

Hysteresis of the Contact Angle

S. J. Gregg

Citation: *The Journal of Chemical Physics* **16**, 549 (1948); doi: 10.1063/1.1746935

View online: <http://dx.doi.org/10.1063/1.1746935>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/16/5?ver=pdfcov>

Published by the **AIP Publishing**

Articles you may be interested in

[Contact angle hysteresis on superhydrophobic stripes](#)

J. Chem. Phys. **141**, 074710 (2014); 10.1063/1.4892801

[Tunable contact angle hysteresis by micropatterning surfaces](#)

Appl. Phys. Lett. **98**, 184101 (2011); 10.1063/1.3576921

[Effect of contact angle hysteresis on thermocapillary droplet actuation](#)

J. Appl. Phys. **97**, 014906 (2005); 10.1063/1.1819979

[Equilibrium contact angle and intrinsic wetting hysteresis](#)

Appl. Phys. Lett. **67**, 2249 (1995); 10.1063/1.115119

[A model for contact angle hysteresis](#)

J. Chem. Phys. **81**, 552 (1984); 10.1063/1.447337



specific results for C_8D_8 which appear to confirm the D_4 structure. If C_8H_8 and C_8D_8 have this structure, these molecules have a species of vibration A_2 (see Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, New York, 1945, p. 252), which is infra-red active and Raman inactive. There are four vibrations of this species in both C_8H_8 and C_8D_8 . We have located unequivocally three strong bands, presumably of this species, at 670, 800, and 3004 cm^{-1} in C_8H_8 and at 527, 720, and 2236 cm^{-1} in C_8D_8 . The location of a fourth vibration will be discussed when this work is published in detail. Here we wish only to make the point that prolonged exposure of the Raman spectrum has failed to reveal any sign of the 670 and 800 frequencies in C_8H_8 or of 527 and 720 in C_8D_8 , although these over-exposed spectra have produced a total of some forty Raman overtones in C_8H_8 .

In the symmetry D_{2d} , which has been suggested on the basis of x-ray and electron diffraction studies,⁷ all infra-red-active species are Raman-active also. The spectroscopic data accordingly appear to favor strongly the D_4 over the D_{2d} structure.

One of the striking features of the Raman spectra of both C_8H_8 and C_8D_8 is the collection of four strong lines of low frequency. These are presumably to be assigned to ring-puckering vibrations analogous to the non-planar benzene ring vibrations. There should be four such frequencies in both the D_4 and D_{2d} structures. In the D_{2d} structure, however, one of the four is forbidden in both Raman and infra-red spectra, whereas four are Raman-active in D_4 . While the assignment of these four lines to the puckering vibrations is not an absolute necessity, the large gap of more than 250 cm^{-1} between the highest of these and the next lowest Raman line in both C_8H_8 and C_8D_8 is convincing support for such assignment and for the D_4 structure.

The authors wish to acknowledge the generous support of the Office of Naval Research (Task Order 10 of Contract N 5ori-78).

¹ Lippincott and Lord, J. Am. Chem. Soc. **68**, 1868 (1946).

² Cf. Cope and Overberger, J. Am. Chem. Soc. **69**, 976 (1947).

³ Flett, Cave, Vago, and Thompson, Nature **159**, 739 (1947).

⁴ Bastiansen, Hassel, and Langseth, Nature **160**, 128 (1947).

* The D_4 structure, which has been called the "crown structure" by some, consists of a puckered eight-membered ring with alternate single and double bonds. The puckering occurs in such a way that a four-fold axis (C_4) is present, so that the ring has a saw-toothed appearance when viewed edgewise. Even-numbered carbon atoms lie in the same plane, which is parallel to the plane in which the odd-numbered carbon atoms lie. An analogous statement holds for the hydrogen atoms. By symmetry all carbon atoms are equivalent as are all hydrogen atoms. It should be noted that the D_4 structure implies optical isomerism.

⁶ R. C. Lord, Jr., Proceedings of the Colloquium on Molecular Structure, Paris, May 27, 1947 (to be published in J. de Chim. physique).

⁷ Lippincott and Lord, Symposium on Molecular Spectra, Ohio State University, June 1947.

⁸ Kaufman, Fankuchen, and Mark, Nature **161**, 165 (1947); J. Chem. Phys. **15**, 414 (1947). Personal communication from Professor V. Schomaker.

Hysteresis of the Contact Angle

S. J. GREGG

Department of Chemistry, University College, Exeter, England

March 12, 1948

THE angle of contact θ of a liquid against a solid is profoundly influenced by the presence of an adsorbed film on the unimmersed portion of the solid (and formed by spreading from the liquid, or by adsorption from the vapor

phase, or both). This is implicit in Harkins and Dahlstrom's treatment¹ of the subject in 1930, but was first explicitly and quantitatively discussed by Bangham and Razouk² in 1937; they arrived at the expression

$$F_L - F_V = \gamma_L \cos \theta, \quad (1)$$

where F_L and F_V are the diminutions in free energy when 1 cm^2 of the *clean* solid (i.e., free from film) is immersed in the liquid and exposed to the vapor, respectively; γ_L is the free surface energy of the liquid. In effect, almost all other workers had taken $F_L = \gamma_L \cos \theta$.

For a mobile film, Bangham³ has shown that F_V may be equated with π , the surface pressure of the film; consequently, Eq. (1) may be written

$$F_L - \pi = \gamma_L \cos \theta. \quad (2)$$

This form of the Bangham-Razouk relationship possesses the merit of expressing the dependence of θ on the adsorbed film in terms of a simple property of the latter, its surface pressure; and this is calculable, in principle^{3,4} and often in practice, from the adsorption isotherm of the vapor on the solid by means of the integrated Gibbs adsorption equation: $\pi = RT \int_0^p \Gamma dp$ (Γ moles = adsorption per unit area of the solid and p = pressure of the vapor). In particular it suggests an immediate connection between hysteresis of the contact angle and hysteresis in adsorption;⁴ in this latter phenomenon the pressure P (and with it the surface pressure π) is greater on the "adsorption-increasing" run than on the "adsorption-decreasing" one, for a given adsorption Γ . It should be noted that hysteresis can occur with non-porous adsorbents⁵ and is not confined to porous bodies, as is often supposed.

Now in measurements of the advancing contact angle, θ_a , the adsorbed film (surface pressure = π_a) is in the process of formation by spreading or by adsorption from the vapor phase; it corresponds to the "adsorption-increasing" run of a vapor adsorption experiment. But in measurements of the receding angle, θ_r , the film ($\pi = \pi_r$) adjacent to the line of contact has recently been covered with the bulk liquid, and it corresponds to the "adsorption-decreasing" run. If adsorption hysteresis occurs, $\pi_a > \pi_r$, consequently $\theta_a > \theta_r$, i.e., there is hysteresis of the contact angle.

To eliminate any difference between θ_a and θ_r it is necessary that $\pi_a = \pi_r$, and this requires (i) that adsorption hysteresis be eliminated, and (ii) that the pressure p over the film shall be the same during both measurements. To achieve (ii) is difficult in practice unless p be chosen as p_0 , the saturated vapor pressure. Attainment of (i) calls for a number of precautions, notably that ample time be allowed for attainment of adsorption equilibrium, and that impurities be absent. Both these points are implicitly, though not explicitly, taken into account in the procedure adopted by Harkins and Fowkes,⁶ whereby they have been able to eliminate hysteresis of the contact angle in a large number of cases.

Nevertheless, Harkins' assertion⁷ that the "advancing and receding angles obtained by nearly all investigators other than those in this laboratory is due to improper preparation of the surface and poor techniques in making the measurements," is, in view of the known characteristics

