Contemporary photochemistry*

É. V. Shpol'skíí Usp. Fiz. Nauk **163**, 87–105 (April 1993)

The study of photochemical processes has made considerable advances in recent years. We have progressed in understanding the mechanism of the chemical action of light further than in all the rest of the fields of chemical kinetics. Photochemistry is indebted to these advances for the contemporary development of the theory of atomic phenomena, in particular the theory of atomic and molecular spectra. It is impossible at present to study photochemical processes apart from connection with the spectral properties of molecules.

We shall present below a brief sketch of the current status of photochemistry, while discussing exclusively the mechanism of the *primary* photochemical process, i.e., the process that occurs directly after the absorption of light, and restrict the treatment to reactions in the gas phase and in solutions. We shall leave aside the photochemistry of crystals, which is of outstanding importance in understanding the nature of the photographic process, since to present it would require treatment of an entire set of distinctive factors and would expand extremely the scope of this article.¹

I. THE PHOTOCHEMICAL LAW OF EQUIVALENCE

The first major stimulus toward understanding the nature of photochemical processes was given by the formulation of the so-called Einstein photochemical law of equivalence.²

According to the original formulation of this law the number of molecules that undergo photochemical transformation must equal the number of absorbed light quanta, or in other words, the quantum yield (= the number of transformed molecules/the number of absorbed quanta) for all photochemical processes must be equal to unity. For at least ten years this law served as the "apple of discord" for photochemists of all countries. In fact, the determinations of the quantum yield for many reactions showed that, although in a number of cases this law is obeyed, in others it fails, in either direction and in the most marked fashion. If we examine tables of quantum yields,³ it immediately strikes the eye that, along with values close to unity, we often find values exceeding unity manyfold (up to 10^5) and values expressed in very small fractions (several thousandths and even ten-thousandths). The final outcome of the bitter polemics on this law was presented only in 1925 at a photochemical conference organized by the Faraday Society.⁴ At present we can state quite definitely that the photochemical law of equivalence in its initial primitive formulation, of course, is not and cannot be valid. But if we conveniently revise this formulation and state that the number of primary photochemical events equals the number of absorbed light quanta, then in this form the law does not arouse any objections, since it is a simple consequence

of the firmly established quantum nature of light absorption. For the contemporary photochemist the value of the quantum yield is a guiding thread in disentangling the nature of the photochemical process since, together with the kinetic data, this quantity allows us directly to decide whether a given reaction is simple or is a chain reaction, and along what line the interpretation of the process must proceed. We shall not discuss further this law here, since the discussion of its theoretical foundations is no longer needed owing to their being generally known, while a treatment of the individual values of the quantum yield makes sense only in connection with the treatment of concrete reactions. In the presentation below we shall repeatedly return to this law for various reasons.

II. PHOTOCHEMICAL REACTIONS OF EXCITED ATOMS

In proceeding to examine the mechanism of elementary photochemical processes, we shall take up first of all the very simple case of reactions between excited atoms and molecules. Although such reactions are relatively rare, it is of interest to treat them since this makes it possible to establish some principles important in the further analysis of more complex cases.

A classic example of photochemical reactions of this type is the reactions of excited mercury atoms. As is known, when mercury vapor is illuminated with light at the wavelength $\lambda = 2537$ Å, the mercury vapor fluoresces intensely, emitting the same wavelength 2537 Å. This is the so-called resonance fluorescence, whose origin is explained by the fact that the value of the quantum corresponding to 2537 Å (4.9 eV = 112.5 kg \cdot cal/mole) is exactly equal to the spacing between the ground state (spectroscopic symbol ${}^{1}S_{0}$) and the *first* excited state (symbol ${}^{3}P_{1}$) of the mercury atom. Therefore mercury atoms that have absorbed hv_{2537} quanta can return after the duration of the mean time of existence in the excited state $\tau = 10^{-8}$ s only to the ground state, while emitting light of the same wavelength $\lambda = 2537$ Å. If, however, we add a *foreign* gas to the mercury vapor, then the fluorescence is partially quenched (sometimes quite significantly). Especially intense quenching is observed upon mixing with oxygen and hydrogen; here one simultaneously observes in the two cases a photochemical reaction: in the former case mercury oxide HgO is formed, while in the latter case free hydrogen atoms together with mercury hydride HgH are formed. Let us discuss somewhat the former case. The processes occurring here can be schematically represented by the equations

$$Hg + h\nu \to Hg^*, \tag{1}$$

$$Hg^* \to Hg + h\nu, \tag{2}$$

$$Hg^{*}+O_{2}\rightarrow HgO+O.$$
 (3)





Here the asterisk denotes an excited mercury atom having the large excess energy of 112.5 kg \cdot cal/mole. Equations (2) and (3) show that an excited mercury atom can undergo a double fate. If it does not collide with an oxygen molecule in the time interval $\tau = 10^{-8}$ s, the absorbed light quantum will be emitted as another quantum-resonance fluorescence will occur. Yet if it undergoes collision during the same time interval, this excess energy can be used for a chemical process, and the fluorescence is quenched. Thus the quenching of fluorescence is a sign of the appearance of a photochemical process. One can easily show^{5,6} that the quantum yield of the reaction in this case is represented by the formula

$$\gamma = \frac{\tau Z p}{1 + \tau Z p} \,. \tag{1}$$

Here Z is the number of collisions at a pressure of 1 mm and p is the pressure in mm.¹⁾ Hence we see that the quantum yield substantially depends on the gas pressure. Only under the condition $\tau Zp \ge 1$, i.e., at high enough pressure, does the value of γ reach unity; at low pressures γ is known to be less than unity. Likewise, at a constant pressure γ substantially depends on the number of collisions Z, which directly involves the temperature. Thus the characteristic signs of reactions of excited atoms are a small value of the quantum yield and a strong dependence of this quantity on the temperature and the pressure.

In addition to Z and p, Eq. (1) also contains τ , the time of existence in the excited state: as τ increases, also the reaction rate increases, and hence also the quantum yield. One can bring about a considerable increase in τ by converting the excited atom to a metastable state in which it (the excited atom) can spend a time interval considerably exceeding 10^{-8} s. Thus, for example, for the mercury atom (Fig. 1), near the excited state ${}^{3}P_{1}$ that we discussed lies the level ${}^{3}P_{0}$ (at a spacing of 0.2 eV from it), for which the transition to the ground level ${}^{1}S_{0}$ is "forbidden". Thus an atom that has entered into this state cannot spontaneously return to the ground state with emission of a light quantum. It will exist in the metastable state, preserving its energy store, until a collision occurs, in which this metastable atom will be able to transfer its excess energy, or until the atom obtains by collision the extra energy needed to return to the ${}^{3}P_{1}$ level, from which spontaneous return to the ${}^{1}S_{0}$ ground state can occur with emission of the

excess energy. If we bear in mind the quite significant increase of τ in the formula (up to 10^{-2} s), evidently in the presence of metastable atoms the reaction rate must increase very strongly.

It turns out that, if we add nitrogen or water vapor to the mercury vapor, the excited mercury atoms $({}^{3}P_{1})$ will impart an energy of 0.2 eV to these foreign molecules and transform to the metastable state. And actually, Wood and Gaviola⁷ established that the addition of N₂ or water vapor to a mixture of Hg and O₂ exerts a strong accelerating influence on the reaction of photochemical oxidation of mercury.

In this regard, interestingly, Mecke and Childs⁸ recently found a metastable state in the oxygen molecule (spectroscopic symbol ${}^{1}\Sigma$), whose duration of existence was estimated as 7 s. Oxygen molecules existing in this state have an excess energy of 37 kg \cdot cal/mole and therefore can exert considerable chemical effects. Recently Kautsky⁹ ascribed the principal role to these metastable oxygen molecules in processes of sensitized photooxidation, photosynthesis of carbohydrates, etc.

In closing we should note another extremely characteristic feature of the interactions of excited atoms. Experiment shows that in a collision the probability of energy transfer from an excited atom to an unexcited atom or molecule increases manyfold if the colliding particle has an energy level close to the value of the energy being transferred. Franck formulated this distinctive resonance condition as follows: the probability of energy transfer will be greater, the smaller the fraction of the transferred energy that goes into kinetic energy of translational motion of the colliding partners. This resonance in energy transfer can be demonstrated most distinctly of all with the case of "sensitized fluorescence" of sodium vapor in the presence of mercury vapor.¹⁰ If one illuminates a mixture of Na and Hg vapors with light of the resonance line of mercury (λ = 2537 Å), one observes sensitized fluorescence of the sodium vapor: the resonance line of Hg is not absorbed by pure sodium vapor; therefore upon illumination with $\lambda = 2537$ Å pure sodium vapor does not fluoresce, but in the presence of Hg vapor fluorescence arises, caused by energy transfer in the collision of excited Hg atoms $({}^{3}P_{1})$ to Na atoms. Here it turns out that the greatest light intensity of this sensitized fluorescence does not belong to the resonance D line of sodium at $\lambda = 5890$ Å, but to the doublet at $\lambda = 4223/4420$ Å $(2^2 P_{3/2,1/2} - 7^2 S_{1/2})$. On the other hand, the excitation energy of Na in the $7^2S_{1/2}$ state, which equals 4.880 eV, almost coincides with the excitation energy of the ${}^{3}P_{1}$ state for Hg (4.86 eV). However, if one adds to the mixture of Na and Hg vapors also a certain amount of nitrogen, then in the collision of an excited Hg atom $({}^{3}P_{1})$ with an N₂ molecule—the former transfers with high probability²⁾ the small excess energy ${}^{3}P_{1} - {}^{3}P_{0}$ to nitrogen molecules and goes over into the metastable state ${}^{3}P_{0}$. Under these conditions the greatest intensity in the sensitized fluorescence spectrum of Na is acquired by a new pair of lines 2752/2748 Å, which arises from transitions 2 ${}^{2}P_{3/2,2/1}$ 5 ${}^{2}S_{1/2}$: but the energy of the state of so-





dium (5 ${}^{2}S_{1/2}$), which equals 4.68 eV, is very close to the ${}^{3}P_{0}$ level of the mercury atom (4.64 eV).¹¹

The physical mechanism on which these resonance phenomena in energy transfer are based can be understood only on the basis of wave mechanics.¹² A discussion of the questions pertaining to this would lead us too far afield. We note only that the phenomena of quantum-mechanical resonance undoubtedly play a large role in processes of photochemical sensitization.

III. PHOTOCHEMICAL DECOMPOSITION OF DIATOMIC MOLECULES

1. Now let us turn to discussing a very important elementary photochemical process---the photochemical dissociation of a molecule-and start with the simplest case-the dissociation of a diatomic molecule. A photochemical dissociation that occurs directly after absorption of a light quantum was first discovered by Terenin¹³ for the case of vapors of the alkali halides. Somewhat earlier Franck¹⁴ had presented a perfectly clear picture of the physical mechanism of this decomposition. As is known, the spectra of molecules differ from atomic spectra in their considerably greater complexity and abundance of lines. This is explained by the fact that a molecule possesses also the levels of vibrational and rotational energy, in addition to the purely electronic energy levels, which are the sole possible ones in the case of atoms. Let A and B (Fig. 2) be two electronic energy levels. In the case of an atom the existence of these levels gives rise to the sole possibility of the transition $A \rightarrow B$ in the case of absorption and $B \rightarrow A$ for emission. Yet in a molecule another series of levels A_1 , $A_2, \dots, B_1, B_2, \dots$, rests on each of these levels, caused by the possibility of vibration of the atoms of the molecule with respect to one another, while in the intervals between the levels A and A_1 , A_1 and A_2 ,..., B and B_1 lies another series of levels (not shown in Fig. 2), corresponding to the different states of rotation of the molecule. Since transitions can occur between all these levels accompanied by absorption (or emission) of light, evidently we obtain, instead of a single line (corresponding to the transition $A \rightarrow B$), a large number of lines grouped into bands, very often characterized by the existence of a sharp edge or border. The position of these borders corresponds to the sequence of vibrational levels. Tracing the course of the vibrational levels¹⁵ shows that these levels, both in the lower, ground state, and in the upper, excited state gradually approach one another up to complete coalescence. Beyond the boundaries of this coalescence lies a continuous region of nonquantized energy values.

This succession of the vibrational levels corresponds to gradual weakening of the bonds in the molecule as the supply of its vibrational energy increases, so that ultimately a bond between atoms breaks, and the molecule dissociates into its constituent atoms. This decomposition precisely corresponds to the point of coalescence of the levels. With further energy increase of the vibrations its excess above the energy necessary to reach the point of coalescence is converted into the kinetic energy of the separated atoms. And since the latter is not quantized, i.e., can have any values, the region lying above the point of coalescence is continuous in type—one cannot distinguish any levels in it.

The gradual approach of the vibrational levels in the spectrum of the molecule corresponds to the gradual approach of the edges of the bands up to complete coalescence. Beyond the point of coalescence on the short-wave side a continuous spectrum must lie, which corresponds to transitions to the cross-hatched region in Fig. 2.

This type of series of bands, which ends at the point of coalescence with the adjacent continuous spectrum, is actually observed. One can trace this entire pattern with especial clarity in the spectrum of molecular iodine.¹⁶ It is evident from the abovesaid that, by determining the position of the point of coalescence, one can calculate the dissociation energy of the molecule. Thus, for the iodine molecule the point of coalescence is observed at $\lambda = 4989.3$ Å. This wavelength corresponds to a quantum energy of 2.468 eV; upon absorbing such a quantum the I₂ molecule decomposes into two atoms, of which one lies in the ground state, and the other in an excited (metastable) state with an excitation energy of 0.937 eV. Consequently the energy taken in the dissociation process itself will be 2.488 - 0.937=1.531 eV, or 35 kcal/mole. Thus a new and highly exact method is opened for determining the dissociation energy of molecules-a quantity so difficult to attain by measurement by the usual physicochemical methods.³⁾

From the photochemical standpoint it is especially interesting that "optical" dissociation must occur in the region of continuous absorption. The fact that this dissociation actually occurs for the case under discussion of molecular iodine has been proved by the most varied methods: from the disappearance of fluorescence upon illumination with wavelengths from the continuum region (λ <4995 Å),¹⁸ from the pressure decrease due to absorption by the walls of the vessel of the free iodine atoms that arise,¹⁹ from the change in heat conductivity of illuminated iodine vapor,²⁰ and finally, by direct spectroscopy from the appearance of the absorption lines of iodine atoms.²¹

The physical mechanism of this dissociation becomes especially clear from examining the potential energy curves of ground-state and excited molecules. The form of these





curves, which show the dependence of the potential energy of the atoms of the molecule on their spacing, is illustrated in Fig. 3. As the atoms approach, their potential energy decreases to a certain minimum that corresponds to the equilibrium distance between the nuclei r_0 ; upon further approach the potential energy increases steeply owing to the onset of repulsive forces. Evidently the ordinate, which equals the magnitude of the arrow D, equals the work that must be expended to remove the atoms from the equilibrium position to an infinite distance, i.e., the dissociation energy. Curve I corresponds to a ground-state molecule, and curve II to an excited molecule. If the electronic excitation is accompanied by weakening of the bonds in the molecule (as very often occurs), curve II must be displaced with respect to curve I to the right (the distance between the nuclei at equilibrium increases), and moreover the dissociation energy D' will be smaller than D. If now a transition occurs owing to electronic excitation from curve I to curve II, then, as Franck⁶ first showed, this transition must occur so that in the first instant the distance between the nuclei does not change (the Franck-Condon principle). Actually, since electronic excitation is an instantaneous process, then at the instant when the excitation is already complete, the heavy nuclei still occupy their previous positions. Consequently, as we can see from the diagram, even when we have a nonvibrating molecule in the ground state (or more exactly, a molecule with zero-point vibration), as happens in most cases at not too high a gas temperature, upon transition to curve II the nuclei acquire excess potential energy and begin to vibrate strongly. If here the point A' where the vertical arrow AA' points proves to lie above the horizontal asymptote of the upper curve II, then in the course of the first half-period of vibration (10^{-13} s) , the molecule will break apart, since its potential energy at point A will be larger than the dissociation energy in the excited state.

2. We have another case presenting features of theoretical interest when the absorption spectrum of the gas possesses no discrete portion at all consisting of separate lines, but is completely continuous. This situation is observed, e.g., in the hydrogen halide molecules HI, HBr, and HCl.²² In this case the potential curve of the excited molecule completely corresponds to an unstable state (Fig. 4). The existence of such states was first substantiated theoretically by London²³ in the construction of the quantum-



FIG. 4.

mechanical theory of the homopolar bond. In the simplest case of interaction of two hydrogen atoms, it turns out that in 25% of the total number of possible cases the interaction of the hydrogen atoms occurs along the "stable" potential curve I, which has a minimum that corresponds to the equilibrium position, while in 75% of the cases the atoms repel one another at all distances. In all these cases the potential curve rises upward monotonically with decreasing distance (curve II in Fig. 5), and at no distance is a stable molecule formed. If now the absorption spectrum of the molecule is continuous throughout its extent, this means that transition to the excited state is always accompanied by dissociation. The mechanism of this process is depicted in Fig. 5, which needs no special explanation after the abovesaid.

3. Finally, let us discuss the case of decomposition in the so-called *predissociation* spectrum. The phenomenon of predissociation, which was discovered by V. Henri,²⁴ is outwardly manifested in the fact that in certain molecular spectra, as one traces the bands toward short wavelengths, beginning at a certain wavelength, sometimes suddenly, sometimes gradually, the fine structure of the bands vanishes. The bands as such continue to exist, and do not coalesce into an entire continuous absorption region, but the individual lines of which they consist, and which are due to the rotation of the molecules, blur and become unresolvable. This type of spectrum is observed very often,









and both in simple and complex molecules $(NH_3, NO_2, CS_2, benzene, formaldehyde, and many others).$

A correct description of the origin of predissociation was first indicated by Born and Franck.²⁵ Briefly. it reduces to the idea that the disappearance of the fine structure of the bands is caused by dissociation within a time comparable to the period of rotation of the molecule $(10^{-12}-10^{-10} \text{ s})$. Since Rayleigh's time we know that an ideally monochromatic, and hence, an ideally fine spectral line is an abstraction. Such a line might arise only in the case that the vibrations that excite it would continue infinitely long, and hence, the wavetrain would be infinitely long. In fact, the vibrations continue for a finite time, which implies in the language of quantum theory that the time of existence τ in the excited state has a finite value. Therefore an actual spectral line always has a finite width, which is further increased by blurring arising from the Doppler effect. The intrinsic width Δv is associated with the time τ during which the vibration occurs (or, as is the same, the time of existence in the excited state) by the relationship

 $\tau \Delta v = 1.$

For a normal value of τ (10^{-8} s), the width $\Delta \nu$ amounts to several hundredths of an Ångstrom unit. Yet if τ decreases, correspondingly $\Delta \nu$ increases. In the case of predissociation the width $\Delta \nu$ is such that it exceeds the spacing between the individual rotational lines of the band. Hence we can estimate the order of magnitude of τ to be 10^{-12} – 10^{-10} s, which corresponds to the period of rotation of the molecule. The fact that decomposition of the molecule actually occurs in the course of this time interval is indicated by the numerous experiments of Henri himself²⁷ and of others.

We shall examine the mechanism of this decomposition with the aid of the diagram of energy levels and potential curves. Here we can trace the onset of decomposition by using the diagram in Fig. 6. Let us assume that, along with the excited state B into which the molecule goes directly upon excitation, there is also a second state B'situated such that the continuous region of state B' corresponds to a discrete level of state B at the same energy.



FIG. 7.

Then for a molecule existing in state B, a certain probability arises of transition to a state of equal energy belonging to the system B'. But, since now the continuous region of system B' lies at the level of B, this transition is effected by decomposition of the molecule. However, it turns out that the transition from the discrete energy level shown in Fig. 7 to the continuous absorption region can occur only when an additional condition is fulfilled, which consists in the fact that the potential curves corresponding to states B and B' must intersect. Let us study two typical cases. Let n be the potential curve of the ground state, and α and α' the curves of the excited states. Transition from curve n leads directly to curve α , since by the Franck–Condon principle this transition must occur without change in the distance between the nuclei. If this transition, as, e.g., the transition AB, leads to a point of curve α lying below the point F of intersection of curves α and α' , then nothing unusual happens. The absorption bands that are obtained have a normal structure. Yet if the transition leads to point D lying below the horizontal asymptote of curve α , but above the intersection of curves α and α' , then in the vibrations in the "potential well" DBEF, the molecule will pass each time through the point of intersection of curves α and α' . and here a probability will arise of transition from curve α to curve α' . Consequently, after several vibrations along curve α , the molecule goes over to curve α' . But once this transition occurs, it unavoidably ends in decomposition, since the potential energy of the molecule will be larger than the dissociation energy corresponding to curve α' . Thus, as long as the transition from curve n lead to the same part of curve α' that lies below the level EG, which corresponds to the intersection of the curves, the bands have a normal form. As soon as a transition arises to a point lying at the level n or above it, it ends in dissociation. and the band acquires a diffuse form.

Another characteristic case is shown in Fig. 8. Here the second curve α' is an unstable repulsion curve. The difference from the previous case consists in the following. Let the molecule exist at the level *H* of curve α . At the same height as this level lies the point *K* of the potential curve α' , and the molecule must undergo decay upon arriving there. But the points *H* and *K* are separated by the





potential barrier *HEK*, and hence one must raise the molecule up to the top of this barrier E in order for it to roll down along curve α' . However, we know from quantum mechanics that tunneling transitions *below* the barrier are possible between two regions of equal energy separated by a potential barrier, although they are improbable. Here, the closer to the top of the barrier the molecule is raised, the greater is the probability of a tunneling transition. Thus we can expect that, in the case in which the potential curves have the described character, diffuseness does not arise immediately, but increases gradually as the probability of transition to the curve α' increases.

4. We saw above that jodine molecules illuminated with light from the region of the continuous absorption spectrum ($\lambda < 4989$ Å) undergo spontaneous dissociation in a time interval comparable to the period of vibration. At wavelengths greater than 5000 Å the absorption spectrum of iodine is discrete and decomposition is not observed, although the molecule in each elementary event can absorb quanta exceeding its dissociation energy. However, it turns out that, if one adds a foreign gas to the iodine vapor, e.g., argon, then one observes dissociation, both in the continuous and in the discrete parts of the spectrum ($\lambda > 5000$ Å).²⁸ Evidently in this case the dissociation in the discrete part of the spectrum is a result of collisions that an excited molecule undergoes in the course of time with a foreign molecule. The reason for this forced decomposition is the phenomenon of the so-called induced predissociation, which plays a large role in photochemical processes. Kronig²⁹ showed that the onset of predissociation requires, in addition to the conditions discussed above, the fulfillment of a number of other conditions. Thus, for example, conservation of the total angular momentum, fulfillment of an entire set of symmetry properties, etc., are required. If any of these conditions is not fulfilled, then, although a discrete level of the one system coincides with the continuous region of the other system, predissociation does not occur, and the molecule can retain its integrity. If, however, factors are present that make possible the breakdown of the selection rules, then transition to the unstable potential curve becomes possible, and absorption is accompanied by decomposition. Precisely iodine has a repulsive



FIG. 9.

potential curve (Fig. 9), transition to which is forbidden under normal conditions.³⁰ However, it suffices to place the vapor being illuminated into a magnetic field to create conditions that remove the forbidden character of the transition. And actually it has already been known for a long time that the fluorescence of iodine vapor is guenched in a magnetic field. This quenching is explained by the realization in the magnetic field of a "forbidden" transition to the repulsive curve, whereby the excitation energy does not return in the form of fluorescence light, but is spent in dissociating the molecule. The same role of a factor that allows a transition to the repulsive curve forbidden under normal conditions can also be played by collisions with foreign molecules. To understand the role of collisions, Kondratjew and Polak³¹ studied the influence of gases with different physical and chemical properties; specifically, they took nitrogen as the inert gas, oxygen as a paramagnetic gas, and hydrogen chloride as a polar gas. It turned out that the order of magnitude of the inducing action of all three of these gases is the same. We can conclude from this that to realize induced predissociation requires only collision with any foreign particle whatever, while the individual properties of this particle play no role. This confirms the hypothesis advanced by Turner,²⁸ according to which the reason for the forbiddenness of the transition to the unstable potential curve is the breakdown in this transition of the law of conservation of total angular momentum. The role of the foreign particle in this case is reduced to taking on the excess angular momentum, so that, for the system iodine+foreign particle, the law of conservation of angular momentum will be fulfilled. Thus we see that spontaneous photochemical decomposition in the continuous spectrum occurs whenever induced decomposition can occur also in the discrete absorption spectrum.

IV. PHOTOCHEMISTRY OF COMPLEX MOLECULES

1. The analysis of the primary photochemical process in the case of complex molecules, of course, involves great difficulties. However, even in this field considerable advances have been attained recently.

Just as in the case of diatomic molecules, the guiding thread for recognizing the primary photochemical event comes primarily from the absorption spectra. It has already been known for a long time³² that certain groups of atoms make themselves known in a certain way in the spectra of various complex molecules in which they enter as constituent parts. Thus, for example, the carbonyl group >C=O yields a characteristic absorption band with a maximum at 2800 Å; the benzene ring or the phenyl group C_6H_5 shows absorption in the region from 3000 to 2300 Å, etc. Such groups are called "chromophoric," where this word is commonly placed in quotation marks since the "light" often proves to be "ultraviolet." On the other hand, as is known, the introduction in addition to a chromophoric group of other groups into a molecule often leads to displacement of the absorption region of the chromophoric group. Moreover, the absorption spectrum of chromophoric groups in complex molecules is usually so diffuse that it can no longer serve as an unambiguous index of the presence of any particular group. In this regard considerable help is rendered by studying the intrinsic vibration frequencies of the molecule. Here the vibration frequencies in the excited state can be found from the absorption spectra if the latter retain their band structure. However, especially rich material exists concerning the vibration frequencies in the ground state of the electron shell, since these latter vibrations can be found very conveniently by using the Raman effect.³³

example, the absorption For spectrum of formaldehyde⁴) H₂CO is discrete in character and shows two vibration frequencies: $\omega'_1 = 1180$ and $\omega'_2 = 830$ cm⁻¹. The Raman effect makes it possible to find in the same formaldehyde the frequencies $\omega_1'' = 1768$ and $\omega_2'' = 1039$ cm^{-1} . Thus the frequencies exhibited in the absorption spectrum are appreciably lower than the frequencies manifested in the Raman effect. This is explained by the fact that the latter makes it possible to find the frequencies in the ground state. Whereas the absorption spectrum yields the frequencies in a state with an excited electron shell in which the bonds are already weakened, and therefore the frequencies naturally are lower. Actually a direct determination of the vibration frequencies in the ground state for the gaseous formaldehyde molecule performed by using the fluorescence spectrum of H₂CO yielded $\omega_1'' = 1713$ and $\omega_2'' = 1039 \,\mathrm{cm}^{-1}$. Undoubtedly the former frequency (1713 cm^{-1}) pertains to the carbonyl group, since it is manifested in all compounds containing this group. According to Herzberg the lower frequencies $\omega_2'' = 1023$ and ω_2' = 830 cm^{-1} arise from the transverse vibrations of the H atoms in the molecule

 $H \to C = 0.$

Another highly characteristic example is given by the benzaldehyde molecule

H C₆H₅CO, which differs from formaldehyde in the introduction of the phenyl group C_6H_5 . This molecule gives a banded absorption spectrum lying in the region from 2700 to 2400 cm⁻¹ and exhibiting the frequencies 945 and 197 cm⁻¹ characteristic of the benzene ring. Remarkably, the presence of the carbonyl group in no way affects the absorption spectrum, since no absorption is observed in the region $\lambda = 2800$ Å. Likewise the absorption spectrum of acetophenone

in its position and in the frequencies that it exhibits is also characteristic of the phenyl group and does not reveal the presence of the carbonyl. The latter two examples are especially interesting from the standpoint of the fact that they show that, if a molecule contains *two* chromophoric groups, absorption can occur from one of them, while the other proves to be unaffected.

2. Turning to discuss different types of photochemical reactions in complex molecules, we first take up the cases in which the elementary event is reduced to the excitation of the molecule. The most interesting example of such reactions might be the so-called conversion of stereoisomers occurring under the action of light. Thus, *trans*-stilbene is converted into *cis*-stilbene:

$$C_{6}H_{5}-C-H \qquad H-C-C_{6}H_{5}$$

$$\parallel \qquad +h\nu \rightarrow \qquad \parallel$$

$$H-C-C_{6}H_{5} \qquad H-C-C_{6}H_{5}^{-1}$$
trans-stilbene cis-stilbene

Maleic acid is converted into fumaric acid:

Analysis of the absorption spectra of these substances showed that the chromophoric character is possessed by the ethylenic double bond C=C: namely, on the electrons forming this bond, and light absorption occurs. But in this case the conversion reactions described above acquire a very simple explanation. Light absorption breaks one of the two bonds of C = C, whereby free rotation is restored about the remaining bond, and the molecule upon returning to the ground state can convert either into the one or the other stereoisomeric form. Here in the case of conversion of maleic acid into fumaric acid, the probabilities of transition from the excited state into the one or the other form differ little from one another, which explains the small quantum yield of this conversion; conversely, in the conversion of trans-stilbene into cis-stilbene the quantum yield is of the order of unity, which indicates a sharply marked preference for transition from the excited state into the form of *cis*-stilbene. Evidently both forms (*trans* and cis) are energetically separated by a potential barrier, to overcome which the molecule must be raised to a higher energy level. But in return from the excited state to the ground state of the cis-isomer, the excess energy must be released either in the form of light of fluorescence or spent in inelastic collisions. In fact the conversion of maleic acid into fumaric acid is not accompanied by emission; consequently the excess energy is released here by an inelastic collision; conversely, *trans*-stilbene fluoresces upon illumination. Since the quantum yield in the latter case equals unity, the emission of light must occur simultaneously with the conversion event.

An experimental proof of the hypothesis presented here for the case of conversion of *trans*- into *cis*-stilbene can be the fact that the quantum yield for wavelengths corresponding to absorption by an electron of the ethylenic bond equals unity.

3. Now we shall proceed to processes of decomposition of complex molecules occurring in a single elementary event in a time interval of the period of vibration, i.e., 10^{-13} - 10^{-14} s. The absorption spectrum in the presence of decomposition in such a time interval must be continuous. However, the converse statement in the case of complex molecules, generally speaking, is false: the absorption spectrum here very often is continuous in character, but far from always the reason for this diffuseness is dissociation occurring upon absorption. The existence of many parts in the molecule and the mutual influence of their electrostatic fields often lead to complete blurring of the spectrum (owing to the Stark effect) without any dissociation.

Thus we cannot decide whether dissociation occurs or not in the case of complex molecules from the form of the spectrum alone.

To discover decomposition and to identify its products, one must apply other methods. However, to "trap" the products of immediate decomposition, one must apply such methods as make it possible to detect these products in the course of the very short time after completion of the decomposition event, since the free atoms or radicals obtained can recombine or react with other molecules. As always, the most refined method is the spectroscopic method. If the magnitude of the absorbed quantum suffices, not only to decompose the molecule, but to convert the decay products to the excited state, then one can determine these products from the fluorescence spectrum that arises here. In the case of complex molecules consisting of H, C, and O atoms, the quanta required for this are so large that the corresponding wavelengths lie in the Schumann ultraviolet (wavelengths of the order of 1000 Å). A. N. Terenin³⁵ was able to overcome the experimental difficulties involved in working in this region of the spectrum, where even air yields a strong absorption, and to study the decomposition of a number of molecules, namely, molecules of water, methyl and ethyl alcohols, formic and acetic acids, CH₃CN, and NH₃. In all these cases it was possible to detect the emission spectra of the radicals OH, CN, and NH₂, which implies that, in decomposition in the Schumann region of the spectrum, the cited radicals are obtained in the excited state.

Another method applied by Terenin for fast trapping of decomposition products is more chemical in character. It is based on using the Paneth method for detecting alkyl free radicals (CH_3 , C_2H_5 , etc.) and consists in the following. On the walls of the vessel (or tube) where the reaction occurs one deposits a mirror made of various pure metals (bismuth, tellurium, lead); when the radicals react with the metal, volatile metalloorganic compounds are obtained, and the mirror disappears. By tracing the disappearance of the metal of the mirror by measuring its transparency, Terenin converted this method from a qualitative to a quantitative one. A distinctive variant of this method was proposed by Mortensen and Leighton. By depositing instead of lead its radioactive isotope (radium D) as the mirror to a trap, it was possible to improve the sensitivity of the method considerably. It was possible in this way to observe a steady-state concentration of radicals corresponding to a partial pressure of 10^{-8} Torr.

By using the described methods Terenin studied the decomposition of the metalloorganic compounds $Hg(CH_3)_2$ and $Pb(C_2H_5)_4$, while Mortensen and Leighton studied the decomposition of $Pb(CH_3)_4$. It was found in all cases that the decomposition is actually accompanied by the detachment of free radicals. We should note that the "half-time" of existence of free radicals is of the order of magnitude on one thousandth of a second.

In all the discussed cases the decomposition occurs in a certain bond and is essentially completely analogous to the dissociation of diatomic molecules in the true continuum.

4. Now let us proceed to discuss the decomposition of complex molecules in a time interval of the order of the period of rotation of the molecule $(10^{-10}-10^{-12} \text{ s})$. This decomposition is effected via predissociation (see III, Sec. 3.4), which is observed in the spectra of complex molecules rather often (e.g., in phosgene, thiophosgene, acetone, formaldehyde, acrolein, etc.). In the case of complex molecules the mechanism of this process of decomposition in the predissociation spectrum, which is reduced to "switching" of energy from the stable excited state to an unstable state of the same energy, shows some highly characteristic and interesting features (Franck, Sponer, and Teller).³⁶ To elucidate these features, let us return to the pattern of potential curves that was discussed in connection with predissociation of diatomic molecules. As we saw, predissociation of diatomic molecules occurs the potential curve of the excited state α intersects with another potential curve α' that corresponds to a less stable or unstable state. In such a case, as was explained, a probability arises of transition from the stable potential curve to the unstable curve-a transition culminating in decomposition. Owing to the considerable shortening of the lifetime of the excited molecule (by a factor of 10^3 to 10^4), the rotational lines of the bands broaden until they coalesce, and the band acquires a diffuse form.

In the case of polyatomic molecules the described process becomes considerably more complicated. The principal complication consists in the fact that, even when the *the energy of the vibrations suffices* to bring the nuclei into a position in which predissociation can occur, a very long time interval can pass before this position will be actually attained.

Let us discuss the reason for this "delay." In the case of diatomic molecules the energy state of the molecule is determined by only one parameter. For polyatomic molecules the relative positions of the nuclei are determined generally by several parameters. Let us discuss a very simple case and assume that we are dealing with a molecule whose state is determined by two parameters.⁵⁾ Correspondingly, the potential curves α and α' are replaced here with the potential surfaces A and A', while the intersection point of the curves is replaced with an intersection line. If we know the state of our polyatomic molecule as given by the values of the two parameters, then this state is represented on the potential surface by some "image" point whose two coordinates are determined by the given values of the parameters. When vibrations (variations of parameters) occur in the molecule, the "image point" will describe a certain curve on the potential surface. Evidently, only at the instant when, in moving over this curve, the "image point" falls on the line of intersection of the potential surfaces A and A', the nuclei in the molecule will be brought into a state in which predissociation can occur. But up to this instant from the onset of excitation of the molecule a very considerable time interval can elapse. In fact, let us discuss in somewhat greater detail the different possible cases of motion of the "image point:"

a) The image point performs a one-dimensional motion on the potential surface. This means that only one of the two "normal vibrations" is excited. If in this uniform motion the image point falls on the intersection line of the potential surfaces A and A', conditions will be created under which predissociation can set in. Evidently, in this case the predissociation process occurs in completely the same way as in diatomic molecules.

b) Both normal vibations are excited. In this case the image point generally describes on the potential surface a highly complex Lissajous curve. In this case it is evident that, before the conditions necessary for existence of predissociation are created, i.e., before the image point reaches the necessary site through the intersection line of the potential surfaces, a considerable time interval can elapse.

c) The image point performs a one-dimensional motion, but its trajectory does not pass at all through the intersection line of the potential surfaces. In this case predissociation does not set in at all. However, if we bear in mind the fact that the forces under whose influence the vibrations occur differ from quasielectric forces, so that the vibrations are anharmonic, then, as is known from the theory of vibrations, we cannot consider the normal vibrations to be uncoupled: if one of them has arisen, then after a certain time interval the other one is necessarily excited. However, in this case the one-dimensional trajectory of the image point is converted in the course of time into a Lissajous figure. As it moves along the latter, the image point finally reaches the intersection line. Thus predissociation ultimately sets in; however, the time interval needed for all the nuclei to occupy positions in which decomposition can occur increases so much that the time of existence in the excited state before decomposition can attain the normal value $\tau \approx 10^{-8}$ s.

As the final result of the discussion that we have conducted, we can state that in the case of polyatomic molecules the time over which the process of predissociation is completed generally is increased by a factor of 10^2-10^3 . But in view of the relationship $\tau\Delta\nu=1$ that we already know between the "unsharpness of the frequency" $\Delta\nu$ and the time of existence in the excited state, as τ increases $\Delta\nu$ declines, and if τ reaches the usual value of 10^{-8} s, the lines again acquire the normal sharpness. In such a case the spectrum maintains its *discrete structure*, despite the fact that the absorption will end in decomposition.

Norrish³⁷ pointed out a number of interesting cases that confirm the ideas of Franck, Sponer, and Teller that we have presented. If dissociation occurs in the discrete part of the spectrum, then the onset of decomposition can be established either by detecting its products or-in considerably more refined fashion-by establishing the disappearance of fluorescence. Actually, in formaldehyde dissociation is observed at wavelengths from 3300 to 2000 Å, but diffuseness of bands can be detected only for wavelengths below 2700 Å; on the other hand, fluorescence ceases already at 3600 Å, i.e., at wavelengths even somewhat larger than those at which appreciable dissociation sets in. Undoubtedly the latter circumstance is explained by the considerably greater sensitivity of the method of detecting quenching of fluorescence as compared with other physicochemical methods.

A very interesting result was found in the case of acetone³⁸ and NO₂.³⁹ Here it turned out that there is a region of about 300 Å where one observes simultaneously both fluorescence and predissociation. This circumstance especially distinctly confirms the view of Franck, Sponer, and Teller presented above, since if fluorescence and dissociation have the same probability, then this means that the times of existence in the excited state in the two cases are the same, i.e., of the order of 10^{-8} s.

A distinctive and interesting type of decomposition is shown by aldehydes and ketones, as well as certain organic acids in the gaseous state. All aldehydes

$$R \rightarrow CO,$$

where R is any radical, and ketones

$$R_1 > CO$$

contain the carbonyl group

which here is "chromophoric." Actually all these compounds have a continuous absorption band characteristic of the carbonyl group that extends from 3500 to 2000 Å with a maximum at 2800–2900 Å;⁴⁰ this band appears both in the gaseous and in the liquid state, and also in solutions. The decomposition of aldehydes and ketones is of the predissociation type. Thus, for example, in the case of formaldehyde and acetaldehyde, in addition to the mentioned continuous spectrum, bands exist, which at first show rotational structure, but at a certain wavelength (at $\lambda = 2750$ Å for formaldehyde, and at $\lambda < 3000$ Å for acetaldehyde) it disappears, with simultaneous onset of photochemical dissociation. Here the decomposition for all the studied simple aldehydes occurs by the same pattern

$$\stackrel{R}{H} > CO + hv = RH + CO.$$

For example, for formaldehyde one observes decomposition into hydrogen and carbon monoxide⁴¹

$$\stackrel{\mathbf{R}}{\longrightarrow} CO + hv = H_2 + CO,$$

while for acetaldehyde the reaction leads to formation of methane and carbon monoxide⁴²

$$\begin{array}{c} CH_{3} \\ H \end{array} > CO + hv = CH_{4} + CO, \end{array}$$

and benzaldehyde decomposes into benzene and carbon monoxide 43

$$\underset{C_6H_5}{\overset{H}{\longrightarrow}}CO+h\nu=C_6H_6+CO.$$

Remarkably, in all cases decomposition and recombination occur in a single elementary event. This can be seen from the following fact. If the first stage of decomposition consisted in splitting off hydrogen or a hydrocarbon radical and in subsequent reaction of them with one another or with the residue of the molecule, then the products of the reaction necessarily must contain molecular hydrogen and molecules that are products of recombination of the radicals with one another (e.g., C_2H_6 in the case of acetaldehyde). But precisely these products are not observed, and the decomposition proceeds almost 100% by the stated patterns. This implies that the entire decomposition is completed within a single excited molecule, and free atoms or radicals do not arise.

We have another pattern in the case of ketones. Here everything indicates that the first stage of decomposition precisely consists of detachment of a free radical. This can be seen especially clearly in the example of mixed ketones. Here the reaction products amount to an almost equimolecular mixture of hydrocarbons according to the scheme:

$$\frac{R_1}{R_2} > CO + hv = \frac{1}{3}(R_1R_1 + R_1R_2 + R_2R_2) + CO.$$

For example, for the case of methylethylketone one obtains

$$CH_{3} > CO + hv = \frac{1}{3}(C_{2}H_{6} + C_{3}H_{8} + C_{4}H_{10}) + CO.$$

The difference in the mechanism of decomposition of aldehydes and ketones was shown with especial clarity by Pearson who detected free radicals upon illuminating simple ketones, but could not do this with aldehydes.

The reason for the difference in behavior of aldehydes and ketones has not yet finally been established. However, one can express a likely hypothesis. For this purpose we shall first formulate the experimentally established fact as follows. The elementary photochemical process for aldehydes consists in a rearrangement in which hydrogen changes in position by combining with a radical, whereas for ketones the elementary photochemical process consists in the detachment of a radical. However, since the hydrogen and the radical in an aldehyde have saturated valencies, then according to quantum mechanics⁴⁴ they repel one another upon approaching. Therefore the rearrangement requires a certain activation energy to overcome the potential barrier separating the two parts of the molecule. On the other hand, in the presence of a potential barrier there is always a certain probability of penetration beneath the barrier ("tunneling effect"). Terenin³⁴ advanced the hypothesis that the possibility of rearrangement in the case of aldehydes is due precisely to the small mass of the hydrogen atom, since this circumstance increases the probability of penetrating beneath the barrier.

5. The photochemical behavior of organic acids in the gaseous state has not yet been studied sufficiently. As is known, all the acids have practically the same absorption (a continuous band with a maximum at 2040 Å), independently of the number of carbon atoms entering into the composition of the acid.^{45,46} Evidently this absorption must be attributed to the COOH group that enters into all the acids.

We can assume on the basis of the existing data that the elementary photochemical event for the acids is analogous to that for the aldehydes. Thus, for formic acid the process is observed⁴⁷

$$H_{HO} \rightarrow CO + h\nu = H_2O + CO,$$

and for acetic acid⁴⁸

$$\frac{CH_3}{HO} > CO + hv = \frac{CH_4}{(50\%)} + \frac{CO_2}{(50\%)}.$$

Moreover, in the case of acetic acid, in addition to the stated process, another process is also observed, in which C_2H_6 , CO_2 , CO, and H_2O are obtained. However, undoubtedly, this process involves double molecules of acetic acid, since it is observed only when these double molecules are present (in the gaseous state and in solution in hexane), and is not observed when there are no double molecules (in aqueous solution; see below). Characteristically, molecular hydrogen is not formed here,⁶⁾ which indicates that the process, as in the case of aldehydes, occurs within the molecule itself and does not involve detachment of free radicals.

6. Let us proceed now to discuss another distinctive phenomenon that is observed among complex molecules and is possible precisely owing to the large number of atoms and different bonds. For this purpose we note first of all that in a polyatomic molecule processes can occur of *stabilization*, in which the energy absorbed by any chromophoric group may be used not to break bonds in this group, but may be transferred to other atoms or groups. This can explain, e.g., the fact that the quantum yield in the decomposition of acetone in the region of the continuous absorption spectrum is not unity, but amounts to only 0.4. In fact, if the process of light absorption by a diatomic molecule occurs precisely at the instant of its collision with another molecule, the excess energy can be transferred to this collision partner and dissociation does not occur. In a gas consisting of diatomic molecules such absorption processes at the instant of collision are rare. A polyatomic molecule contains within itself a constant reservoir in the form of the different groups constituting it, to which the excess energy can be transferred. Therefore, in a polyatomic molecule processes of stabilization are far more probable than in diatomic molecules.

However, the following fact is considerably more interesting. If a polyatomic molecule absorbs light, then, as we have seen, this usually occurs at some definite site in the molecule–wherever the absorbing bond of a chromophoric group exists. Here the remaining bonds lying in other parts of the molecule can prove to be completely unaffected at the instant of absorption. It turns out, however, that the absorbed energy can undergo fluctuations within the molecule, as a result of which its action can be manifested, not where it was absorbed, but at a completely different site. Let us give several examples. Acetophenone

$$CH_3 > CO$$

and benzaldehyde

contain two chromophoric groups: carbonyl >C=O and the phenyl radical C_6H_5 (the benzene ring). It turns out upon comparing the absorption and fluorescence of these molecules⁴⁹ that absorption in the one and the other substance occurs at the phenyl group (absorption maximum at 2600 Å, with the presence of frequencies at 900 cm⁻¹ characteristic of the benzene ring), whereas the emission (fluorescence) spectrum is characteristic of the carbonyl group (presence of the frequency 1750 cm⁻¹ characteristic of the >C=O group).

From the photochemical standpoint the facts discovered by Norrish³⁷ are even more interesting. It turned out that, in the decomposition of long-chain aldehydes and ketones, the decomposition occurs at a site in the molecule considerably remote from the site where the absorption of a quantum occurs. As always, the absorption occurs at the carbonyl group, yet the decomposition occurs in the long chain attached to the carbonyl group. For example, methylbutylketone decomposes according to the scheme

$$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{1}$$

$$\stackrel{^{1}}{=}O+h\nu$$

$$=CH_{3}CO+CH_{3}CH:CH_{2}.$$

Here the arrow \downarrow indicates the site where the quantum is absorbed, while the double arrow $\uparrow\uparrow$ indicates the site

where decomposition occurs. In exactly the same way, in the case of valeraldehyde the principal decomposition occurs by the scheme

$$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}$$

$$\downarrow H$$

$$\downarrow O + h\nu$$

$$\rightarrow CH_{3} CO + CH_{3}CH:CH_{2}.$$

The magnitude of the absorbed energy amounts to 90–95 kg \cdot cal/mole, whereas the energy spent in effecting the decomposition that occurs lies between 25 and 65 kg \cdot cal. Such an amount of energy cannot be transferred via *vibrations* of parts of the molecule (the energy of vibrations is of the order of tenths of a kilocalorie per mole). Thus we arrive at the conclusion that processes of energy transfer can occur within a complex molecule analogous to inelastic collisions-a distinctive type of internal inelastic collisions. As is known, these collisions amount to a quantum-mechanical effect of resonance type, and the problem of theoretical physics is to offer an explanation of this interesting phenomenon.

V. PHOTOCHEMICAL REACTIONS IN SOLUTIONS

1. Photochemical reactions in solutions are of greatest interest to a chemist. Yet for a physicist who is called on to interpret the mechanism of elementary processes, the liquid state presents the greatest difficulties. In fact, up to now we know even least of the nature of liquids, and if previously we transferred to liquids all that we knew about gases, now we are inclined to consider them closer to solids than to gases.⁵⁰ Despite all these well known difficulties, in recent years we have advanced rather far also in understanding photochemical processes in solutions.

Unfortunately, in this case the absorption spectra tell us even less than in the case of complex molecules. Actually the absorption spectra of solutions, especially aqueous ones, with rare exceptions are continuous. However, the diffuseness of the spectrum in a given case is in no way an unambiguous sign of occurrence of dissociation. In fact, a molecule in solution is surrounded by a vast number of solvent molecules, and one can say that it exists continually in a state of collision. Thus the diffuseness of spectra in solutions is due primarily to two factors: a) the influence of the electric fields of the surrounding molecules (the Stark effect), and b) the shortening of the lifetime of the excited state owing to collisions with the surrounding molecules. These collisions, in turn, can lead to a) dissociation, and b) dissipation of the excitation energy and degradation into thermal energy. Thus we see that dissociation or photochemical decomposition is only one of an entire set of factors that cause the diffuseness of the spectrum. This implies that, in the case of solutions, the onset of dissociation can be established solely from the appearance of decomposition products; spectroscopic methods here do not yield an unambiguous answer.

2. The most characteristic feature of a reaction in solution is the small quantum yield observed in such reactions. The reason for this can be understood if we bear in mind precisely the fact that we can consider a molecule of a dissolved substance to be continually in a state of collision with the surrounding solvent molecules. We have already mentioned above that in gases absorption at the instant of collision can lead to stabilization of the absorbing molecule, since the excess energy acquired by the latter can be transferred to the collision partner and, in particular, can be transformed into the kinetic energy of translational motion of the collision partners. But in a gas the probability of such an absorption at the instant of collision, or even of collision in the time interval that passes between the instant of absorption and the decomposition event, has an insignificant magnitude ($\sim 10^{-4}$ at atmospheric pressure), since the lifetime of a molecule that absorbs in the true continuum is small ($\tau = 10^{-13}$ s). Yet in a liquid the dissolved molecule constantly exists in the sphere of influence of surrounding molecules. Therefore in a solution conditions are constantly present that favor stabilization. Consequently the probability of stabilization becomes quite significant, despite the fact that the probability of conversion of the excitation energy into translational energy is generally very small.

But if even the absorption by the dissolved molecule ends in its decomposition, there is a large probability that the results of this decomposition will be nullified by subsequent recombination of the products. In fact, in a solution the "crowding" is such that the decomposition products cannot separate far during a considerable time interval, and remain near one another. Consequently the possibility of repeated collisions arises for them, in which recombination can occur. The number of such collisions can reach several hundred before the decomposition products separate to a sufficient distance (if, of course, recombination has not occurred earlier).⁵¹

The possibility of secondary reactions of the decomposition products with solvent molecules plays a no less important role. In fact, there are no factors that would hinder the *atoms* or *radicals* that arise in the photochemical process from reacting with the solvent. If this reaction proves reversible, then after illumination the initial state is restored, and the energy is simply dissipated. Yet if the reaction is irreversible, then it yields some additional products whose possible appearance must be taken into account.

All of the discussed factors diminish the quantum yield, even in the continuous spectrum, i.e., in the region where in gases we obtain a quantum yield equal to unity (or close to unity).

Moreover, we note that, whenever decomposition occurs in the discrete part of the spectrum, e.g., owing to induced predissociation, the probability of predissociation itself in solution will be incomparably larger than in a gas, since in solution successive collisions are made possible for the molecule that has absorbed light. However, this heightened probability of decomposition is fully covered by the discussed factors that lead to a reduced final yield. 3. In studying reactions in solutions, especially aqueous solutions, another distinctive factor appears on the scene-electrolytic dissociation. Therefore we shall discuss separately photochemical processes in undissociated molecules and in ions. Of course, the mechanism of the process in the two cases is completely different.

Let us start with reactions in undissociated molecules. The absorption spectra of such molecules in solution are continuous throughout, and therefore differ strongly from the corresponding spectra of the gas. But the course of the absorption coefficient, i.e., the absorption curve itself, is almost identical in the two cases, and sometimes even completely identical.⁷⁾ For example, in solutions of I₂ in chloroform and carbon disulfide the absorption maximum lies between 5000 and 6000 Å, whereas in gaseous iodine it lies at 5000 Å. Also for the other halogens Br_2 and Cl_2 the absorption spectra in solution are close to those for the gas. In H₂O₂ the absorption spectra in the gaseous state and in aqueous solution are completely identical. The same is observed in complex organic molecules: the absorption spectra of aldehydes in solution, apart from those cases in which solvation or hydration occurs, are identical to the spectra of the same substances in the gaseous state, which indicates the identity of the chromophoric groups in the two cases. Likewise, the organic acids in solution yield, as in the gases, an absorption spectrum identical for all acids and pertaining to the chromophoric group COOH.

The similarity or identity of the absorption curve in solution and in the gas indicates the identity of the elementary photochemical processes in the two cases. Thus the various reactions in which the absorbing component is the I_2 molecule, undoubtedly, are caused by the photochemical dissociation of I_2 and the appearance in solution of free iodine atoms. From this standpoint the photoreaction between I_2 and oxalate salts has been studied in especial detail.⁵³

Reactions in which the Cl_2 molecule participates also involve the preliminary photochemical dissociation of this molecule and the appearance of free Cl atoms. However, these reactions are always complicated by the interaction between the chlorine atoms that are obtained and the solvent. This pertains to the reaction in chlorine water⁵⁴ and the chlorination of trichlorobromomethane. Unfortunately, it is precisely these simpler cases that have been studied extremely insufficiently from the photochemical standpoint, so that the existing experimental data provide little material for discussion.

4. The photochemical behavior of the aliphatic carboxylic acids has been studied more fully.²⁵ The most interesting point here is that these acids in aqueous solution exhibit the same elementary process as in the gases, namely: they decompose in *one elementary event*, i.e., without preliminary detachment of radicals, into carbon dioxide and paraffin hydrocarbons. Thus, acetic acid yields methane and CO_2 :

$$\underset{\text{HO}}{\overset{\text{CH}_3}{>}} CO + h\nu \rightarrow CH_4 + CO_2,$$

propionic acid yields ethane and CO2:

$$\frac{CH_3CH_2}{HO} \xrightarrow{CO+h\nu \to C_2H_6+CO_2}$$

A more complex pattern is observed with butyric acid. Here, in addition to the reaction following the same scheme as for acetic and propionic acid, namely:

$$\begin{array}{c} \text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\\ \text{HO} \xrightarrow{} \text{CO} + h\nu \rightarrow \text{C}_{3}\text{H}_{8} + \text{CO}_{2}, \end{array}$$

one observes the formation of ethylene, probably owing to the reaction

$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\\ \text{HO} \end{array} \begin{array}{c} \text{CO} + h\nu \rightarrow \text{CH}_2 = \text{CH}_2 + \text{CH}_3\text{COOH.} \end{array}$$

Here we are dealing with a case fully analogous to that found by Norrish in the decomposition of aldehydes and ketones having long chains: Absorption of light occurs at the COOH group, while the reaction occurs in a part of the molecule remote from this group.

Another very interesting fact specifically characteristic of reactions in solution consists in the following. If we compare the number of molecules of the acid decomposed with the number of them found in the form of gaseous decomposition products, it turns out that the former quantity is always considerably greater than the latter. This means that, along with the gaseous products, also soluble products are formed. Actually, in one of the experiments 55 millimoles of acetic acid was decomposed, while 38 millimoles was found in the form of $CH_4 + CO_2$, but in addition, 13 millimoles was found in solution in the form of formic acid. The latter fact-the production of formic acidcan be explained most simply and naturally by the participation of water in the reaction:

CH₃COOH,
$$H_2O + h\nu \rightarrow CH_3OH + HCOOH$$
.

Exactly the same results were found also in other acidspropionic, butyric, and succinic: in all cases the amount of decomposed acid proved to be larger than the amount corresponding to gaseous products, and in all cases the production of formic acid was observed.

5. Now let us turn to photochemical processes involving ions. The nature of these processes was first established with the example of the halide ions I^- , Br^- , and Cl^- . In studying the absorption spectra of aqueous solutions of different halide salts,⁵⁴ it was shown that these spectra in the range 2500-1800 Å are determined solely by the anions and do not depend on the nature of the cation. These spectra are continuous, while for iodine and bromine two maxima are observed, separated in frequency units by the spacing $\sim 8000 \text{ cm}^{-1}$ for iodides and 3000 cm⁻¹ for bromides. If we find the energy value (hv) corresponding to these spacings, for I⁻ ions we obtain 0.9 eV, and 0.3 eV for Br⁻. These values are characteristic of the iodine and bromine atoms. Namely: 0.9 eV is nothing other than the spacing between the ground level of iodine $({}^{2}P_{3/2})$ and the first excited (metastable) level of the same atom (spectroscopic symbol ${}^{2}P_{1/2}$). Likewise for bromine 0.3 eV is the spacing between the same levels of the neutral atom. On this basis Franck and Scheibe⁵⁵ gave the following interpretation of the nature of the process giving rise to these spectra. The elementary process that occurs in the absorption of a quantum, e.g., by an iodide ion I^- , according to Franck and Scheibe, consists in the detachment of an electron from this ion; here the remaining neutral I atom can exist either in the ground state or in the excited state. In the two cases a different energy must be expended on the detachment process. Namely, let the magnitude of the quantum needed for the former process be hv_1 ; then

$$I^- + h\nu = I(^2P_{3/2}) + e^-;$$

the magnitude of the quantum needed for the second process will be hv_2 :

$$I^- + hv_2 = I(^2P_{1/2}) + e^-.$$

Then the energy difference will be

$$hv_1 - hv_2 \equiv h\Delta v = {}^2P_{3/2} - {}^2P_{1/2}.$$

This value of ${}^{2}P_{3/2} - {}^{2}P_{1/2}$, as is known from analyzing the spectrum of iodine, is precisely equal to 0.9 eV, or in frequency units $\Delta v = 8000 \text{ cm}^{-1}$. Analogously for the bromine atom the energy difference of the first levels is precisely equal to 0.3 eV.

Since the energy relationships in the two cases are determined by how strongly the electron is bound to the bromine and iodine atoms, the spectra themselves have been called *electron-affinity spectra*. However, the attempt to determine from these spectra the value of the electron affinity, which is highly important for atomic phenomena, vielded no satisfactory results. Therefore the interpretation of the spectra in the latest study of Franck and Haber⁵⁶ was somewhat altered by the following refinement. One cannot consider an ion dissolved in water to be isolated. It is surrounded by a shell of water molecules, i.e., it is hydrated. Therefore the elementary process, according to Franck and Haber, occurs in the complex I^- , H_2O , and consists in detaching an electron from the iodine atom and attaching it to the hydrogen of a neighboring water molecule. As a result we obtain

$$\mathbf{I}^{-}, \quad \mathbf{H}_{2}\mathbf{O} + h\mathbf{v} \rightarrow \mathbf{I} + \mathbf{H} + \mathbf{O}\mathbf{H}^{-}. \tag{1}$$

Thus the final result of the elementary photochemical process must consist in formation of free iodine and hydrogen atoms and in increasing the alkalinity of the solution. However, we should note that we can expect *a priori* that the quantum yield of this process will be very small. In fact, although process (1) occurs with a quantum yield equal to unity, the products that arise in this process in solution cannot depart to great distances, but undergo repeated collisions (see above). Therefore, even at the following instant, the charge-exchange reaction must occur with high probability:

$$\mathbf{I} + \mathbf{H} \to \mathbf{I}^- + \mathbf{H}^+, \tag{2}$$

which restores the initial state. Only a small fraction of the atoms that arise remains in the free state, and upon recombining yields the molecules

$$2I \rightarrow I_2 \rightarrow$$
 and $2H \rightarrow H_2$

The existing experimental material confirms this scheme. Thus, according to Warburg and Rump,⁵⁷ aqueous solutions of hydrogen iodide upon illumination with ultraviolet light decompose with liberation of free iodine. The quantum yield of this reaction is very small and only in very concentrated solutions (7.5 mole/L) reaches the value of two that is normal for decomposition of hydrogen iodide. But in this latter case the primary processes (1) and (2) are complicated by the secondary processes

$$\mathbf{H} + \mathbf{H}\mathbf{I} \rightarrow \mathbf{H}_2 + \mathbf{I},$$

 $H+I^{-}(H_2O) \rightarrow H_2+I+(OH)^{-}$.

The photochemical reactions of solutions of the alkali halides were studied by Butkow,⁵⁸ who showed that, in solutions of iodides and bromides, iodine and bromine are liberated, and the alkalinity of the solutions increases. Here the region of photochemical sensitivity of the solutions coincides with the absorption spectrum of the corresponding ions. The quantum yield in all cases proved to be very small, since the reverse reactions

$$I+H \rightarrow I^- + H^+$$
,
 $Br+H \rightarrow Br^- + H^+$

occur at rates close to the rate of the forward reaction. For the chlorides no formation of free chlorine was observed at all, evidently because the reverse reaction

$$Cl + H \rightarrow Cl^- + H^+$$

has a probability equal to unity.

6. Now let us discuss a more complex case of an elementary process in the electron-affinity spectrum, but one that presents especial interest for the interpretation of photochemical reactions in solutions. The topic is the reaction of sulfite ions $SO_3^{2^-}$. The reaction of oxidation of sodium sulfite by oxygen is one of the most interesting photochemical reactions in solution, and has been studied in detail.⁵⁹ This reaction is typically a chain reaction, since the number of molecules of sulfite undergoing oxidation per absorbed quantum amounts to 5×10^4 ; in this same reaction Bäckström first showed the identity of the chains in the photochemical and dark processes.

The absorption spectrum of solutions of sodium sulfite has been subjected to special investigation,⁶⁰ where it turned out that, at a certain acidity of the solution $(pH \ge 7)$ this spectrum fully belongs to the sulfite ions. This spectrum is interpreted by Franck and Haber as an electronaffinity spectrum; the elementary process (3) that occurs here, in accord with what has been said above, can be written as:

$$SO_3^{2^-}$$
, $H_2O + hv \rightarrow SO_3^- + H + OH^-$. (3)

The energy relationships in this process can be established from the following considerations. The quantum energy is spent in detaching one electron from the $SO_3^{2^-}$ ion (evidently the work performed in this detachment equals the electron affinity of the SO_3^- ion, E_{SO_3}) and in decomposing a molecule of water into H and OH (dissociation energy $D_{\rm H,O}$). But, moreover, in this process the energy of combination of the electron with OH is released (electron affinity E_{OH}). Finally a certain *potential* energy X of the products of decomposition arises. This potential energy is caused by the possible repulsion of the decomposition products if they have charges of the same sign, and also by the potential energy of the surrounding water molecules, which tend to arrange themselves in an ordered fashion around the ions that arise (hydration energy). However, since the elementary process involves electronic excitation that occurs instantaneously, while the listed sources of potential energy involve displacement of heavy nuclei, which cannot change in position in the time during which the electronic process is completed, the corresponding energy figures only as potential energy, and cannot be used in the process itself. We can easily see that these ideas amount to a modification and expansion of the Franck-Condon principle discussed above for the case of elementary processes in solutions.

On the basis of what has been said, the energy balance of the reaction can be represented by the equation

$$hv = D_{\rm H,O} + (E_{\rm SO_1} - E_{\rm OH^-}) + X.$$
 (4)

The presence in this equation of the term X, which is difficult to estimate, renders the process itself unsuitable for exact determination of the electron affinity. Thus, the initial hope of Franck, who saw in this process the possibility of directly determining the value of the electron-affinity energy, was not borne out. However, from the photochemical standpoint it will be justified if it turns out that the products to which this process leads are actually obtained.

Let us discuss the question from this standpoint. The primary event, as Eq. (3) shows, leads to formation of SO_3^- , H, and OH^- . However, even at the next instant, owing to the equilibrium between the SO_3^- ions that appear and the H⁺ ions present, undissociated molecules of HSO₃ must be obtained. The HSO₃ radical, unknown in the free state, Franck and Haber called monothionic acid, and attributed to this radical a large role in the development of the subsequent chain process. Thus we can say that, for each absorbed quantum in the elementary process, the following products arise: one H atom, one molecule of HSO₃, and two OH⁻ ions. However, we can easily convince ourselves that the final quantum yield of the reaction (in the absence of oxygen) must be very small. In fact, the primary process (1) and the appearance of monothionic acid are followed by a number of secondary processes that completely restore the initial situation. First, between H and HSO₃, which remain as neighbors for a long time, the charge-transfer reaction occurs:

$$H + HSO_3 \rightarrow H^+ + HSO_3^-.$$
 (5)

This reaction has the character of ordinary analytical charge-transfer reactions. It occurs practically without an activation energy, and therefore its probability is very large.

The reaction (5) can be followed by the onset of the process

$$H^{+} + HSO_{3}^{-} + 2OH^{-} \rightarrow SO_{3}^{2^{-}} + 2H_{2}O_{3}$$

which completely restores the initial situation.

Part of the products of the primary photochemical event still escapes the reverse reactions and is subjected to further transformations. Namely, first, reactions can occur of the atoms and radicals that are formed with participation of water molecules (disproportionation):

 $H + HOH + HSO_3 \rightarrow H_2O + H_2SO_3$,

 $H + HOH + HSO_3 \rightarrow H_2 + H_2SO_4;$

second, H atoms and HSO₃ radicals can undergo dimerization to yield stable products

$$2H = H_2$$
, $2HSO_3 = H_2S_2O_6$.

Thus, on illuminating sulfite in the *absence of oxygen* we should expect the appearance of the following products: hydrogen, dithionic acid $H_2S_2O_6$, and sulfuric acid. Special experiments designed to test this theory enabled finding all these products, and thus confirmed the theory of Franck and Haber. In the *presence* of oxygen the obtained products are subjected to further oxidation, and a chain arises. The mechanism of development of this chain was also pointed out by Farkas and Wansbrough-Jones⁴⁸ and somewhat modified by Bäckström.⁶² However, since these problems are no longer related to primary photochemical processes, we shall not take them up here, while referring those interested to the original literature or to the review by the author cited above.

7. To the examples discussed above we should add another interesting and instructive case of photochemical reactions in ions of organic acids. The spectra of the ions of acetic, formic, and succinic acids are very similar to one another. Farkas and Wansbrough-Jones interpreted these spectra as the electron-affinity spectra of the anions. In such a case the elementary process must occur according to the scheme

$$A^-$$
, $H_2O + h\nu \rightarrow A + H + OH^-$,

where A^- is the symbol of any anion. Owing to the reverse reaction

$$A+H \rightarrow A^- + H^+$$
,

which restores the original situation, the final quantum yield should be very small.

The experimental study led to the following results. Acetate ion yields as the principal products of photochemical decomposition carbon dioxide and methane. The quantum yield referred to CH_4 , as in the case of sulfite, is very small. In the most favorable case ($pH \approx 8.0$), it equals 0.065. That is, in 93.5% of the cases the products of the primary photochemical process react to restore the original situation. According to Farkas and Wansbrough-Jones, the formation of carbon dioxide and methane is a result of subsequent reaction of the CH_3COO^- ion at the instant of its appearance in the process of charge transfer. This process is accompanied by the evolution of a large amount of heat, which in some cases proves sufficient for a reaction with *water* to occur according to the scheme



The fact that the latter reaction does not occur every time is explained, in the opinion of Farkas and Wansbrough-Jones, by the rapid dissipation of the excess energy: the newly formed CH_3COO^- ion is immediately hydrated and proves capable of transferring its excess energy to several water molecules bound to it.

The CH₃COO radical that arises in the primary photochemical process escapes charge transfer in a small number of cases and continues to exist for a certain time interval, while entering into side reactions. In the case of sulfite one of these reactions was the formation of dithionic acid owing to dimerization of monothionic acid and the formation of sulfuric acid via reaction involving a water molecule. The former reaction corresponds in the case being discussed to formation of succinic acid

 $2CH_3COO \rightarrow COOH-CH_2-CH_2-COOH$,

and the latter to formation of peracetic acid. The formation of succinic acid could be detected after a 28-hour illumination of a solution 0.1N in sodium acetate +0.1N in NaOH; however, the formation of the peroxy acid was not found, evidently because from the thermodynamic standpoint the conditions for obtaining it are considerably less favorable than in the case of formation of sulfuric acid from HSO₃.

The phenomena observed upon illumination of the ions of formic and succinic acids are analogous to those discussed. The only difference consists in the fact that in the case of formate one observes evolution also of CO in addition to CO_2 . Farkas and Wansbrough–Jones ascribe the source of CO to the reaction

HCOO⁻,
$$H_2O \rightarrow H_2O + CO + OH^{-1}$$

In the dimerization of the HCOO radical that arises in the primary event, evidently, one should obtain oxalic acid, as is actually observed: upon illuminating formate for 4.5 hours, 0.0068 moles of oxalic acid was found.

In summarizing all that we have said thus far, we see that the elementary photochemical processes for ions can be considered to be fully established in those cases in which the absorption spectrum can be interpreted as an electronaffinity spectrum.

²⁾This ease of transfer is also based on the resonance between the ${}^{3}P_{1} - {}^{3}P_{0}$ level difference and the vibrational levels of the N₂ molecule.

^{*}First published in Uspekhi Fizicheskikh Nauk 16, 165–198 (April 1936). Expanded presentation of a lecture read on 12 December 1935 at the N. D. Zelinskii University of Physical Chemistry at Moscow University.

¹⁾It is assumed that a reaction occurs in each collision of an excited mercury atom with an oxygen molecule.

³⁾Cf. the tables of spectroscopically determined dissociation energies compiled by Gerta Sponer.¹⁷

⁴⁾This example and the following ones are taken from the study by A. N. Terenin.³⁴

⁵⁾Actually, even in the case of a triatomic molecule, one must know three parameters. However, even a simplified model with two parameters enables one conveniently to trace all the characteristic features of the phenomenon. Yet the complications, which involve the increase in the

number of parameters, only enhance considerably the features that are manifested in treating the simplest model.

- ⁶⁾Actually one sometimes observes the formation of hydrogen in small amounts. However, it is explained by secondary causes.
- ⁷⁾For the literature on absorption spectra in solutions, see Leu.⁵²

A. Monographs

- K. Bonhoeffer and P. Harteck, Fundamentals of Photochemistry, ONTI, 1935.
- A. N. Terenin, Photochemistry of Vapors of Salts, GTTI, 1934.
- V. N. Kondrat'ev, Structure of Molecules and Elementary Chemical Processes, GTTI, 1934.
- V. N. Kondrat'ev, Photochemistry, GTTI, 1933.
- V. N. Kondrat'ev and M. A. El'yashevich, Energy Exchange, GTTI, 1933.
- A. C. G. Mitchell and M. W. Zemansky, Resonance Radiation and Excited Atoms, Cambridge, 1934.

B. Literature cited in the text

- ¹For a review of photochemistry in crystals, see the article: M. V. Savost'yanova, Usp. Fiz. Nauk 11, 451 (1931).
- ²A. Einstein, Ann. Phys. (Leipzig) 17, 132 (1905); 37, 832 (1912); J. Stark, Phys. Z. 9, 898 (1912).
- ³See, e.g.: K. Bonhoeffer and P. Harteck, Fundamentals of Photochemistry, pp. 9-18.
- ⁴Photochemical Processes, Trans. Faraday Soc. 21 (1925); see also the German translation: Z. Phys. Chem. 120 (1926).
- ⁵O. Stern and M. Volmer, Phys. Z. 20, 186 (1919).
- ⁶I. M. Frank, Acta Physicochim. URSS 1, 833 (1935).
- ⁷R. Wood and Gaviola, Philos. Mag. 6, 271 (1928).
- ⁸Childs and Mecke, Z. Phys. 68, 344 (1931).
- ⁹Kautsky, de Bruijn, and R. Neuwirth, Ber. 66, 1588 (1932).
- ¹⁰ Beutler and Josephy, Z. Phys. 53, 747 (1929).
- ¹¹Cf., e.g.,: W. Grotrian, Graphische Darstellung der Spektren, Part II.
- ¹² H. Kallmann and F. London, Z. Phys. Chem. 2, 207 (1929).
- ¹³A. Terenin, Z. Phys. 37, 120 (1926).
- ¹⁴J. Franck, Trans. Faraday Soc. 21, 3 (1925).
- ¹⁵See, e.g.,: Weizel, Bandspektren.
- ¹⁶R. Mecke, Ann. Phys. (Leipzig) 71, 104 (1923).
- ¹⁷ Landolt-Börnstein, Physicalisch-chemische Tabellen, II. Ergänzungsband.
- ¹⁸Dymond, Z. Phys. 34, 553 (1925).
- ¹⁹ Bonhoeffer and Farkas, Z. Phys. Chem. 132, 255 (1928).
- ²⁰Senitleben, Ann. Phys. (Leipzig) (5) 2, 847 (1929).
- ²¹Turner, Phys. Rev. 27, 396 (1926).
- ²² Bonhoeffer and Steiner, Z. Phys. Chem. 122, 287 (1926).
- ²³F. London, Z. Phys.
- ²⁴ V. Henri, Structure des Molecules, Hermann, Paris, 1926.
- ²⁵M. Born and J. Franck, Z. Phys. 31, 411 (1925).

- ²⁶L. De Broglie, Einführung in die Quantenmechanik, Leipzig, 1929.
- ²⁷V. Henri, Leipziger Vorträge, 1931.
- ²⁸L. Turner, Phys. Rev. 41, 627 (1932). ²⁹ R. de L. Kronig, Z. Phys. 50, 347 (1928).
- ³⁰I. H. Van Vleck, Phys. Rev. (1930).
- ³¹ Kondratjew and Polak, Phys. Z. Sowjetunion 4, 770 (1933). ³²Cf., e.g.,: H. Leu, Lichtabsorption und chemische Konstitution (Handb. d. Physik von Geiger u. Scheel, Vol. 21).
- ³³K. W. F. Kohlrausch, Der Smekal-Raman-Effekt.
- ³⁴A. N. Terenin, Acta Physicochim. URSS 3, 181 (1935).
- ³⁵A. Terenin and H. Heumin, Nature 134, 255 (1934).
- ³⁶J. Franck, H. Sponer, and F. Teller, Z. Phys. Chem. 18, 88 (1932).
- ³⁷R. G. W. Norrish, Acta Physicochim. URSS 3, 171 (1935).
- ³⁸R. G. W. Norrish, Crone, and Saltmotsh, J. Chem. Soc. (Lond.) 1456 (1934).
- ³⁹ R. G. W. Norrish, J. Chem. Soc. (Lond.) 761 (1927); 1158, 1604, 1611 (1929).
- ⁴⁰Cf.: Bonhoeffer and Harteck, Fundamentals of Photochemistry, p. 160, and literature cited there.
- ⁴¹Kirbride and Norrish, Trans. Faraday Soc. 27, 404 (1931).
- ⁴² V. Henri, Leipziger Vorträge, 132 (1931).
- ⁴³V. Henri, *ibid.*, p. 134.
- ⁴⁴ F. London, Sommerfeld Festschrift.
- ⁴⁵ V. Henri, Photochimie, p. 90.
- ⁴⁶Leu and Arends, Z. Phys. Chem. 4, 234 (1929).
- ⁴⁷E. Gorin and H. Taylor, J. Am. Chem. Soc. 56, 2042 (1935).
- ⁴⁸L. Farkas and O. H. Wansbrough-Jones, Z. Phys. Chem. 18, 124 (1932).
- ⁴⁹N. Prileshajewa, Acta Physicochim. URSS 3, 195 (1935).
- ⁵⁰Bernal and Fowler, J. Chem. Phys.
- ⁵¹Ya. K. Syrkin, Zh. Fiz. Khim.; Acta Physicochim. URSS.
- ⁵²H. Leu, Handb. d. Physik.
- ⁵³ Berthoud and Bellenot, J. Chim. Phys. 21, 308 (1934); see the analysis of this reaction in the article: É. Shpol'skiĭ, Zh. Fiz. Khim. 2, 468 (1931).
- ⁵⁴Allmand, Cunliffe, and Madison, J. Chem. Soc. (Lond.) 127, 822 (1925)
- ⁵⁵G. Scheibe, Z. Elektrochem. 34, 497 (1928); Z. Phys. Chem. 5, 355 (1929); Fromherz and Menschik, Z. Phys. Chem. 7, 439 (1930); J. Franck and G. Scheibe, Z. Phys. Chem. Haber-Band, 22 (1928).
- ⁵⁶J. Franck and F. Haber, Sitzung Ber. Preuss. Akad. Wissensch. Phys.-Math. Klasse (1931), XIII,
- ⁵⁷E. Warburg and Rump, Z. Phys. 47, 305 (1928).
- ⁵⁸K. Butkow, Z. Phys. 62, 71 (1930).
- ⁵⁹É. Shpol'skiĭ, Zh. Phys. Khim. 2, 468 (1931).
- ⁶⁰Albu and Goldfinger, Z. Phys. Chem. (B) 16, 338 (1932); see references there to earlier studies.
- ⁶¹É. Shpol'skiĭ, Zh. Fiz. Khim. 6 (2-3) (1935).
- ⁶²H. L. Bäckström, Z. Phys. Chem. Abt. B 25, 122 (1934).
- ⁶³H. Leu and B. Arends, Z. Phys. Chem. Abt. B 17, 177 (1932).

Translated by M. V. King