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Joseph S. Mitchell

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JOSEPH S. MITCHELL,** *Laboratory of Colloid Science, Cambridge, England*

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The theory of the dependence, on the molecular orientation, of the velocity of photochemical reactions in monolayers at the surface of aqueous substrates is developed. The molecular extinction coefficient in the film is discussed and a definition is given of the "apparent quantum efficiency." Consideration of the molecular thermal agitation suggests the possibility of a phase boundary potential gradient of the order of 10^8 volts per cm. Under certain conditions, the apparent quantum efficiency is proportional to the absolute temperature. Factors modifying the absorption spectrum of a compound in a monolayer are discussed. By an application of the general theory of radiation, a relation is obtained between the molecular orientation and an integral of the molecular extinction coefficient in the film over the absorption band. The molecular extinction coefficient in the film cannot be deduced *a priori* from that in solution; it is proportional to the mean value of $\sin^2 \theta$ (where θ is the angle between the molecular dipole axis and the direction of the incident light) and is usually of the order of $3/2 \sin^2 \theta$ that in solution. The theoretical accuracy of the $\sin^2 \theta$ relation is discussed and both quadrupole absorption and reabsorption of coherently scattered radiation are shown to be of no practical importance. Direct measurement of the absorption spectrum of a monolayer is essential for the absolute determination of the quantum efficiency of a photochemical reaction.

I N a number of recent investigations,[1-4] chemical reactions occurring in organic compounds spread in monolayers at the surface of aqueous substrates have been studied by observation of the phase boundary potential and surface pressure. The results of these experiments show clearly the importance and reality of the Hardy-Langmuir principle of molecular orientation in the realm of two-dimensional chemical kinetics. In photochemical processes in monolayers, a similar dependence of the reaction velocity on the orientation of the absorbing molecules has been found. (A detailed account of these experiments will be published shortly.) In the present paper, the theory of this orientational effect is given and the general processes of light absorption by monolayers are discussed in relation to the absolute measurement of the quantum efficiency of the photochemical processes occurring.

The optical anisotropy of monolayers at air-water interfaces has been demonstrated by Tronstad and Feacham[5] using the Jamin-Rayleigh method. With the aid of Strachan's development of the Drude equation,[6] they showed that, in the case of monolayers of myristic acid, the scattering index in the plane of the film is of the same order as that in bulk, while the index for the direction normal to the film is smaller by a factor of the order of 10^{-2}.

THE MOLECULAR EXTINCTION COEFFICIENT IN A MONOLAYER

It is evident that for the absorption of light by a two-dimensional monomolecular array, Beer's law in its usual form has no precise meaning. The absorbing oscillators are independent and each can capture energy from an area of incident wave-front of the order of λ^2/π (where λ is the wave-length of the incident light)[7] so that it is permissible to apply the differential analog of Beer's law, to define the molecular extinction coefficient in the film and to calculate the light absorption from a beam of given intensity. Thus the energy ΔJ absorbed by the monolayer per cm² per sec. from a normally incident beam of intensity J is given by

$$\Delta J = (2.303/6.06 \times 10^{20}) \epsilon n J, \qquad (1)$$

where n is the surface density specified by the number of molecules per cm², and ϵ by definition is the molecular extinction coefficient in the monolayer. The thickness of the film does not appear explicitly, but the formal analogy of Eq. (1) to Beer's law leads to a functional

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** Beit Memorial Research Fellow.
[1] Hughes and Rideal, Proc. Roy. Soc. **A140**, 253 (1933).
[2] Fosbinder and Rideal, Proc. Roy. Soc. **A143**, 61 (1933).
[3] Schulman and Rideal, Biochem. J. **27**, 1581 (1933).
[4] Gee and Rideal, Proc. Roy. Soc. **A153**, 116 (1935).
[5] Tronstad and Feacham, Proc. Roy. Soc. **A145**, 115 (1934).
[6] Strachan, Proc. Camb. Phil. Soc. **29**, 116 (1932).
[7] Rayleigh, Phil. Mag. **32**, 188 (1916).

relation, in terms of the molecular-orientation, between the molecular extinction coefficient of the compound in the film and in solution.

For examining the orientational effect, since ϵ is not known accurately, it has been found satisfactory to express the experimental data of photochemical processes by means of the "apparent quantum efficiency" ϕ_a, which is defined as the quantum efficiency calculated with the aid of Eq. (1) on the assumption that the molecular extinction coefficient in the film has the same value as that in solution in a polar solvent.

THE STRUCTURE OF MONOLAYERS IN RELATION TO LIGHT ABSORPTION

In liquid expanded and liquid homalic films, there is little doubt that the constituent molecules are partially sunk in the water, the polar groups being completely immersed. In liquid condensed, gelatinous and solid films, there are probably a few water molecules interspersed among the lower parts of the hydrophobic groups, but the polar groups are still surrounded by water molecules. The dielectric constant in the neighborhood of the dipoles is not known with certainty, but probably varies, usually lying between 5 and 10.

The effect of thermal agitation on the molecular orientation is a problem of great importance. At the limiting area in the liquid expanded state, the terminal dipole might be expected to be free to rotate as a result of collisions with the substrate molecules. The very low experimental value of the temperature coefficient (Fosbinder and Rideal, 1933)[2] of the vertical component of the dipole moment, as deduced from Helmholtz's equation, shows that this is not true and suggests that an orienting electric field normal to the surface must be present. An application of Langevin's theory[8] shows that an effective potential gradient of the order of 10^8 volts per cm is required in the region of the electric dipole. That a field of this order of magnitude is reasonable physically is supported by the following considerations. The total potential step at an air-water interface has not been measured directly but must be

equal to the difference between the photoelectric work function for water and the contribution to the work function of the image forces. The work function for water, and solutions of electrolytes up to $N/2$ concentration, has been found by Gorlich[9] to be 6.08 volts. The order of the contribution from the image forces ϕ' can be calculated by Schottky's equation[10] $\phi' = 300e/2r_0$ volts, where r_0 is the inter-atomic distance; taking the radius of a water molecule as 1.38A, ϕ' is found to be 2.6 volts. Thus at an air-water interface there must exist a potential step of the order of 3.5 volts, which is probably due to a preferential orientation of the superficial polar water molecules. The distance over which this phase boundary potential change occurs must be of the same order as the minimum thickness of the optical transition layer, which was found by Rayleigh[11] to be 3A and by Raman and Ramdas[12] to be 5A. If a value of 4A is taken the potential gradient present is of the order of 10^8 volts per cm.

In solid and liquid condensed monolayers, the variation of orientation of the dipoles at any given area is almost certainly limited to small angular oscillations about the mean position, which is determined by the van der Waals adhesion of the hydrophobic groups in conjunction with the packing limitation set by the intermolecular repulsive fields. It will be shown below that the probability of light absorption by a molecule is proportional to $\sin^2 \theta$, where θ is the angle between the molecular dipole axis and the direction of the incident light, which will be assumed throughout this paper to be normal to the surface. In monolayers of certain compounds it can be demonstrated, by means of molecular models constructed with the aid of x-ray crystallographic data, that the vertical component of the dipole moment $\bar{\mu}$, deduced from the phase boundary potential and molecular area measurements by the Helmholtz equation, is proportional to the mean value of $\cos \theta$. The important quantity for light absorption is the mean value of $\sin^2 \theta$, which is less than $1 - \overline{(\cos \theta)}^2$ by $(a^2/2) \sin^2 \theta_0$, where θ_0 is the mean equilibrium value of θ and a the amplitude of the small

[8] Langevin, J. de physique 4, 678 (1905).

[9] Gorlich, Ann. d. Physik 13, 831 (1932).
[10] Schottky, Zeits. f. Physik 14, 63 (1923).
[11] Rayleigh, *Scientific Papers* (1892), Vol. 3, p. 496.
[12] Raman and Ramdas, Phil. Mag. 3, 220 (1927).

angular oscillation about θ_0. The amplitude a, cannot be calculated a priori, but if it is sufficiently small with respect to unity, no error is introduced in identifying $\overline{\sin^2 \theta}$ with $1 - \overline{(\cos \theta)^2}$. If, however, a is not negligible, the interesting result is obtained that at $\theta_0 = 0$, $\overline{\sin^2 \theta} = a^2/2$, so that the apparent quantum efficiency of a photochemical reaction under these conditions, which should be realized at the limiting area of certain condensed films, will be proportional to the absolute temperature. For any value of θ_0, the deviation of the observed ϕ_a from that calculated on the assumption of negligible thermal oscillation is proportional to the absolute temperature, but owing to the usual variation of with molecular area, it is only at and near the limiting area that such an effect could be detected.

General Features of the Absorption of Light by Monolayers

Accurate measurements of the absorption spectra of organic compounds spread in monolayers at an air-water interface have not yet been made, but the velocity of simple photochemical reactions shows that the molecular extinction coefficient in the film at any given wave-length is of the same order as that in solution in a polar solvent and that the absorption bands are usually not displaced by more than 100A from the position in solution. Hughes and Allsopp[13] have shown directly that magnesium naphthalocyanine gives visible green monolayers in which the molecular extinction coefficient is of the same order as in solution. Modification of the absorption spectrum in monolayers of various organic compounds adsorbed on transparent laminae of inorganic salts has been examined in considerable detail by de Boer[14] but the results are not capable of direct extension to monolayers on aqueous substrates.

In relation to the absorption of light, the general physical conditions in a monolayer at a water surface are closely analogous to those present in solution in a polar solvent. The collision damping is of similar importance, pro-

ducing a Lorentz wave-length half-breadth $\Delta\lambda$[15] for the collision broadened line of wave-length λ, of the order of $\Delta\lambda = \lambda^2 Z/c\pi$. Z, the collision frequency between a film molecule and the substrate molecules, can be obtained from the approximate equation $Z = 3\pi\eta\sigma/2m$ where σ and m are the diameter and mass of the film molecule and η is the viscosity of the solvent. For molecules such as stearic acid on water, Z is of the order of 10^{13} per second, so that at $\lambda = 2400A$ $\Delta\lambda = 10A$. The collision displacement of a line is of the order of $\Delta\lambda/2$[16] and is thus negligible with respect to that produced by the inhomogeneous Stark effect of the electric fields of the colliding substrate molecules. According to the theory of Stern[17] the fields of water molecules can, during collisions, produce wave-length displacements of the absorption spectrum of the order of 100–1000A, such as were found for mercury atoms in solution by Reichardt and Bonhoeffer.[18]

It is possible that there is a not inconsiderable modification of the absorption spectrum in a monolayer due to the homogeneous Stark effect produced by the orienting field at the phase boundary. Analogy with the linear Stark effect for a diatomic molecule with a permanent electric dipole suggests that the order of the wave-length displacement $\Delta\lambda$ of an absorption line of wave-length λ is given by $\Delta\lambda = (\lambda^2/hc)p \cdot E$, where p is the molecular dipole moment and E the applied electric field. A phase boundary potential gradient of the order of 10^8 volts per cm may produce a shift of the ultraviolet absorption spectrum of the order of 100A, and accurate measurement of the absorption spectrum of a monolayer may provide evidence for the existence and magnitude of the orienting field.

It is now necessary to consider briefly the transition probability which determines the absorption intensity, in the presence of the inhomogeneous, and possibly also the homogeneous, electric fields. The molecules dealt with experimentally are extremely complex, so that even in the simplest cases, an exact treatment of the Stark effect is quite impossible. Analogy

[13] Hughes and Allsopp, Nature 137, 503 (1936).
[14] de Boer, Electron Emission and Adsorption Phenomena (Cambridge, 1935), Chap. 8.

[15] Lorentz, Proc. Amst. Acad. 18, 134 (1915).
[16] Lenz, Zeits. f. Physik 80, 423 (1933).
[17] Stern, Physik. Zeits. 23, 476 (1922).
[18] Reichardt and Bonhoeffer, Zeits. f. Physik 67, 780 (1931).

with diatomic molecules possessing a permanent electric moment[19] suggests that under certain, probably very restricted, conditions the summation rule may still hold, so that the oscillator strength corresponding to a given transition is invariant. Although the field strengths are very great, and the electron transition is at the periphery of the atom, the validity of the summation rule has been confirmed by Reichardt[20] for the 2537A absorption line of mercury, modified by solution in hexane.

Light Absorption and Molecular Orientation

We must first consider a simplified model in which the thermal agitation of the molecules is absent and the perturbing fields, apart from the incident light, are small. The monolayer consists of a two-dimensional array of molecules represented by electric dipoles whose axes are inclined at a constant angle θ to the normal to the surface. The azimuthal orientation is random. No details of the molecular distribution are specified but macroscopic uniformity is necessary. The incident light is normal to the surface; it is unpolarized and has a continuous spectral distribution with $N(\nu)$ quanta per cm² per second per unit frequency range at ν, so that the intensity J_ν per unit frequency range at ν is $J_\nu = N(\nu)h\nu$. n is the total number of molecules per cm². The molecular resonance frequencies do not coincide on account of the perturbing fields and $n_\nu d\nu$ is the molecular surface density of molecules with proper frequencies between ν and $\nu+d\nu$. ϵ_ν is the molecular extinction coefficient in the film at the frequency ν. Thus two spectral distributions have to be considered:

1. That of the incident light; in which J_ν varies very slowly with frequency.
2. That of the proper frequencies of the absorbing oscillators. ϵ_ν varies rapidly with frequency over the absorption band and has only non-zero values over a narrow range.

The probability P_ν of absorption by a molecule with a permanent electric dipole moment of a quantum per second from an incident beam of $N(\nu)$ quanta per cm² per second per unit fre-

quency range at frequency ν is proportional to $|(p\cdot E)|^2$, the square of the modulus of the scalar product of the electric moment p and the electric vector E of the incident light beam.

When the beam is plane polarized with the electric vector parallel to the x axis and the molecular dipole axis is also in the direction of the x axis, P_ν is given, to a first approximation, by

$$P_\nu = (8\pi^3 e^2/hc)|x_{ik}|^2 N(\nu)\nu, \qquad (2)$$

where i, k signify the upper and lower molecular energy levels involved and x_{ik} is the corresponding matrix element of the x coordinate:

$$x_{ik} = \int \psi_i^*(\sum_n x_n)\psi_k dx_1 \cdots dx_n dy_1$$
$$\cdots dy_n dz_1 \cdots dz_n, \quad (3)$$

where $x_l y_l z_l$ are the coordinates of the lth particle and the summation is extended over the n particles (electrons and nuclei) in the molecule. This result can be obtained by two methods by means of Dirac's perturbation theory[21] and contains an integration over the whole spectrum of the incident light.

Thus the number of quanta absorbed per cm² of the model film per second in the frequency range ν, $\nu+d\nu$ from an incident unpolarized beam of $N(\nu)$ quanta per cm² per second per unit frequency range at frequency ν, is, averaging over all directions of polarization of the incident beam and of azimuthal orientation of the molecules, given by

$$P_\nu n_\nu d\nu = \frac{8\pi^3 e^2}{hc}|r_{ik}|^2 \frac{\sin^2\theta}{2} N(\nu)\nu n_\nu d\nu, \qquad (4)$$

where r_{ik} is the matrix element of the coordinate vector r, whose components are x, y, z.

In terms of the molecular extinction coefficient in the film, Eq. (1) shows that

$$P_\nu n_\nu d\nu = \frac{2.303}{6.06\times10^{20}}n_\nu d\nu \int_0^\infty \frac{\epsilon_\nu J_\nu d\nu}{h\nu}. \qquad (5)$$

J_ν varies very slowly with frequency so that

$$P_\nu n_\nu d\nu = \frac{2.303}{6.06\times10^{20}}n_\nu d\nu N(\nu)\nu \int \frac{\epsilon_\nu d\nu}{\nu}, \qquad (6)$$

where the frequency range of integration is now

[19] Kronig, *Band Spectra and Molecular Structure* (Cambridge, 1930), p. 99.
[20] Reichardt, Zeits. f. Physik **70**, 516 (1931).

[21] Dirac, *Principles of Quantum Mechanics* (Oxford, 1930), Chaps. 9, 12.

extended over the absorption band. Hence from Eqs. (4) and (6)

$$\frac{8\pi^3 e^2}{hc}|r_{ik}|^2 \frac{\sin^2\theta}{2} = \frac{2.303}{6.06\times10^{20}}\int \frac{\epsilon_\nu d\nu}{\nu}. \quad (7)$$

This equation is analogous to the well-known relation[22-25] between the Einstein B coefficient and the integral of the absorption coefficient of a line:

$$B_{ki} = c/N_k \int (\alpha' d\nu/h\nu), \quad (8)$$

where B_{ki} is Einstein's absorption probability coefficient defined in terms of the radiation density, N_k is the number of absorbing molecules per cm^3 in the lower state k and α' is the "natural extinction coefficient." Introduction of the usual expression for B_{ki} shows more clearly the relation between Eqs. (7) and (8):

$$\frac{g_i 8\pi^3 e^2}{g_k 3hc}|r_{ik}|^2 = \frac{2.303}{6.06\times10^{20}}\int \frac{\epsilon_\nu' d\nu}{\nu}, \quad (9)$$

where ϵ_ν' is the molecular extinction coefficient in bulk. The statistical weights of the upper and lower states g_i and g_k, are usually unity.

Eqs. (7) and (9) are deduced assuming the presence of weak or negligible perturbing fields, and the formal difference between them is due to the averaging over all values of $\sin^2\theta$ in Eq. (9). When strong perturbing fields are introduced, so that Eq. (7) corresponds to a real monolayer and Eq. (9) to a solution, $|r_{ik}|^2$ in each case is replaced by a sum $\sum_{i'k'}|r_{i'k'}|^2$ and the absorption integrals may change, but if the summation rule is valid, these quantities are invariant; there is however no *a priori* demonstration that in any given case this is true.

Eq. (7) shows the relation between the molecular extinction coefficient in the film and the molecular orientation. As discussed above, $\sin^2\theta$ must be averaged over those values of θ allowed by the thermal agitation and orientational oscillation at any given molecular area. Thus the fundamental result capable of experi-

mental test is that the molecular extinction coefficient in the film is proportional to $\overline{\sin^2\theta}$. Comparison of Eqs. (7) and (9) demonstrates that no exact relation exists between ϵ_ν' the molecular extinction coefficient in solution and ϵ_ν, that in the film. In general,

$$\epsilon_\nu = 3/2f(\nu)\overline{\sin^2\theta}, \quad (10)$$

where $f(\nu)$ is an extremely complicated function of ν, which cannot be calculated theoretically in terms of ϵ_ν', but which usually is of the same order as ϵ_ν'. From these considerations it is evident that direct measurement of the absorption spectrum of a monolayer is essential for the absolute determination of the quantum efficiency of a photochemical process occurring in the monolayer.

ACCURACY OF THE SIN² θ RELATION

There are three factors which one may envisage as capable of causing departures from the $\sin^2\theta$ relation, namely:

1. Inaccuracy of Eq. (2) due to neglect of significant terms of higher order of approximation.
2. Reabsorption of light coherently scattered in the monolayer.
3. Quadrupole absorption.

Each of these will be considered briefly and shown to be of no importance under experimental conditions.

Eq. (2) is obtained by the perturbation theory as a second-order term. The higher order approximations can be easily calculated and it is found that, while the third-order term vanishes, the fourth-order term does not and leads to the following modification of Eq. (2):

$$P_\nu = 8\pi^3/hc|(\alpha'|p|\alpha'')|^2 N(\nu)\nu$$
$$-\frac{16\pi^6 N(\nu)^2\nu^2}{h^2c^2}\sum_{\alpha'''}|(\alpha'|p|\alpha'')|^2|(\alpha''|p|\alpha''')|^2, \quad (11)$$

where $\nu = \nu(\alpha'\alpha'')$ the frequency of the absorbed radiation being connected with states α', α'' and the summation in the second term is over all other states α'''. Under the conditions in photochemical experiments, an incident beam with $N(\nu)$ of the order of one quantum per cm^2 per second per unit frequency range in the wavelength band 2350–2400A is employed, so that the first term in Eq. (11) is of the order of

[22] Becker, Zeits. f. Physik 18, 325 (1923).
[23] Tolman, Phys. Rev. 23, 693 (1924).
[24] Milne. Mon. Not. Roy. Astronom. Soc. 85, 117 (1924).
[25] Joos, *Handbuch der Experimental Physik* (Leipzig, 1927), Vol. 21, p. 102.

1.10^{-3}, while the second term is of the order of 5.10^{-7} and hence is negligible.

The process of equating the expressions on the right sides of Eqs. (4) and (6) neglects the negative absorption, and is equivalent to omitting from the left side of Eq. (7) a factor $(1 - g_i N_i / g_k N_k)$. Under experimental conditions, light absorption is the only important mechanism responsible for the formation of excited molecules, so that the proportion of excited molecules in the film N_i/N_k is of the order of 10^{-12}.

The coherent scattering in the film can be calculated by regarding the molecules as Hertzian oscillators. With an unpolarized normally incident beam of intensity J_{inc}, the order of the intensity $J_{r\theta}$ scattered by a molecule at a distance r of the order of the molecular radius a in a direction making an angle θ with the normal is, on the assumption that the molecular polarizability is of the order of a^3, given by the expression

$$J_{r\theta}/J_{inc} = (a^6/r^4)(2\pi/\lambda)^2((1+\cos^2\theta)/2). \quad (12)$$

Only the immediately adjacent molecules can have an appreciable effect, and even at $r = 2a$, for $\lambda = 2400A$, $J_{r\theta}/J_{inc}$ is of the order of 10^{-6}. For large r, $J_{r\theta}/J_{inc}$ is of the order of $a^6/r^2\lambda^4$ which cannot be greater than 10^{-18}. Thus it is certain that coherent scattering can never be of importance in photochemical processes in monolayers.

It is not evident *a priori* that a film molecule can be adequately represented by an electric dipole and absorption by an electric quadrupole molecule will now be considered.[26] The Einstein probability coefficient B_{ki}, for absorption of radiation of frequency ν_{ik} by a quadrupole is easily found to be

$$B_{ki} = (g_i/g_k)(4/5)(\pi^5\nu_{ik}^2/c^2h^2)|Q_{ik}|^2 \quad (13)$$

in the usual notation, where Q_{ik}, the matrix component of the quadrupole moment is defined by

$$Q_{ik} = -e \int \psi_i^*(\sum_n r_n^2)\psi_k dx_1 \cdots dx_n dy_1 \\ \cdots dy_n dz_1 \cdots dz_n. \quad (14)$$

By induction from Eqs. (7) and (8), it can be seen that the molecular extinction coefficient in a film of quadrupoles is of the order of $15 \overline{\sin^4\theta}/8$ that in solution, where θ is the angle between the quadrupole axis and the direction of the incident beam. However, for $\lambda = 2400A$ and $r = 3A$, B_{ki} (quadrupole)$/B_{ki}$ (dipole) is of the order of 10^{-5}, so that no photochemical reaction due to quadrupole absorption could possibly be detected.

I wish to thank Professor E. K. Rideal for his stimulating criticism and continued help throughout this investigation.

[26] Rubinowicz, Physik. Zeits. 19, 440 (1918).

The Evaluation of Molecular Dipole Moments from the Data of Electrical Stern-Gerlach Experiments

R. G. J. FRASER, *Imperial Chemical Industries Limited,*
AND
J. V. HUGHES, *St. John's College, Cambridge, England*

RODEBUSH, Murray, and Bixler[1] report measurements of the electrical dipole moments of the alkali halides by the molecular beam method, which gave values for KCl and KI much greater than those obtained by Scheffers,[2] also by a beam method. Scheffers used a wire and concentric cylinder to obtain the necessary inhomogeneous electric field, whereas Rodebush Murray, and Bixler used the Rabi type of field (parallel plate condenser), and they suggest that

[1] W. H. Rodebush, L. A. Murray, and M. E. Bixler, J. Chem. Phys. 4, 372 (1936). See also W. H. Rodebush, ibid. p. 536.

[2] H. Scheffers, Physik. Zeits. 35, 425 (1934).