

Monolayers Adsorbed on Metal Surfaces

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Citation: *The Journal of Chemical Physics* **16**, 841 (1948); doi: 10.1063/1.1747012

View online: <http://dx.doi.org/10.1063/1.1747012>

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where h is Planck's constant and m the electronic mass. There are $N = Z + 1 = 2\nu + 10$ π -electrons belonging to the gas (each carbon atom in the chain contributes one electron, and the two nitrogen atoms altogether three); in the ground state, the $N/2$ levels of lowest energy are occupied by these electrons, each level containing two electrons. The first absorption band corresponds to a jump from the highest filled level with quantum number $n = N/2$ to the next higher level. From Eq. (1) can easily be obtained an expression for the wave-length λ_{vac} of the peak of this band.

$$\lambda_{vac} = \frac{8mc}{h} \frac{L^2}{N+1} = \frac{8mb^2c}{h} \frac{N^2}{N+1} \quad (2)$$

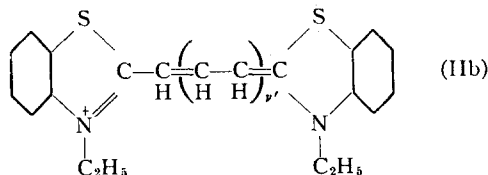
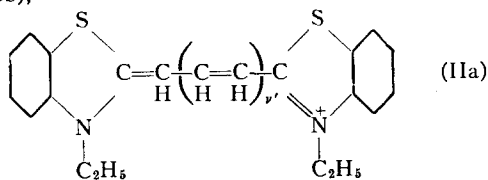
(c = velocity of light). By introducing the numerical values of m , l , c , and h into (2) we obtain for some values of N (or ν):

$N = 10 (\nu = 0)$	$\lambda_{vac} = 5790 \text{ \AA}$	(exp. $\lambda_{vac} = 5900 \text{ \AA}$)
$N = 12 (\nu = 1)$	$\lambda_{vac} = 7060 \text{ \AA}$	(exp. $\lambda_{vac} = 7100 \text{ \AA}$)
$N = 14 (\nu = 2)$	$\lambda_{vac} = 8340 \text{ \AA}$	(exp. $\lambda_{vac} = 8200 \text{ \AA}$)
$N = 16 (\nu = 3)$	$\lambda_{vac} = 9590 \text{ \AA}$	(exp. $\lambda_{vac} = 9300 \text{ \AA}$)

The experimental values given in brackets are those obtained by Brooker and co-workers³ from the spectra of dyes of structure (Ia), (Ib). These values are seen to be in good agreement with the theoretical values.

This one-dimensional free electron model can equally well be used for determining (in good agreement with the experiment) the position of the absorption peaks of a number of colored compounds, such as symmetric oxanole and cyanine dyes, triphenylmethane dyes, and aromatic hydrocarbons, such as anthracene, naphthalene and pentacene.²

The intensity of the absorption bands of these compounds, measured by the oscillator strength f , can easily be determined on the basis of our free electron model. For a molecule for which it can be assumed that its chain of resonating single and double bonds possesses all *trans*-configuration, such as symmetric cyanine of structure (IIa), (IIb),



the oscillator strength of the first absorption band is found to be given by the equation:

$$f = \frac{4}{3\pi^2} \cos^2(\beta/2) \cdot \frac{N^2(N+2)^2}{(N+1)^3} \quad (3)$$

$180^\circ - \beta$ is the valence angle between the chain members, and N , as mentioned above, the number of electrons be-

longing to the one-dimensional gas. (In the case of cyanines [see structure (IIa), (IIb)], N is equal to $2\nu + 6$, and $180^\circ - \beta$ is equal to 124° (i.e., equals the $C \equiv C - C$ valence angle).) By introducing this value into (3), we obtain for some values of N (or ν):

$N = 6 (\nu' = 0)$	$f = 0.71$	(exp. $f = 1.2$)
$N = 8 (\nu' = 1)$	$f = 0.93$	(exp. $f = 1.2$)
$N = 10 (\nu' = 2)$	$f = 1.14$	(exp. $f = 1.6$)
$N = 12 (\nu' = 3)$	$f = 1.35$	(exp. $f = 1.9$)

The experimental values in brackets, obtained from the data given by Brooker,³ are in rough agreement with the theoretical values.

The problem of absorption of organic dyes and related compounds has been treated by earlier workers throughout on the basis of the bond orbital and molecular orbital method.⁵ The wave functions of the π -electrons are considered in these latter treatments as simple combinations of atomic wave functions. The treatment proposed here, which is similar to Sommerfeld's treatment on metals,⁶ does not refer to atomic wave functions, but considers a given π -electron as a particle in the potential field of the molecular frame. It is seen that this treatment is simpler and more powerful for the purpose considered here than the bond and molecular orbital treatments; according to the latter treatments, the position of the absorption peaks are dependent upon parameters that have to be determined empirically (in most cases from the position of the corresponding peaks in related compounds), while our equations do not contain such parameters.

¹ N. S. Bayliss, J. Chem. Phys. **16**, 287 (1948).

² H. Kuhn, Helv. Chim. Acta, in print; lecture at the chemistry colloquium in Basel, January 22, 1948.

³ This Brillouin zone appears in non-symmetric cyanine dyes, where one of the two resonating structures that correspond to Ia and Ib is energetically preferred relative to the other. We thus expect by substituting a symmetric by a non-symmetric polymethine dye that there is a shift of the absorption band towards shorter wave-length. Such a shift has been found empirically by Brooker and co-workers [see L. G. Brooker, Rev. Mod. Phys. **14**, 275 (1942)]—further references are given here] in a great number of examples.

⁴ See, for instance, L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York 1935), Section 14.

⁵ A. L. Sklar, J. Chem. Phys. **5**, 669 (1937), **10**, 521 (1942); Rev. Mod. Phys. **14**, 233 (1942); K. F. Herzfeld and A. L. Sklar, Rev. Mod. Phys. **14**, 294 (1942); L. Pauling, in Gilman's *Organic Chemistry* (New York, 1938), p. 1864, Proc. Nat. Acad. Sci. **25**, 577 (1939); T. Förster, Zeits. f. Elektrochemie **45**, 548 (1939).

⁶ See for instance: A. Sommerfeld and H. Bethe, *Handbuch der Physik*, Vol. **24**, second edition.

Monolayers Adsorbed on Metal Surfaces

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June 15, 1948

IN a recent paper, Halsey and Taylor¹ have considered the interpretation, in terms of statistical mechanics, of extensive measurements by Frankenburg² on the adsorption of hydrogen on tungsten powders. They quote the formula given by Fowler and Guggenheim³ for the adsorption isotherm for a random distribution of particles (that is, an immobile film) on an array of localized⁴ sites, taking account of closest neighbor interactions. Halsey and

Taylor point out, as is well known to be the case for an immobile film (each particle of which occupies one site on a localized array)⁶ that this leads to a linear variation of heat of adsorption, q , with the fraction of the surface covered, θ . From the fact that Frankenburg's data does not follow such a law, they conclude that a theory of interactions on a surface in which all the sites involve the same energy of adsorption cannot account for the experimental results.

Their conclusion, in this respect, appears not to be well founded. Their rejection of interaction theories appears to be based primarily on the fact that the experimental results do not reproduce a linear variation of the heat of adsorption with the fraction of the surface covered. But this is not a characteristic of all possible types of adsorbed film, even for the kind of fixed interaction theory used in the case which they quote; such a linear variation is only to be expected on this theory for a random distribution, that is, an immobile film, of adsorbed particles, each of which occupies only one site on the surface. For mobile films⁶ and for all films, mobile or immobile, in which each adsorbed particle occupies more than one site⁷ on the array of the localized sites, the variation of the heat of adsorption may depart very much from a linear law in θ . Consequently, the experimental fact that a linear relation is not observed can provide no justification for rejecting out of hand an interaction theory.

Furthermore, it should be noted that the interaction theories to which reference has been made, and to one application of which Halsey and Taylor make appeal, assume that there is a fixed interaction energy between particles adsorbed on closest neighbor sites. It was pointed out by Roberts⁸ that for an actual surface this will not be so; that, in fact, the surface provides a two-dimensional periodic potential field, the local sites postulated by Langmuir⁹ being the potential minima of this field. It has been shown¹⁰ that when this periodic variation of the potential field* provided by the surface and the variation with distance of the interaction energy between two adsorbed particles are taken into account, neither a mobile nor an immobile film gives anything like a linear variation of the heat of adsorption with the fraction of the surface covered. As this physical model is a much closer representation of an actual surface than the fixed interaction model which was used in the earlier theoretical treatments of adsorption, it can be concluded that for an actual surface a linear variation of q with θ is scarcely to be expected in any case. This is entirely neglected by Halsey and Taylor, and it provides an additional reason for doubting the validity of the conclusion which they seek to deduce from the absence of a linear variation. There is not space in a letter to consider all the effects of the periodic potential field provided by an actual surface but a qualitative discussion has been given elsewhere.⁸ Miller and Roberts discussed theoretically a linear chain only, but by the use of other statistical methods it appears that the two-dimensional case can also be discussed and work is proceeding on this point.

Halsey and Taylor invoke the assumption that the energy difference between the lowest state in the gas phase and the lowest adsorbed state varies from site to site and that the interactions between adsorbed molecules can be neglected. It has been pointed out above that their argu-

ment depends on the neglect of a particular case of the fixed interaction theory and on the complete neglect of refinements of the theory which indicate that all adsorbed films give a variation of the heat of adsorption quite different from that which is the basis of their argument. Their rejection of theories which depend upon the interaction between adsorbed particles can scarcely be considered even to have been made plausible. Any effect which can be explained by the type of heterogeneity postulated by Halsey and Taylor is probably due to the fact that in the experiments which they discuss powdered metal is used and adsorbed gas on such a substratum forms a highly complex system.

¹ G. Halsey and H. S. Taylor, *J. Chem. Phys.* **15**, 624 (1947).

² W. G. Frankenburg, *J. Am. Chem. Soc.* **66**, 1827, 1838 (1944).

³ R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Teddington, England, 1939), Ch. X, p. 421.

⁴ For a precise definition of the terms mobile and immobile films and of localized arrays of sites in this connection see J. K. Roberts, *Some Problems in Adsorption* (Cambridge University Press, Teddington, England, 1939), p. 22; A. R. Miller, *Proc. Camb. Phil. Soc.* **43**, 232 (1947); A. R. Miller, *The Adsorption of Gases on Solids* (Cambridge University Press, Teddington, England, in press), Section 2.2.

⁵ J. K. Roberts, *Proc. Camb. Phil. Soc.* **34**, 399 (1938).

⁶ J. S. Wang, *Proc. Roy. Soc. A* **161**, 127 (1937), Fig. 1; A. R. Miller, *The Adsorption of Gases on Solids* (Cambridge University Press, Teddington, England, in press), Sections 2.4 and 2.5.

⁷ J. K. Roberts, *Proc. Camb. Phil. Soc.* **34**, 577 (1938), Fig. 4; A. R. Miller, *Proc. Camb. Phil. Soc.* **43**, 232 (1947), Figs. 2 and 5.

⁸ J. K. Roberts, *Some Problems in Adsorption* (Cambridge University Press, Teddington, England, 1939), Section 2.7.

⁹ I. Langmuir, *J. Am. Chem. Soc.* **40**, 1361 (1918).

¹⁰ A. R. Miller and J. K. Roberts, *Proc. Camb. Phil. Soc.* **37**, 82 (1941).

* Still assuming, however, that the adsorption energy of a particle adsorbed at one of these minima is the same for all the sites.

Carbon-Carbon and Carbon-Hydrogen Bond Energies

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June 14, 1948

WHEN the force constants ($k(\text{CC})$ and $k(\text{CH})$) for the aliphatic structures given in Table I are plotted as a function of internuclear distance ($R(\text{CC})$ and $R(\text{CH})$) as in Fig. 1, the well-known result is obtained that the larger force constants are found for the shorter bonds.¹ In order to obtain the corresponding carbon-carbon bond energies ($D(\text{CC})$) and the average carbon-hydrogen bond energies ($D(\text{CH})$), the atomic heats of formation (Q_a) of the molecules in Table I were calculated, using for the heat of sublimation of carbon $L(\text{C}) = 5.888 \text{ ev}^2$ or 7.334 ev^3 . For the $D(\text{CC}):R(\text{CC})$ curve only two points are known: $D(\text{C}_2(^3\Pi_u)) = 3.6 \text{ ev}$ from Herzberg⁴ and $D(\text{diamond}) = L/2 = 2.944 \text{ ev}$ based on $L(\text{C}) = 5.888 \text{ ev}$. For the $D(\text{CH}):R(\text{CH})$ curve two known points are $\bar{D}(\text{CH in CH}_4) = Q_a/4 = 3.88 \text{ ev}$ and $D(\text{CH}(^2\Pi_r)) = 3.47 \text{ ev}$ from Shidei.⁵ Skinner⁶ assumes a straight line relation for $D(\text{CH}):R(\text{CH})$. In the present calculations, however, the other points (C_2H_2 , C_2H_4 , C_2H_6) were found by dividing the corresponding Q_a values of these molecules in such a manner that both types of curve, $D(\text{CC}):R(\text{CC})$ and $D(\text{CH}):R(\text{CH})$ would have the same kind of curvature as the corresponding $k(\text{CC}):R(\text{CC})$ and $k(\text{CH}):R(\text{CH})$ curves. The procedure