

The Correlation of Spectroscopy and Photochemistry

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FROM a historical standpoint photochemistry and spectroscopy have one fact in common: they developed largely as empirical sciences. It seems today almost a truism that a photochemical study should be accompanied by a sound spectroscopic investigation, but this has not been true in the past nor is it, unfortunately, adequately recognized by many workers in the field today. The difficulties may not be inherent in the minds of the investigators, but may be ascribed to the lack of adequate spectroscopic equipment in many chemical laboratories and to the fact that the chemist is frequently concerned with complex molecular species which have been treated with little success from a theoretical standpoint.

In its early days photochemistry consisted largely of chemistry and little of physics. Polychromatic radiation of unknown and variable intensity was often employed, thus making impossible any real discussion of reaction mechanism. To the synthetic chemists such studies were often useful. Thus the reactions of many organic compounds with the halogens are accelerated by sunlight, and certain other reactions proceed more smoothly when exposed to radiation than under more usual conditions. Occasionally a new field of chemistry was opened up through the discovery of some photochemical reaction. One needs only cite the discovery of organic mercury compounds by Frankland¹ through the action of sunlight on methyl iodide in the presence of liquid mercury.

In October, 1925, at a meeting of the Faraday Society in Oxford, Franck² first proposed the potential energy curves which have become so useful in correlating spectroscopic facts and which have proved of inestimable value to the photochemist in picturing the mechanisms of

reactions. Condon³ has extended the ideas of Franck to explain intensity distributions in band spectra. One may estimate the shape of the Franck-Condon curve for a given diatomic molecule from a few fundamental constants with the help of a very useful equation given by Morse.⁴ The quantitative extension of these same ideas to polyatomic molecules has encountered many difficulties, but the foundation is such that one feels justified in using them with a great deal of certainty in at least a qualitative discussion of spectroscopic and photochemical facts.⁵

The Einstein law of photochemical equivalence,⁶ which followed logically not long after the successful application of elementary quantum ideas to the photoelectric effect, led to quantitative studies of the relationship between intensity of absorbed radiation and quantity of chemical action. It was soon shown⁷ that some reactions exhibited quantum yields not differing markedly from unity, whereas others showed either very low or very high yields. Reactions of very high quantum yield are frequently referred to as chain reactions and few conclusions of interest to the spectroscopist can usually be drawn from them. Thus in the much studied hydrogen-chlorine reaction the reaction may be initiated either photochemically or by ionization with alpha-particles or electrons.⁸ In all cases the number of molecules reacting in a chain is very large and depends greatly on the presence of impurities and the nature of the walls of the

¹ E. U. Condon, *Phys. Rev.* **28**, 1182 (1926).

² P. M. Morse, *Phys. Rev.* **34**, 57 (1929).

³ See, for example, J. Franck, H. Sponer and E. Teller, *Zeits. f. physik. Chemie* **B18**, 88 (1932).

⁴ A. Einstein, *Ann. d. Physik* **37**, 832 (1912).

⁵ See M. Bodenstern, *Zeits. f. physik. Chemie* **85**, 333 (1913) for a summary of early work.

⁶ S. C. Lind, *The Chemical Effects of Alpha Particles and Electrons*, The Chemical Catalog Co., New York, p. 180, 1928.

¹ Frankland, *J. Chem. Soc.* **3**, 322 (1850); *Ann. d. Chemie* **85**, 361 (1853).

² J. Franck, *Trans. Faraday Soc.* **21**, 536 (1926).

vessel. It is true that a study of the band spectrum of chlorine leads one to believe that the photochemical reaction is initiated by the production of chlorine atoms, but the photochemical facts alone scarcely afford justification for this statement.

Long chain reactions will not be considered further in this article and we shall confine our attention to those cases in which a combination of spectroscopy and photochemistry gives some promise of elucidating the mechanism.

In order to afford a basis for discussion, the following brief summary lists the possible effects of radiation on molecular systems. Pure rotation-vibration transitions have been ignored.

(1) Change of electronic state accompanied by change in rotation or vibration leading to an excited molecule which may suffer several different fates.

(2) Change of electronic state accompanied by a transition to a point above the horizontal portion of the Franck-Condon curve of the upper state. In this case dissociation results, the products being either in their ground or upper levels depending on the character of the upper electronic state of the molecule. Any energy in excess of that required to produce dissociation must appear as kinetic energy (or energy of vibration and rotation in the case of polyatomic molecules). This was shown to be the case in the dissociation of sodium iodide vapor by Hogness and Franck⁹ who studied the Doppler effect in the *D*-lines of sodium emitted as fluorescence radiation.

(3) Transition to an upper electronic level may be followed by a radiationless transition to a perturbing level resulting in dissociation. This phenomenon is termed predissociation.¹⁰ It is usually detected by a diffuseness of the absorption bands. Collisions may also be effective in inducing predissociation from certain energy levels. Predissociation should be quite common among polyatomic molecules, but is infrequently encountered among diatomic molecules.

With these hastily summarized facts in mind we shall proceed to a more detailed discussion of

certain specific cases. No attempt has been made to give a complete bibliography for any of the reactions mentioned.

A. THE OXYGEN-OZONE SYSTEM

The normal state of the oxygen molecule is described as ${}^3\Sigma_g^-$.¹¹ This designation satisfactorily agrees with the fact the oxygen gas is paramagnetic and has permitted calculation of the entropy of oxygen which is in good agreement with values obtained with the aid of the third law of thermodynamics.¹² Several upper states are predictable and a few have been found.¹¹ Thus a ${}^1\Sigma_u^-$ state with an electronic term of 1.62 electron-volts is the upper state for the atmospheric absorption bands.¹³ There are several absorption regions in liquid oxygen which may be interpreted in terms of energy levels of the O_2 molecule and some evidence is found from heat capacity measurements for a level lying between the ${}^1\Sigma_u^-$ and ground levels.¹⁴

A ${}^3\Sigma_u^-$ state with an electronic term of 6.10 electron-volts is the upper level for the well-known Schumann-Runge bands.¹¹ These bands converge at $\lambda 1751$ and absorption of radiation of shorter wave-length by oxygen leads to the production of normal 3P and excited 1D oxygen atoms.

From a chemical standpoint one would expect a tendency toward polymerization on the part of molecules in a triplet state. Some evidence for such a polymerization is found in magnetic susceptibility data¹⁵ as well as in the variation of absorption coefficient with pressure.¹⁶ There would certainly be appreciable van der Waals forces between O_2 molecules, but whether any such definite molecule as O_4 exists in appreciable quantity seems uncertain. Oxygen does show absorption bands extending from approximately $\lambda 2800$ to about $\lambda 2400$, with a continuum extending to shorter wave-lengths.¹⁷ At moderate

¹¹ W. Jevons, *Report on Band-Spectra of Diatomic Molecules*, The Physical Society, London, p. 290, 1932.

¹² W. F. Giaque and H. L. Johnston, *J. Am. Chem. Soc.* **51**, 2300 (1929).

¹³ R. S. Mulliken, *Phys. Rev.* **32**, 880 (1928).

¹⁴ B. Lewis and G. von Elbe, *ibid.* **41**, 678 (1932).

¹⁵ G. N. Lewis, *J. Am. Chem. Soc.* **46**, 2027 (1924).

¹⁶ O. R. Wulf, *ibid.* **50**, 2596 (1928).

¹⁷ For a discussion of earlier work on these bands see O. R. Wulf, *Proc. Nat. Acad. Sci.* **14**, 609 (1928).

⁹ T. R. Hogness and J. Franck, *Zeits. f. Physik* **44**, 26 (1927).

¹⁰ V. Henri and M. C. Teves, *Nature* **114**, 894 (1924); *Comptes Rendus* **179**, 1156 (1924).

pressures and with very long path lengths a series of weak absorption bands which converge about $\lambda 2400$ has been observed. Herzberg¹⁸ finds that these bands involve probably an upper $^3\Sigma_u^+$ state with an electronic term of 4.68 electron-volts which will separate adiabatically into two normal 3P oxygen atoms. A weak quadrupole transition is involved, therefore, in the absorption process. In addition to these bands another set lying in the same region with an intensity depending on the square of the pressure has been studied by Finkelnburg and Steiner.¹⁹ Rather than ascribe these bands to the chemical combination of two oxygen molecules, these authors suggest that the customary selection rules break down when an absorbing O_2 molecule is in close proximity to another molecule. They believe, therefore, that the upper state of these bands is $^3\Delta_u$ and that it will separate also into two normal atoms.

The photochemical formation of ozone from oxygen has been known for many years. The earliest quantitative work is due to Warburg²⁰ who investigated the reaction at high pressures and at two wave-lengths, $\lambda\lambda 2070$ and 2530 . He found at the shorter wave-length approximately two molecules of ozone to be formed per quantum absorbed, the number decreasing slightly with increasing pressure and becoming 1.5 at a pressure of 300 kg/cm^2 . At the longer wave-length the number was distinctly smaller, varying from 1.2 at 47.5 kg/cm^2 to 0.6 at 300 kg/cm^2 . At atmospheric pressure and with radiation in the fluorite region (largely below the convergence limit of the Schumann-Runge bands, $\lambda 1751$) 2.0 molecules of ozone are formed from oxygen per quantum absorbed.²¹ From this fact and others it is evident that oxygen atoms (either 3P or 1D) will react readily with oxygen molecules to form ozone. The reaction mechanism would be, therefore, $O_2 + h\nu = 2O$; $2O + 2O_2 = 2O_3$.

¹⁸ G. Herzberg, *Naturwiss.* **20**, 577 (1932).

¹⁹ W. Finkelnburg and W. Steiner, *Zeits. f. Physik* **79**, 69 (1932).

²⁰ O. Warburg, *Zeits. f. Elektrochemie* **27**, 133 (1921). For references to earlier work see G. B. Kistiakowsky, *Photochemical Processes*, The Chemical Catalog Co., New York, p. 221, 1928.

²¹ W. E. Vaughan and W. A. Noyes, Jr., *J. Am. Chem. Soc.* **52**, 559 (1930).

At wave-lengths longer than the convergence limit of the Schumann-Runge bands a variety of interpretations must be considered. Kistiakowsky²² has studied the oxygen-hydrogen reaction in two spectral regions, $\lambda\lambda 1719$ – 1725 and $\lambda\lambda 1854$ – 1862 and finds markedly different behavior in the two cases. At the longer wave-length ozone is formed to nearly the same extent as if the hydrogen were replaced by nitrogen, while at the shorter wave-length hydrogen peroxide is formed in addition. Two interpretations of these facts seem possible: (1) As suggested by Kistiakowsky 1D but not 3P oxygen atoms may be capable of reacting with hydrogen to form hydrogen peroxide. There are some theoretical reasons in favor of this explanation. (2) At the longer of these two wave-lengths ozone may be formed from excited oxygen molecules without oxygen atoms being produced (in more than small numbers) at any step in the process. The first interpretation seems much more logical than the second.

Energy corresponding to 5.1 electron-volts is necessary to dissociate the normal oxygen molecule¹¹ so that absorption of wave-lengths in the Schumann-Runge band system could be followed either by dissociation upon collision²³ or by a reaction of the type $O_2' + O_2 = O_3 + O$. Whether spectroscopic evidence could be obtained for the presence of oxygen atoms at wave-lengths longer than $\lambda 1751$ is doubtful due to certain experimental difficulties. It is possible that this matter would be worthy of further investigation.

It has been assumed generally that triple collisions are about 10^{-3} times as numerous as ordinary collisions at a pressure of one atmosphere. This ratio will depend obviously on the nature of the gas and on the definition of a triple collision. If ozone formation at wave-lengths longer than the convergence limit were due to triple collisions one could write $O_2' + 2O_2 = 2O_3$. The difficulty in studying ozone formation over a large pressure range at these wave-lengths makes experimental test of this mechanism difficult. Unless the lifetime of the excited molecules is large the yield should depend

²² G. B. Kistiakowsky, *J. Am. Chem. Soc.* **52**, 1868 (1930).

²³ cf. L. A. Turner, *Phys. Rev.* **41**, 627 (1932).

markedly on the pressure. The data of Eucken,²⁴ which were obtained with polychromatic radiation (mostly $\lambda \sim 1860$ and $\lambda \sim 1720$) indicate a more rapid rate of ozone formation at 90°K than at room temperature at low pressures, the difference being less near atmospheric pressure. These results are not sufficiently precise to warrant much discussion, but could be explained by the increased chance of triple collisions (slight polymerization?) at low temperatures. Eucken advances an explanation based on the shorter life of molecules in high rotation states, there being some theoretical justification for this assumption. A quantitative study of the fluorescence of oxygen under various conditions might provide an answer to some of these questions.

In discussing the results of Warburg²⁰ it must be kept in mind that the quantitative determination of ozone at the pressures used is very difficult and that ozone is known to be decomposed at least by the longer of the two wave-lengths he employed. The variation of quantum yield with pressure is, therefore, not much greater than possible experimental errors. It is true that the molecule O_4 would offer a possible explanation for most of Warburg's results, but since the evidence for this molecule does not rest on a very secure foundation it seems wise to inquire whether other mechanisms would suffice.

The shorter of the two wave-lengths employed by Warburg ($\lambda 2070$) lies on the long wave side of the Schumann-Runge band system. Pressure broadening might conceivably lead to absorption in this region but this seems doubtful. However the weak ${}^3\Sigma_g^- \leftarrow {}^3\Sigma_u^+$ bands¹⁸ and the ${}^3\Sigma_g^- \leftarrow {}^3\Delta_u$ bands¹⁹ both converge about $\lambda 2400$. The upper states of these band systems probably have shallow Franck-Condon curves and dissociate into normal atoms. $\lambda 2070$ lies, therefore, in a continuous absorption region beyond the convergence limit of these band systems and absorption of radiation of this wave-length should lead directly to the production of two normal oxygen atoms. This is an adequate explanation of the quantum yield of two obtained by Warburg. The decrease in yield with increasing pressure, although not great, could only be explained by assumptions of doubtful validity.

²⁴ A. Eucken, *Zeits. f. physik. Chemie* **107**, 436 (1923).

Warburg²⁰ ascribes the change to a peculiar effect of neighboring molecules on the absorbing molecule leading to a dissipation of energy. So little is known from a theoretical standpoint concerning such matters that this question must be left open.

The longer of the two wave-lengths ($\lambda 2530$) lies to the long wave side of the convergence limit of the above bands. Here production of atoms in a primary process is impossible. The energy deficiency is not great (about 0.2 electron-volt) and an appreciable fraction of the collisions made by an activated molecule could supply enough energy to produce dissociation. Part of the energy would be lost by fluorescence or by collision of the second kind, thus giving a very logical explanation of the quantum yield below two. The variation of the yield with pressure is again difficult to explain unless one ascribes different behaviors to the ${}^3\Sigma_u^+$ and ${}^3\Delta_u$ molecules which would be formed by the absorption of radiation. At such high pressures the absorption in this region would be largely continuous and the exact theoretical interpretation again a matter for future investigation.

Many of the facts of photochemical ozonization have, therefore, been elucidated with the aid of spectroscopy although much remains to be done.

The reverse reaction, namely the formation of oxygen from ozone, has been the subject of numerous investigations. Most of the results in this field have been summarized by Schumacher,²⁵ who has shown that the photochemical results are consistent with the primary process $O_3 + h\nu = O_2 + O$.

The absorption spectrum of ozone has been the subject of numerous studies. Aside from work in the infrared and on the Raman spectrum, probably the most recent work is that of Wulf²⁶ and of Wulf and Melvin.²⁷ Numerous bands extending from the infrared to the limit of the quartz region are known. The bands in the visible have been shown by Wulf to be diffuse and in all probability of the predissociation type. The products resulting from such a predissocia-

²⁵ H. J. Schumacher, *J. Am. Chem. Soc.* **52**, 2377 (1930).

²⁶ O. R. Wulf, *Proc. Nat. Acad. Sci.* **16**, 507 (1930).

²⁷ O. R. Wulf and E. H. Melvin, *Phys. Rev.* **38**, 330 (1931).

tion process must be normal ${}^1\Sigma_g^-$ oxygen molecules and normal 3P oxygen atoms. Since the reaction $O_3 = O_2 + O$ is endoenergetic only to the extent of about one electron-volt, optical dissociation must lead to products with fairly high kinetic energy. In the region $\lambda\lambda 3400-2300$ ozone exhibits a large number of absorption bands appearing against a background of continuous absorption. Various electron states of ozone are possible. For example dissociation products might be a normal oxygen molecule and a 1D atom (about 3 electron-volts) or a ${}^1\Sigma_u^-$ molecule and a 1D atom (about 4.6 electron-volts).

The tendency for the combination between oxygen molecules and oxygen atoms to take place is quite large so that one would expect the reaction to be inhibited by oxygen.

It is of interest to inquire as to whether one may obtain by spectroscopic means further evidence for some of the steps in these reactions. Since the absorption bands of ozone (at least in the visible) are diffuse and of the predissociation type, one should expect by the principle of microscopic reversibility to find them in emission under certain conditions. They should be expected under conditions such that oxygen atoms could combine with oxygen molecules in the absence of a third body. Attempts have been made to find such bands in emission.²⁸ At first oxygen atoms were produced by the irradiation of oxygen with wave-lengths lying below the convergence limit of the Schumann-Runge bands. Calculations based on many assumptions tended to show, however, that the emission of the ozone bands would be too feeble to be observed. This is especially true since the oxygen atoms must possess appreciable kinetic energy at the moment of combination with oxygen molecules. Further attempts to observe these bands in the afterglow in oxygen also failed, due also to the rather weak intensity. Finally a method capable of less exact interpretation was employed and the spectrum of a high potential discharge in oxygen was obtained. In this case many bands and lines due to O_2^+ and atomic oxygen were observed. There was obtained,

however, a series of bands with approximately the same spacing as the ozone bands, although there remains a slight doubt as to the interpretation of these results. Walles²⁹ in studying the emission spectrum of boric acid in the carbon arc claims to have found a series of bands extending from $\lambda 6400$ to $\lambda 3750$ which he believes to be the bands of ozone occurring in emission.

Finally it is worthy of note that the thermal decomposition of ozone is, if sufficiently rapid, accompanied by the emission of radiation. Wave-lengths even as short as $\lambda 2200$ are emitted, including the well-known ultraviolet bands at about $\lambda 2450$. Wulf³⁰ has considered various possible interpretations of this phenomenon and calls attention to the fact that radiation is generated of wave-length shorter than corresponds to any reaction of unexcited ozone. This phenomenon is very obscure and may possibly be due to traces of impurity.³¹ It is barely possible that the emission of radiation may be ascribed to the recombination of oxygen atoms and oxygen molecules, but to account for such short wave-lengths both would have to be in energy levels much above the normal.

Thus we see that spectroscopy and photochemistry together have solved many of the important problems concerning the formation and decomposition of ozone, but much careful work is still needed before the entire picture is complete.

B. COMPLEX MOLECULES

The absorption spectra of complex molecules have been studied extensively from an experimental standpoint, but aside from some success in interpreting Raman and infrared spectra, most of the conclusions reached have been in the nature of empirical generalizations.

Among organic molecules certain groups or radicals are usually associated with absorption in certain spectral regions.³² Thus all of the ketones, which contain the group $>C=O$ absorb in the neighborhood of $\lambda 3000$, the organic

²⁸ E. Walles, *Zeits. f. Physik* **80**, 267 (1933).

²⁹ O. R. Wulf, *Proc. Nat. Acad. Sci.* **12**, 129 (1926).

³¹ For discussion see E. Q. Adams, *Bull. Nat. Research Council*, No. 59, p. 31, 1927.

³² See V. Henri, *Etudes de Photochimie*, Gauthier-Villars et Cie., Paris, 1919.

³³ W. M. Manning, Ph.D. thesis, Brown University, 1933.

acids possess an absorption region located at shorter wave-lengths, etc. If a given molecule contains more than one strongly absorbing group, absorption due to both groups will be observed but displaced, usually toward the red, to an extent depending on how closely the groups are associated in the molecule. While great progress is being made in the theoretical interpretation of possible electron states of these complex molecules the surface has only been scratched.

Attention will be confined to the simplest of the ketones, acetone, $(\text{H}_3\text{C})_2\text{CO}$. The absorption spectrum of acetone vapor has been investigated and is found (in the quartz region) to extend from about $\lambda 3400$ toward the ultraviolet with a maximum about $\lambda 2800$.³³ No fine structure or discontinuities in the absorption curve have been reported. Further investigation at low pressures and long path lengths failed to show anything but continuous absorption,³⁴ although high dispersion has not been used by any of the investigators. At least there seem to be no variations in the spectrum of spacing appropriate to be ascribed to vibration levels. Whether one is justified in assuming a primary dissociation process by analogy with the spectra of simpler gases is an open question. At least it has been pointed out frequently that resonance effects in complex molecules will lead to a sufficient overlapping of energy levels to prevent any very marked banded structure from appearing.

The photochemical decomposition of acetone has been investigated. In the absorbing region there seems to be no variation of quantum yield with wave-length^{35, 36} and the main products of the reaction are ethane (C_2H_6) and carbon monoxide (CO).^{36, 37} Other products, particularly methane (CH_4) and hydrogen are formed in smaller quantities. Fluorescence has been observed,³⁸ the amount of energy reemitted in this form being less than 3 percent of the total energy

absorbed. The quantum yield as determined by Damon and Daniels at two different wave-lengths ($\lambda 3130$ and 2650) is low (0.1–0.3 molecule per quantum), increases with decrease in intensity and increases with increase in pressure. Independent determination of the quantum yield at $\lambda 3130$ ³⁸ agreed well with values obtained by interpolation from the data of Damon and Daniels. The variation of quantum yield with temperature has not been investigated but is probably not large. (The data of Damon and Daniels were obtained at 56° .)

Usually a low quantum yield accompanied by fluorescence is taken as an indication that molecules in an upper electron state are formed by the absorption of radiation and that these molecules may (1) decompose; (2) lose energy by collision without decomposing; (3) lose all or part of the energy by fluorescing without decomposing. In this case the fluorescent radiation lies in the green part of the spectrum and is changed to blue by the presence of oxygen.³⁶

The exact interpretation of these results with the aid of the spectroscopic data presents many difficulties. Kirkbride and Norrish³⁷ are inclined to the belief that the primary process is $(\text{H}_3\text{C})_2\text{CO} \rightarrow (\text{CH}_3)_2 + \text{CO}$, thus yielding directly the final products of the main reaction. Several facts seem at least superficially to disagree with this hypothesis and we shall examine the various possibilities in more detail.

Even though the absorption region under investigation is characteristic of ketones it is obviously not the carbon-oxygen bond which dissociates. One could suggest various possible electron states for acetone, but there would be little of a definite nature in the results. We shall confine ourselves to a speculation based on suggestions made by Urey and Johnston³⁹ in their analysis of the absorption bands of chlorine dioxide.

The structure of the acetone molecule is almost certainly such that the three carbon atoms do not lie in the same straight line.⁴⁰ For

³³ V. Henri and Wurmser, *Comptes Rendus* **156**, 1013 (1913); C. W. Porter and C. Iddings, *J. Am. Chem. Soc.* **48**, 40 (1926).

³⁴ W. M. Manning, unpublished results.

³⁵ C. W. Porter and C. Iddings, reference 33.

³⁶ G. H. Damon and F. Daniels, *J. Am. Chem. Soc.* **55**, 2363 (1933).

³⁷ F. W. Kirkbride and R. G. W. Norrish, *Trans. Faraday Soc.* **123**, 407 (1931).

³⁸ W. A. Noyes, Jr., unpublished results, obtained at 25° .

³⁹ H. C. Urey and Helen Johnston, *Phys. Rev.* **38**, 2131 (1931).

⁴⁰ See L. Pauling, *J. Am. Chem. Soc.* **53**, 1367 (1931) and succeeding papers for a discussion of the theoretical aspects of this problem of bond angles.

each electron state there will be an angle between the two carbon-carbon bonds leading to a minimum of potential energy. In the polydimensional surface representing the potential energy of such a complex molecule, this angle would be one of the coordinates.⁵ When the electron state of the molecule is changed the angle corresponding to minimum potential energy will undoubtedly change. Use of the Franck-Condon principle leads to the prediction that the vibration quantum number corresponding to changes in this angle will be relatively high after the change in electron state.

There remains the explanation of the continuous absorption combined with a low quantum yield. The energy required to break the carbon-carbon bond in acetone is not known with certainty but is fairly high, probably between 3.3 and 4.0 electron-volts.⁴¹ Even without including energy from other degrees of freedom in a manner analogous to that used in the explanation of homogeneous unimolecular gas reactions, the disruption of this bond at the long wave end of the absorption region would be energetically possible. There is no evidence, aside possibly from the variation of quantum yield with intensity, that we are dealing with a reaction proceeding through intermediate free radicals. The reaction $(\text{H}_3\text{C})_2\text{CO} \rightarrow (\text{CH}_3)_2 + \text{CO}$ is very slightly endoenergetic (not more than 0.5 electron-volt).

It is possible, therefore, that in the absence of water (which induces a polymerization reaction) the primary process is of the type of a predissociation by collision. This explanation satisfactorily accounts for the effect of pressure on the quantum yield observed by Damon and Daniels. Actually one should expect a fairly constant quantum yield at relatively high pressures and that the yield would begin to fall off at pressures comparable to those at which the rates of unimolecular reactions begin to deviate markedly from the so-called high pressure rate. The main primary process would be, therefore, similar to the one postulated by Kirkbride and Norrish.³⁷ The effect of increasing intensity in lowering the quantum yield is much more

obscure. Ordinarily this would suggest a reverse reaction between some of the intermediate dissociation products. In the present case this is scarcely a reasonable assumption to make. It is possible that collision between two activated molecules is more effective in deactivating one of them than a collision between an activated molecule and a normal molecule. In this connection a study of the variation of the intensity of the fluorescence both with the intensity of the incident radiation and the pressure of the acetone might provide the key to the solution of this problem.

The continuous absorption must then be due to the following causes: (1) a general overlapping of energy levels; (2) the very close spacing of the vibration levels in the upper electron state when the quantum number of the vibration corresponding to variation in the angle between the carbon-carbon bonds is large; (3) a possible pressure effect. The absorption spectrum of acetone should be examined with higher dispersion and at very low pressures. Acetaldehyde⁴² shows a region of distinct structure merging into a region of diffuse bands.

All of the hydrocarbons absorb in the Schumann region. Acetone should also have another absorption maximum in this region of the spectrum. If the absorption in this region should be due to the hydrocarbon part of the molecule one might expect not only a different quantum yield but different products from those obtained at longer wave-lengths. Conceivably ketene ($\text{CH}_2=\text{C}=\text{O}$) and methane would be formed. Methane is formed in appreciable quantities even at $\lambda 2650$ and $\lambda 3130$.³⁶ Thus a photochemical investigation would aid materially in interpreting the spectrum of acetone in this region. Work of this type is projected.

C. GENERAL CONCLUSIONS

One can scarcely examine carefully either spectroscopic or photochemical studies of any molecular types without realizing that the two must go hand in hand. It is truly surprising, however, to find so few cases in which both types

⁴¹ See F. O. Rice, W. R. Johnston and B. L. Evering, *J. Am. Chem. Soc.* **54**, 3529 (1932); G. B. Kistiakowsky and H. Gershinowitz, *J. Chem. Phys.* **1**, 432 (1933).

⁴² For recent work on this substance see P. A. Leighton and F. E. Blacet, *J. Am. Chem. Soc.* **55**, 1766 (1933). This article contains references to earlier work.

of investigation have been carried out with adequate care. The two cases which we have discussed in some detail are by no means satisfactorily elucidated at all points and numerous problems for future investigation immediately suggest themselves.

Particularly in dealing with complex molecular species it seems doubtful whether a spectroscopic study alone will ever succeed in adequately describing and correlating the various electron states and the possible dissociation products.

Photochemistry must be used as an aid. Due care must be used, however, in interpreting results because chain reactions and various secondary steps may lead to products altogether different from those produced during the primary process. One cannot emphasize too strongly that conditions must be varied over a wide range and some guiding principle kept in mind which will lead the investigator to observe all of the useful information which can be obtained from a given experiment.