H_2$, but this cannot be the real primary process, as the hydrogen has to be set free in form of atoms, most of which will recombine under ordinary experimental conditions, but will not always do so.

According to Norrish and Kirkbride (51), some photo-decomposition of formaldehyde occurs with wave-lengths belonging to the region of banded structure below the point of predissociation.* This is due to bands involving excited vibrational levels of the ground term. A similar suggestion has already been put forward by Herzberg (50). At each C−H vibration means 8 and each C−O vibration means 5 kcal./mole, this

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* The long wave fluorescence of acetone has now been found to be due to diacetyl, cf. reference (53).

amount of energy is not to be neglected. This view is well supported by the experiments of Leermaker (54) in the identical case of acetone, who found that for longer waves the quantum yield increases with temperature, from 0.4 at 67° to 1.0 at 167°; i.e., with the increase in population of the excited vibrational levels. Similar results have been obtained for acetaldehyde and propionaldehyde by Smith (54) and by Leighton and Blacet (54). Norrish's result, therefore, is easily explained by the fact that his experiments were conducted at 100°. The above representation therefore indicates two essential conclusions:

(*a*) The repulsive curve $CO(^1\Sigma)+2H$ is the lowest of all repulsive states, even lower than that involving H+CHO. For molecules which do not possess a low excited stable state, such as is associated with the low excitation energy of the electrons of the carbonyl group, this repulsive curve will even form the very lowest of all excited levels of the molecule, both repulsive and stable.

(*b*) In a case of predissociation, in which besides the repulsive also a stable excited state must be taken into consideration, the dissociation products are in the same way determined by the unstable and not by the stable term. No special mechanism is required for transferring to other parts of the molecule energy stored by excitation inside the carbonyl group, as sometimes assumed. The intersection of the excited carbonyl term with another unstable one provides this mechanism.

From formaldehyde we now turn to related substances. Bergmann and Samuel (55) have pointed out a good agreement of observed and calculated data for similar processes of other aldehydes and ketones. The data for some typical molecules are collected in Table XIV; points of predissociation (PrD) have been observed by Henri and colleagues (56), long wave-length limits in the vapor state (LWL) and in solution (Sol) are those, measured by Bergmann and Samuel. The calculations have been carried out in the following way: from the atomic energy of formation D the contributions (d) of all the C−H and C−C bonds have been deducted so as to obtain the formation energy of the inner groupings C−CO−C and H−CO−C, respectively. For propionaldehyde, for instance, 333.6 kcal./mole obtain for this value, i.e., D(H−CO−C). From this value that of $D(CO, {}^1\Sigma)$ is again deducted. In our example this leaves 92.2 kcal./mole, which is the energy necessary for the process

$$H\cdot CO\cdot C_2H_5 \rightarrow CO(^1\Sigma)+C_2H_5+H$$

and which compares favorably with the predissociation value of 88. It may be mentioned that in this calculation the value of D(CO) has been used twice, once before in the calculation of the energy of dissociation of a molecule from its heat of formation. This involves the sublimation energy of carbon, which itself is derived from D(CO). The calculations of Table XIV are therefore quite independent of the precise value of D(CO).

Considering that neither optical nor even some of the thermochemical data are entirely accurate, the agreement is good. The present interpretation, if we assume a reversal of the carbonyl group into unexcited CO, permits one to depict the slow and gradual shift of the predissociation from 2750 of formaldehyde to 3500A of acetone. But most striking is the fact that even the enormous shift from formaldehyde to 4395A of diacetyl is accurately represented by this theory. Evidently, the conventional interpretation cannot do this. If the photolytic process would involve the breaking of a single bond, then the predissociation points of all ketones should have about the same value, namely that of the energy of the C−C bond and all the aldehydes should either exhibit the same predissociation or another one corresponding to the energy of the C−H bond. Only a theory as that offered here can represent such shifts from the ultraviolet to the visible, because it deducts a constant value, i.e., D(CO) from the varying energies of formation of the respective groupings.

All such molecules possess a second region of continuous absorption at shorter waves. For instance, for acetone a second long wave-length limit has been observed in hexane solution at between 2300 and 2000A, with a maximum in the Schumann region at 1800A, and it probably is in this region that the methyl and acetyl radicals are formed, which have been observed by Spence and Wild (57) as their light filter apparently was transparent for the 2300 to

TABLE XIV. Aldehydes and ketones.

Molecule	D	Observed abs. spectr. A	Observed abs. spectr. kcal./mole	Calculated	For dissociation products
Formaldehyde	345.6	2750	103(PrD)	104	$CO(^1\Sigma)+2H$
Acetaldehyde	617.0	2730 3120	104(PrD) 91(Sol)	91	$CO(^1\Sigma)+H+CH_3$
Propionaldehyde	883	3250	88(PrD)	92	$CO(^1\Sigma)+H+C_2H_5$
Acetone	886	3500	81(PrD)	75	$CO(^1\Sigma)+2CH_3$
Diacetyl	1118	(*A*) 4395	65(PrD)	66	$CO(^1\Sigma)+CH_3+CH_3CO$
		(*B*) 2800	102(LWL)	106	$CH_2(^1\Sigma)+H+CO\cdot CO\cdot CH_3$
Acetylacetone	1401	(*A*) <3290	>85(LWL)	84	$CO(^1\Sigma)+CH_3+CH_2\cdot CO\cdot CH_3$
		(*B*) 2457	116(LWL)	125	$CH_3+CO\cdot CH_2\cdot CO\cdot CH_3$

2000A region. As pointed out above, the true bond energy $D_B(C^{IV}-C^{IV})$ should be at about 125 kcal./mole, corresponding to 2270A. The interpretation of these short wave spectra is, however, still difficult because the margin between figures, calculated for different types of processes, often is rather small. We have included in Table XIV plausible interpretations for these "*B*" regions of absorption for diacetyl and acetylacetone on a tentative basis.

Furthermore, Bergmann and Samuel have applied the same considerations successfully to a number of organic molecules for which the data are listed in Table XV. For formic and acetic acid in the vapor state, we possess measurements of the long wave-length limit by Scheibe and collaborators (58). However, these have been carried out with a small fluorite spectrograph, which did not permit a sufficient investigation of the ultraviolet region. In fact, the absorption coefficient of the long wave-length limits in their curves is higher than that of the following minimum, which is physically impossible. The true long wave-length limits therefore lie at longer waves and lower energies. This was confirmed by a reinvestigation of ethyl acetate in the vapor state, and the limits measured in solution therefore have been added to Table XV.

The electronic levels of formic acid are given in Fig. 11. The atomic energy of formation is 469.6 kcal./mole, $D(OH)$ is 100, and the level $C(s^2p^2-{}^3P)+H+O+OH$ therefore lies 396.6 kcal./mole above the ground level of the molecule. Hence the level $CO(^1\Sigma)+OH+H$ is 128.6 above the same level and the approach of H and OH towards $CO(^1\Sigma)$ produces a repulsive curve only. This latter will be the first excited term of the molecule and the first absorption will be the transition from the ground level to this nonbonding state. The long wave-length limit of the first region of selective absorption lies at >2170A (<131 kcal./mole) in the vapor state and at 2360A (=121 kcal./mole) in solution. As the spectrum is invariably shifted to longer waves in solution, we use a mean value of 126 in Fig. 11.

Bergmann and Samuel then measured the absorption spectra of the vapors of similar molecules in which oxygen atoms had been replaced by sulphur, and the spectrum therefore lies at longer waves. For these molecules, only the heat of combustion of thiourea is experimentally known; the atomic energies of dissociation of thio- and dithio-acetic acid had to be extrapolated. However, this can be done with ease and sufficient accuracy. The difference between $D(CH_3\cdot OH)$ and $D(CH_3\cdot SH)$ is 44.2 kcal./mole; that between the corresponding ethyl compounds is 46. Hence $D(CH_3\cdot CO\cdot SH)$ is calculated as $D(CH_3\cdot CO\cdot OH)$ minus 45. The difference between urea $(NH_2)_2CO$ and thiourea $(NH_2)_2CS$ is 60 kcal./mole, that between $D(CO_2)$ and $D(COS)$ is 59, and between $D(COS)$ and $D(CS_2)$ is 60. Hence $D(CH_3\cdot CS\cdot SH)$ is calculated as $D(CH_3\cdot CO\cdot SH)-60$. This gives the values, listed in Table III, namely 700 and 640 kcal./mole, respectively. The inaccuracy of such thermochemical extrapolations is probably less than the experimental error in $D(CS, {}^1\Sigma)$ which is needed for the following calculations. For the latter, extrapolation of the vibrational levels of the band spectrum yields 7.7 ev or 178 kcal./mole. We know that such extrapolations often give only upper limits and depend on the accuracy with which the anharmonic constant has been determined. There are some cases known in which the Birge-Sponer values are 50 percent incorrect, and more (59). However, this appears not to be true for the ground level of CS the spectrum and fine structure of which are well analyzed. $D(CS_2)$ is 248 kcal./mole. If we add to it 100 kcal./mole as the best value for the energy of excitation which makes the carbon atom tetravalent, we obtain 348 for the adiabatic dissociation of CS_2 into two S atoms and $C(sp^3)$. One-half of this value, or the true bond energy of the $C=S$ bond in CS_2 is 174, closely approximating $D(CS)=178$. It appears, therefore, that we are on safe grounds and that this value will not be more than a very few kcal./mole too high. The calculations can be carried out in the same way as earlier, $CS(^1\Sigma)$ taking the place of $CO(^1\Sigma)$. Thus, the atomic energy of formation of thiourea is 596. The contribution of four $N-H$ bonds according to $D(NH_3)$ is 333, which leaves 263 for the atomic heat of formation of the inner grouping $(N\cdot CS\cdot N)$. If we deduct $D(CS)$, we obtain 85 as the minimum energy for a process of which the dissociation products are $CS(^1\Sigma)+2NH_2$. The long wave-length limit of the continuous absorption spectrum has been determined as between 3300 and 3000A, 86 to 94 kcal./mole. All the other calculations are carried out in the same way. As $D(OH)$ is not equal to $\frac{1}{2}D(H_2O)=109$ but less, we have taken for (SH) the proportionate part of $D(H_2S)$, namely, $D(HS)=77$ instead of 83. The data are included in Table XV.

Considering the many spectroscopical and thermochemical difficulties, the agreement of calculated and observed values again may be called very good. To our mind, there are two facts of particular significance. First the successive replacement of one and two oxygen atoms shifts the spectra precisely to those wave-lengths required by the present interpretation. Secondly, for the keto-acids and their esters, we obtain two different values for the inner groupings, according to the well-known energy difference of the $C=O$ bond in the carbonyl and carboxyl groups (on account of genuine resonance in the latter). Hence two different values obtain for a fission of the molecule at either group. The spectra of ethylacetoacetate and of pyruvic acid at the bottom of Table XV show clearly that the two corresponding regions of selective absorption both are exhibited by such compounds. For ethylacetoacetate the long wave-length limits are in good agreement with the figures calculated according to the present interpretation. The spectrum of pyruvic acid so far has only been measured in solution where it is always shifted to longer waves; nevertheless the agreement is still quite bearable. One other remark may not be out of place. The continuous absorption

TABLE XV. Various organic molecules.

Molecule	Energy of inner grouping	Observed LWL		Calculated D_R	Dissociation products
		A	kcal./mole		
$H\cdot CO\cdot OH$	$D(H\cdot CO\cdot O)=370$	vap >2170	<131	129	$CO(^1\Sigma)+H+OH$
		sol ~2360	~121		
$CH_3\cdot CO\cdot OH$	$D(C\cdot CO\cdot O)=360$	vap >2125	<134	119	$CO(^1\Sigma)+CH_3+OH$
		sol ~2320	~122		
$CH_3\cdot CO\cdot OC_2H_5$	$D(C\cdot CO\cdot O)=350$	vap 2630–2420	108–117	109	$CO(^1\Sigma)+CH_3+OC_2H_5$
$CH_3\cdot CO\cdot SH$	$D(C\cdot CO\cdot S)=338$	vap 2960–2820	96–101	97	$CO(^1\Sigma)+CH_3+SH$
$CH_3\cdot CS\cdot SH$	$D(C\cdot CS\cdot S)=278$	vap 3010	94	100	$CS(^1\Sigma)+CH_3+SH$
$(NH_2)_2CS$	$D(N\cdot CS\cdot N)=263$	vap 3300–3000	86–94	85	$CS(^1\Sigma)+2NH_2$
$CH_3\cdot CO\cdot CH_2$	$D(C\cdot CO\cdot C)=335$	vap 2596	109	94	$CO(^1\Sigma)+CH_3+CH_2\cdot CO\cdot OC_2H_5$
|		sol 2850	99		
$C_2H_5\cdot O\cdot CO$	$D(C\cdot CO\cdot C)=354$	vap 2225	127	113	$CO(^1\Sigma)+OC_2H_5+CH_3\cdot CO\cdot CH_2$
		sol 2175	131		
$CH_3\cdot CO\cdot CO\cdot OH$	$D(C\cdot CO\cdot C)=331$	sol 3700	77	90	$CO(^1\Sigma)+CH_3+CO\cdot OH$
	$D(C\cdot CO\cdot C)=349$	sol 2850	99	108	$CO(^1\Sigma)+OH+CH_3\cdot CO$
$CH_3\cdot OH$	$D(H_3C\cdot O)=368$	vap 2000	142	140	$CH_2(^1\Sigma)+H+OH$

spectra exist and indicate some photolytic process. Their long wave-length limits therefore have to be explained. As it happens, they lie at rather low energy values. The only other possible assumption would be to attribute them to a breaking of bonds like O—H, S—H, and C—H. The corresponding energy values would be 109 to 118 for O—H, 83 to 99 for S—H, and 95 or 120 for C—H (although the former figure is theoretically hardly tenable for C—H). Such figures would not explain the individual differences between the spectra, but in some cases they could be compatible with the observed values. Then, however, the question arises why do great differences exist between the spectra of different types of organic molecules? If the long wave-length limit, e.g., of a thio-acid indicates the fission of an S—H bond, why do not the mercaptanes show the same spectrum, the alcohols the same as the acids, and the hydrocarbons the same as those where a breaking of the C—H bond is assumed? The long wave-length limit of methyl alcohol vapor lies at about 2000A, 142 kcal./mole (48). It is not very well determined, but certainly 15 to 20 kcal./mole higher than that of the acids. None of the above explanations would be acceptable and there is certainly none compatible *both* with the spectra of methyl alcohol and formic acid. However, the atomic energy of formation of $CH_3 \cdot OH$ (468.2) minus $D(OH)$ leaves 368 kcal./mole for the energy of $H_3C \cdot O-$. With the same value for $D(CH_2, {}^1\Sigma)$ as before, 228, we obtain 140 for the process $CH_3 \cdot OH \rightarrow CH_2({}^1\Sigma) + H + OH$. This figure is in much better accord with the observed value of 142 than any of the other possible ones, and it makes it understandable why the spectra of the alcohols are at shorter waves than those of the acids, and so forth.

Bergmann and Samuel also discussed the possible photolytic processes related to the short wave maxima of selective absorption which some of these molecules exhibit in the near Schumann region. In general one gets the impression that such substances do not differ in their behavior from the inorganic molecules in which the central atom is in its maximal state of valency. The presence of a second or third carbon atom seems not to produce fundamental changes of the optical properties.

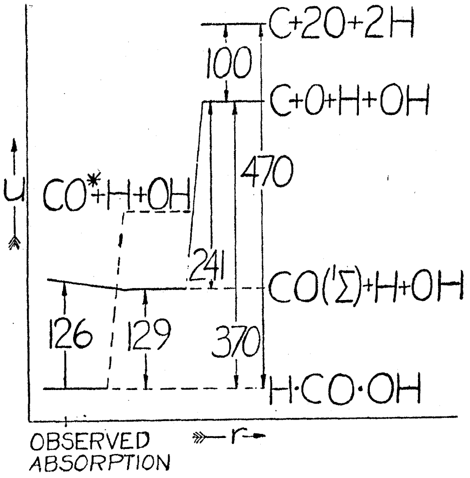

FIG. 11. Energy terms of H—CO—OH in the system C+2O+2H.

Three more molecules should be mentioned in this connection namely CO_2, CS_2, and COS. For the latter the first long wave-length limit (60) (at such experimental conditions which permit observing the structure of the continuum) lies at 2380A = 119.4 kcal./mole; taken at that value of the absorption coefficient which characterizes the following transmission point, we obtain about 2300A or about 124 kcal./mole. Dissociation into CS $({}^1\Sigma) + O({}^3P)$ would need an energy of 130. For CS_2 a point of predissociation was found (56) at 2820A or 102 kcal./mole, but this appears to be only an upper limit. Under quite reasonable experimental conditions it shifts easily to lower energy values, i.e., with a pressure of 15 mm Hg in a 10-cm tube the predissociation lies already at 2965A or 96 kcal./mole (61). The dissociation into unexcited CS and S needs 70 kcal./mole only.

The best interpretation on strictly experimental grounds would be to assume dissociation into $CS({}^1\Sigma)$ plus excited $S({}^1D)$. For this process an energy of 96 kcal./mole is needed, in almost exact agreement with the observed predissociation. The agreement is less good for COS, dissociation into $CO({}^1\Sigma) + S({}^1D)$ needs 93 kcal./mole, still much below the long wave-length limit. But the dissociation of CO_2 into $CO({}^1\Sigma)$ plus $O({}^1D)$ takes place with an energy of $(126+45) = 171$ kcal./mole, and this is almost exactly the point where the diffuse absorption bands merge into a continuum; this takes place at 1620A = 177 kcal./mole (61*a*). It is quite possible that these molecules form an exception and dissociation into unexcited products does not take place. One reason might be their linear structure resulting in such a different position of the energy surfaces in space that the repulsive curve due to unexcited O or S atoms cannot be reached in transitions from the ground level. Another reason might be that here the selection rules are rigorously applicable which do not permit transitions from the $^1\Sigma$ ground state to the repulsive triplet state formed by $CO(^1\Sigma)$ plus an atom in ^3P. They are valid only for not too heavy molecules and have been derived under the assumption that no deformation of the molecule takes place in the excited state which would change its symmetry properties. It is likely that these linear molecules approach nearer to this condition.

Incidentally there is some doubt about thermochemical data; the heats of formation of Berthelot vary greatly from those of Thomsen which have been used here. Hence other interpretations are not impossible, and that is why we have not included these molecules in Table XV.

Finally we possess spectroscopical data for phosgene, acetyl chloride, and related substances, while Bichowsky and Rossini's book provide the heats of formation for many of these substances for the first time. A comparison is made in Table XVI. For each substance we have listed first the energy necessary for the dissociation into $CO(^1\Sigma)+2R$, and secondly that for the breaking of a bond by adiabatic dissociation, leading to R+RCO. For the latter we have not taken the contributions towards the atomic energy of formation, i.e., $d(C-Cl)=\frac{1}{4}D(CCl_4)=74$, but what we consider the true bond energy, counting from the excited state of the truly tetravalent carbon atom. With about 100 kcal./mole of excitation energy, we obtain, as explained above, $D_B(C^{IV}-Cl)=99$.

At a first glance it appears as if most of these molecules break up by the ordinary adiabatic fission of a single bond, and for the first six of them the bond energies appear to be in better agreement with the spectroscopical values. The theory applied here successfully to so many molecules simply means that the repulsive state $CO(^1\Sigma)+2R$ often is the lowest of the excited levels, but this must not always be the case. The different chemical properties and greater reactivities of most of these substances of Table XVI may be connected with a particularly low position of a repulsive term which permits dissociation into a free radical and a halogen atom.

However, some points of interest may be mentioned. First, some of the spectroscopical values are questionable. In some cases we know that they have been obtained with low dispersion and in such heavy and complicated molecules the observed continuous spectrum may be nothing but the envelop of the band system characteristics of so many aldehydes and ketones. This point has been made already earlier (62). It appears to be very clear in a case like chloral; as in the original paper we have therefore excluded the long and extended absorption at longer wave-lengths and have taken the first point of retransmission as the true long wavelength limit (87 kcal./mole), and immediately agreement is reached with the energy of dissociation into $CO(^1\Sigma)+Cl+CCl_3$, which is 90 kcal./mole. But even the results of other laboratories and without knowledge of experimental details appear not to be entirely clear. Thus it is at least very unusual, that the predissociation of Cl_2CS is recorded at shorter waves than that of Cl_2CO. A new investigation with larger dispersion is urgently called for.

Furthermore, the photolysis of actyl halides has been studied by Etzler and Rollefson (64). They find CO plus CH_3X as the main end-products, if light of the first absorption region is used. This indeed suggests dissociation into $CO(^1\Sigma)+X+CH_3$ as the primary step.

Under these conditions we have included these molecules for the sake of completeness but a definite correlation of light absorption and photodissociation has to await a clarification of the experimental data.

VII. CONCLUSIONS

In the course of the preceding review of dissociation spectra it has been shown that the empirical data agree with the theory outlined in the introduction. Not only do the long wavelength limits agree within the experimental error with the energies calculated on this basis,

TABLE XVI. Phosgene, acetyl chloride, and derivatives.

Molecule	Energy of inner grouping	Observed predissociation or long wave-length limit: A	kcal./mole	Calculated kcal./mole	Dissociation products	Ref.
Cl_2CO	$D(Cl\cdot CO\cdot Cl)=325$	2750	103	84 99	$CO(^1\Sigma)+2Cl$, or $Cl+ClCO$	(56)
Cl_2CS	$D(Cl\cdot CS\cdot Cl)\sim 265$	2710	104	87 99	$CS(^1\Sigma)+2Cl$, or $Cl+ClCS$	(56)
$CH_3\cdot CO\cdot Cl$	$D(C\cdot CO\cdot Cl)=330$	2900–2750	98–103	89 99	$CO(^1\Sigma)+Cl+CH_3$, or $Cl+CH_3\cdot CO$	(62)
$CH_3\cdot CO\cdot Br$	$D(C\cdot CO\cdot Br)=317$	3100	91	76 87	$CO(^1\Sigma)+Br+CH_3$, or $Br+CH_3\cdot CO$	(63), (64)
$CH_3\cdot CO\cdot I$	$D(C\cdot CO\cdot I)=302$	4000	71	61 71	$CO(^1\Sigma)+I+CH_3$, or $I+CH_3\cdot CO$	(64)
$ClCH_2\cdot CO\cdot Cl$	$D(C\cdot CO\cdot Cl)=329$	2625	108	88 99	$CO(^1\Sigma)+Cl+ClCH_2$, or $Cl+ClCH_2\cdot CO$	(62)
$CCl_3\cdot CO\cdot Cl$	$D(C\cdot CO\cdot Cl)=335$	2975	96	94 99	$CO(^1\Sigma)+Cl+CCl_3$, or $Cl+CCl_3\cdot CO$	(62)
$CCl_3\cdot CO\cdot H$	$D(C\cdot CO\cdot H)=331$	3280	87	90 114 100	$CO(^1\Sigma)+H+CCl_3$, or $H+CCl_3\cdot CO$, or CCl_3+HCO	(62)
$CBr_3\cdot CO\cdot H$	$D(C\cdot CO\cdot H)=325$	2925	98	84 114 100	$CO(^1\Sigma)+H+CBr_3$, or $H+CBr_3\cdot CO$, or CBr_3+HCO	

but of equal significance is the existence of precisely that number of absorption regions and maxima, as can be predicted for both types of molecules with the central atom in its maximal or a lower state of valency. As these mechanisms of both these classes have been discussed in detail, no further remarks appear necessary at this time.

There are, however, a few questions of more general interest, which at least should be mentioned here. They concern the photochemical behavior of these compounds, the general theory of spectra and various aspects of the theory of valency.

The relation of the present theory and *the results of preparative photochemical experiments*[*] already has been discussed by Bergmann and Samuel (55). It must be understood that the absorption spectrum reveals the primary step of the breaking up of the molecule while photolytic experiments reveal the end products, after the freed molecules, atoms, or radicals have undergone a number of stabilization reactions. Hence a correlation of these two entirely different types of investigations is not always easy even in the gaseous phase.

A complete confirmation of the present view may be obtained, however, in some of the simpler cases. The end products of photolysis of formaldehyde are carbon monoxide and molecular hydrogen according to Norrish and colleagues (51). But this cannot be the primary process as hydrogen does not exist in molecular form in the formaldehyde molecule. Combining both the spectroscopical and photochemical results, we can now write:

$$H_2CO \xrightarrow{h\nu} CO(^1\Sigma)+2H \rightarrow CO(^1\Sigma)+H_2.$$

Here $h\nu$ denotes the first absorption region about 2600A or more.

Similarly carbon tetra-iodide on irradiation gives molecular iodine and tetra-iodoethylene, but again the I_2 molecule does not exist as such in CI_4 and this molecule cannot break up this way in a single step. By taking account of the spectrum and Terenin's experiments on the fluorescence of the similar SnI_4, discussed above,

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[*] For detailed literature cf. e.g., K. Rollefson and M. Burton, *Photochemistry* (Prentice Hall, Inc., New York, 1939); also references (51) and (55).

we can now write:

$$2(CI_4)\xrightarrow{h\nu}2(CI_2(^1\Sigma)+2I)\rightarrow C_2I_4+2I_2.$$

Here $h\nu$ denotes any of the first three absorption regions, about 2500 to 3500A.

Such immediate recombinations of the freed molecules, atoms, and radicals, however, are only the most simple case and a number of factors may influence the subsequent stabilization and produce entirely different end products. Two of these factors may be mentioned.

It happens that in the formaldehyde molecule the distance between the hydrogen atoms is 1.88A. As we know from the potential curve of the H_2 molecules, this means that in the moment of liberation they are well in the sphere of mutual attraction, which extends to more than 2.5A. Hence they recombine immediately if not disturbed. But if there should be a collision of the breaking-up H_2CO molecule with some other molecule or atom during the time interval between the absorption of light and the recombination of the H atoms, they will be thrown out of the sphere of mutual attraction. In such a case the very high reactivity of free atoms or free radicals will lead to quite different and complicated stabilization reactions. Actually an increase of pressure produced by the addition of a foreign gas or by raising the temperature has been shown in many cases to cause different and more complicated secondary reactions. The results of photolytic experiments therefore depend in a large degree on the experimental conditions.

Again, the unexcited hydrogen atoms liberated from formaldehyde possess spherical symmetry and may combine in any collision. But in higher aldehydes and ketones they are replaced by radicals and if two of them collide a recombination probably takes place only if the collision is nearly end-on. Otherwise the collision will be elastic, no immediate recombination takes place, and different secondary reactions set in. Hence also the geometry of the molecules plays an important part. This again is borne out by experiments. The above type of reaction with immediate recombination becomes less and less important, the larger the radical, and less important for the ketones with two radicals than for the aldehydes with one radical and one H atom. It is interesting to note that the above type of reactions, for instance, is valid for 37 percent of photolyzed molecules of di-*n*-propyl ketone but not for 44 percent of di-iso-propyl ketone. The long chain-structure apparently is less favorable for immediate recombination.

Also, if a shorter wave-length of the same absorption region is used, this recombination becomes less probable on account of the higher kinetic energy of the colliding radicals. Unfortunately in photolytic experiments filters are rarely selected with a view to isolate light of one particular selective absorption region simultaneously on the long and short wave side, and hence results are sometimes misleading. As discussed earlier (55) light of the second and third absorption region will lead to entirely different processes, because different repulsive states are involved.

In general it may be stated that photolytic experiments fully bear out the present theory.

Selection Rules of transitions between electronic states have been formulated on theoretical grounds and it is generally assumed that intercombinations are permissible only between terms of equal multiplicity. But while the ground states of the diamagnetic, chemically saturated molecules all have the character of ($^1\Sigma$) terms, many of the repulsive levels to which dissociation is due will have to be classified as triplet terms; incidentally, this will be true in any theory of dissociation spectra. However, these rules are not rigorously valid for molecules composed of heavier atoms, nor if strong geometrical deformation of the molecular structure in the excited state changes the symmetry properties on which these rules are based. Such deformations, however, probably play an important role. The great decrease of vibrational frequencies on excitation indicates a great increase in the intermolecular distances together with a great loosening of the binding forces. In the case of SeO_2, for instance, the symmetric and antisymmetric valence vibrations change from 901 and 1189 cm^{-1} in the ground state to 663 and 790 cm^{-1} in the excited level (65) and a strong deformation of the molecule is highly probable.*

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* These figures are 917 and 1173, 658 and 782 according to another analysis (65b).

Some further remarks concern the *theory of valency*. The connection is obvious: the process of dissociation is the converse of the process of formation and therefore such spectroscopical data should be taken into account in the formation of the theory of covalent linkage.

The first remark concerns the bond energies. The division of the atomic energies of dissociation into bond energies has become an accepted method in molecular physics. But as long as we confine ourselves to division of a grand total into more or less arbitrary parts, the bond energies exist as a merely arithmetic quantity without experimental verification. At least for the class of molecules of lower valence state, the continous spectra immediately and directly *confirm the existence of approximately additive bond energies.*

From this follows another conclusion: It has been pointed out recently (1) that additivity of molecular constants is hardly compatible with a theory in which the ground level of a molecule is conceived as resonating between several structures. Of these one would be the lowest, all the others would constitute excited terms of the molecule. Their percentage contributions would depend to a large extent on the energy of excitation. As this would necessarily vary from molecule to molecule (for instance from $SeCl_4$ to $SeOCl_2$), the molecular constants could not remain the same and therefore not additive (for instance the bond energy $Se^{IV}-Cl$ would be changed by entirely different contributions). The bond energies not only are such an additive molecular constant but their individual existence is confirmed by the dissociation spectra. Hence we have to conclude that resonance—although theoretically always present—is negligible for molecules formed by a marked central atom.

This, of course, is not so for molecules for which rigorous energetic degeneracy of several structures exists. Indeed our molecules include one case which comes near this condition, namely, the carboxyl group. It has been known for a long time that the contributions to the energies of formation for the carbonyl group ($d(C=O)=167$) and the carboxyl group ($d(C=O)=184$) are different. The dissociation spectra of these two types of molecules and the agreement of long wave-length limits or predissociation with figures calculated with these two different values show that this difference is not merely formal, but a real variation of the energy content, which has to be located in these groups.

Moreover, the dissociation spectra also throw light on some fundamental problems of the theory of covalency.

In wave mechanics two different approaches to the problem of covalent linkage have been formulated. One is the theory of molecular orbitals (Herzberg, Hund, Lennard-Jones, Mulliken), the other is the electron pair-bond theory (Heitler and London, Slater, Pauling). The former operates with the concept of independent electrons which are not localized between two definite atoms. In the other the covalent bond is caused by Heitler-London's electron degeneracy, or in other words by Lewis' sharing.

In our opinion—as expressed in detail earlier (66)—there is no doubt that the pair-bond theory is the only one which gives an accurate description of the covalent bond as existing in these molecules formed by a marked central atom. Indeed, to our mind, this is already clear on theoretical grounds, because the orbital theory on account of its excessive over-ionization gives an entirely incorrect picture precisely of the process of formation of such a molecule. Even if we cancel the ionic terms of the wave function entirely, as in Heitler and London's original paper, we are much nearer to reality with a hydrogen molecule formed entirely by atoms, than with the molecule of the orbital theory which is formed in part by hydrogen ions. In order to make the orbital theory a real theory of valency, the interaction of the electrons would have to be taken into account from the very beginning and this would lead directly to the pair-bond concept. But such an attempt has never been seriously undertaken, because it also would lead directly to the great mathematical difficulties of the latter method. The great simplicity of the orbital theory would be lost, which makes it supreme—not as a theory of valency, but—as a theory of the electron configurations and the term system of the molecule when it is already formed and is not dissociating.

Under these circumstances, however, it is of interest to compare the experimental spectroscopical results with these two theoretical concepts. We can do so on two counts.

If in these molecules, under discussion, the electrons really would be independent and their interaction negligible, then clearly the sulphur-chlorine bond in SCl would be entirely different from the same bond in SCl_2, and so on. But then the additivity of the bond energy could not be understood. The dissociation spectra establish an approximate additivity of the bond energies as a direct and experimental fact, and this shows the existence of electrons which to a great extent at least are localized between two definite atoms and therefore are not independent.

The other point is that in the Heitler-London concept electrons of a completed group cannot act chemically. This is the unavoidable corollary to Lewis' sharing. If the electrons were independent and their interaction were negligible, there would be no reason why the ground level of SO_3 should not be formed by a combination of an unexcited O atom with SO_2 in its $^1\Sigma$ ground state. Dissociation spectra (and diamagnetism) of all the molecules of maximal valency clearly indicate that this is not the case.

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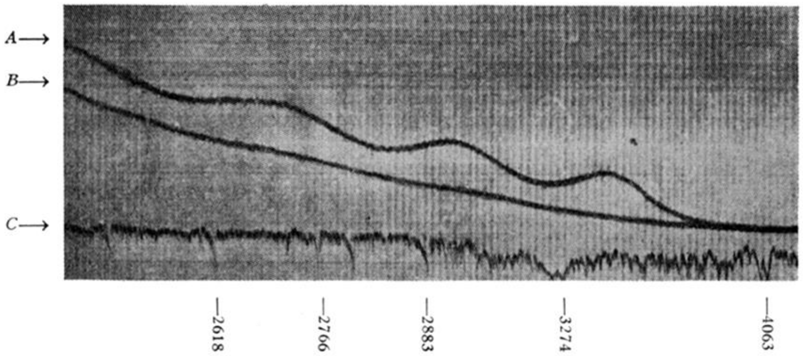

FIG. 2. Photogram of absorption spectra of CHI_3 (vapor). This was taken with a recording microphotometer from original plate. (*A*) Absorption spectrum of iodoform, (*B*) source of light (continuous hydrogen spectrum), (*C*) standard lines. Three different regions of selective absorption of CHI_3, their absorption maxima and long wave-length limit can be clearly distinguished.