

A Theoretical Calculation of the Parameters α and β Used in the Molecular Orbital Method

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TABLE I.

Vapor	Number of molecules in stable nucleus	Nucleus radius r in angstroms	σ^* σ_0	P/P_∞ calculated using σ	P/P_∞ calculated using σ_0	P/P_∞ measured
Water, 275.2°K	80.0	8.9	0.82	2.9	4.2	4.2 ± 0.1
Water, 261.0°K	72.0	8.0	0.80	3.2	5.0	5.0
Methanol, 270.0°K	32.0	7.9	0.80	1.5	1.8	3.0
Ethanol, 273.0°K	128.0	14.2	0.88	2.0	2.3	2.3
<i>n</i> -propanol, 270.0°K	115.0	15.0	0.88	2.6	3.2	3.0
Isopropyl alcohol, 265.0°K	119.0	15.2	0.88	2.4	2.9	2.8
<i>n</i> -butyl alcohol, 270.0°K	72.0	13.6	0.88	3.5	4.5	4.6
Nitromethane, 252.0°K	66.0	11.0	0.85	4.2	6.2	6.0
Ethyl acetate, 242.0°K	40.0	11.4	0.85	6.4	10.4	8.6 to 12.3**

* Ratio of surface tension predicted from Tolman's results to the surface tension measured in the bulk liquid phase.

** The higher value is assumed to be more nearly correct.

supersaturated vapor is strongly dependent on the surface tension. This is illustrated by Fig. 1 where calculated values of the ratio of critical supersaturation pressure to equilibrium vapor pressure of the bulk liquid phase, P/P_∞ , are plotted as a function of assumed values of surface tension, σ , for the case of condensing water vapor at 275.2°K. The surface tension values are assumed for the purpose of calculating P/P_∞ as a function of σ by means of the Becker and Döring⁵ treatment. It is seen that a value of surface tension very close to that measured for the bulk liquid phase is required if calculated and experimental values of P/P_∞ are to agree.

The present authors have computed the critical droplet size for a number of vapors by the Becker and Döring⁵ method, using the measured critical supersaturation ratio and the value for surface tension measured on the bulk liquid phase. Then, using Tolman's¹ theoretical results for decrease in surface tension with droplet radius, a value for surface tension at the critical droplet size was obtained. This new value of σ was used to calculate P/P_∞ for comparison with the experimental quantity. The results are summarized in Table I. It is seen that in most of the cases fair agreement is obtained between measured values of P/P_∞ and values calculated using the surface tension σ_0 as measured on the bulk liquid phase. On the other hand, values of P/P_∞ calculated

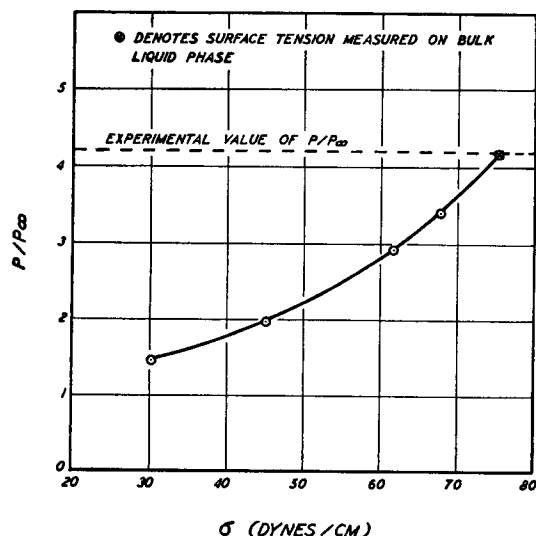


FIG. 1. Calculated values of critical supersaturation pressure ratio versus assumed values of surface tension for the case of condensing water vapor at 275.2°K.

using the surface tension σ , as predicted from Tolman's results, are in poor agreement with the data. The inconsistency between the work on nucleation and the current theoretical studies on surface tension of droplets is evident. It may be that some revision of the present theoretical approach is in order.

It is interesting to note that in the two anomalous cases, methanol and ethyl acetate, the number of molecules per stable nucleus is considerably smaller than in the other cases. Further, these anomalies could be resolved by employing a value for surface tension somewhat higher than that measured on the bulk liquid phase.

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A Theoretical Calculation of the Parameters α and β Used in the Molecular Orbital Method

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THE molecular orbital method in the usual L.C.A.O. approximation enables us to express the energy of the r -electrons in two parameters: the Coulomb integral

$$\alpha \equiv \int \varphi_1 H \varphi_1 d\tau$$

and the exchange integral

$$\beta_{12}' \equiv \int \varphi_1 H \varphi_2 d\tau - S_{12} \alpha', \quad S_{12} = \int \varphi_1 \varphi_2 d\tau.$$

φ_1 and φ_2 are the P_z -orbitals of adjacent C atoms.

Hitherto β_{12}' (and α) were empirical parameters. There is, however, a large discrepancy between the values calculated for β_{12}' from resonance energies and from electronic-transition processes. We have therefore tried to calculate α and β_{12}' theoretically to get some insight into the nature of this discrepancy.

For benzene we put for the Hamilton operator:

$$H = -\frac{\hbar^2}{2m} \nabla^2 + \sum_k H_k + V_r.$$

For the part

$$-\frac{\hbar^2}{2m} \nabla^2 + \sum_k H_k,$$

we refer to Goeppert-Mayer and Sklar;² V_r is the potential energy of one r -electron (ν) in the field of the other five r -electrons (μ) which are supposed to be distributed among the six P_z -orbitals of the C atoms. The electron is also supposed to be equally distributed, which is numerically equivalent to a localization on one carbon atom. This gives

$$V_r = \frac{5}{6} e^2 \sum_{\mu} \frac{1}{r_{\nu\mu}} \quad \text{and} \quad \int \varphi_1(\nu) V_r \varphi_2(\nu) d\tau = V_r \cdot S_{12}.$$

For this calculation of α and β_{12}' we further need integrals as

$$\int \varphi_i(\nu) \varphi_j(\nu) H_k(\nu) d\tau$$

and

$$\int \varphi_i(\nu) \varphi_j(\nu) \frac{e^2}{r_{\nu\mu}} \varphi_k^2(\nu) d\tau.$$

They are reduced to known integrals by substituting

$$S_{ij} \int \varphi_m^2(\nu) \dots \quad \text{for} \quad \int \varphi_i(\nu) \varphi_j(\nu) \dots$$

$\varphi_m(\nu)$ is a virtual P_z function located midway between the original i and j functions.^{3,4}

With this approximation and using the values of Parr and Crawford,⁶ we obtain as a value for $\alpha = 4.20$ ev and for $\beta_{12}' = 2.42$ ev.

The only experimental data we have used are the effective nuclear charge for a C atom $Z = 3.18^6$ and the C—C distance 1.39 Å in benzene.⁷ In the calculation of α we used for $W2p$, the energy of a $2p$ -electron in the unexcited carbon atom, instead of the experimental ionization potential of -11.24 ev, a value of -10.82 ev calculated theoretically with the effective nuclear charge of 3.18; β_{12}' is independent of $W2p$.

From these and analogous calculations we conclude:

(1) β_{12}' is with good approximation, independent of the potential field of the r -electrons (the term $V_r \cdot S_{12}$ cancels).

(2) For a definite C—C bond β_{12}' is proportional to S_{12} . This was already known from empirical data.⁸

(3) β_{12}' is strongly dependent on the environment of the bond in the molecule (e.g., for naphthalene $\beta_{12}' = -1.93$ ev and $\beta_{910}' = -2.26$ ev).

(4) The quantitative results of the molecular orbital method are improved if we consider as a second approximation also the exchange and lack of orthogonality integrals between non-adjacent atoms. Following our method with a , for this correction reasonable approximation, we obtain for benzene

$$\beta_{13}' = \frac{S_{13}}{S_{12}} \beta_{12}'; \quad \beta_{14}' = \frac{S_{14}}{S_{12}} \beta_{12}',$$

$$(S_{12} = 0.26; \quad S_{13} = 0.04; \quad S_{14} = 0.02).$$

In this second approximation we compute for the resonance energy (R.E.) of benzene, $0.76\beta_{12}'$ (zero-approximation R.E. $2\beta_{12}$, first-approximation R.E. $1.06\beta_{12}'$). With the experimental value for the R.E. (39 kcal.⁹), we compute for $\beta_{12}' = -2.23$ ev. The calculated R.E. with our theoretical value for β_{12}' is 42 kcal.

For the energy difference ΔE between the ground state and the first excited state we evaluate in second approximation $2.14\beta_{12}'$, which gives 2410 Å with our theoretical value of -2.42 ev as compared with the experimental value of 2550 Å.

For the quantity $\Delta E/\text{R.E.}$, which is independent of β_{12}' , we obtain experimentally, 2.86; calculated, 2.82. Thus the well-known discrepancy between the spectroscopical and the thermochemical value is eliminated in our second approximation.

For ethene we find with the same method ($S_{12} = 0.287$) $\beta_{12}' = -2.95$ ev, in agreement with the experimental spectroscopical value $\beta_{12}' = -3.0$ ev¹⁰ (They are, however, not strictly comparable.) The theoretical value for α is 8.0 ev.

For naphthalene, we compute in second approximation, R.E. is $1.22\beta_{12}'$; for anthracene, $1.61\beta_{12}'$. We have taken into account β_{13}' , S_{13} etc., but β_{12}' , contrary to our third conclusion, was not varied with the environment in the molecule.

For the ultraviolet spectrum, we obtain with the calculated values of $\Delta E/\text{R.E.}$ with the experimental values of R.E.⁹

	0° approx.	1° approx.	2° approx.	obs.
benzene	7143 Å	3630 Å	2600 Å	2550 Å
naphthalene	11,430 Å	5461 Å	3524 Å	2750 Å
anthracene	17,212 Å	8236 Å	5037 Å	3800 Å

A further improvement might be obtained from a variation of β_{12}' .

If this method leads to reasonable results it will, in the future, be possible to calculate β_{12}' for an arbitrary bond in a molecule by a simple addition if we know the internuclear distances of that molecule, and to expand this method, e.g., to heterocyclic molecules.

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Infra-Red Absorption Spectra at Low Temperatures*

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October 17, 1949

VERY and Ellis¹ and Avery and Morrison² have shown that for certain hydrocarbons many of the infra-red absorption bands are very considerably narrowed when the temperature is reduced. The above authors give conclusive evidence that Bjerrum's formula is valid even in the liquid and solid state for the particular cases which they have investigated.

Walsh and Willis³ have recently questioned the phenomenon of temperature narrowing of infra-red bands in a single phase (liquid or solid) attributing the effect to change in phase. Study of the papers of Avery and Ellis¹ and Avery and Morrison² does not support the contention of Walsh and Willis.³ Comparison of the low temperature spectrum of Avery and Ellis with A.P.I. Spectrogram No. 245 for liquid 2, 2 dimethylbutane is completely unjustified since comparison of line breadth is impossible due to widely different instrumental factors entering into the two above mentioned spectra.

We have recently investigated⁴ the infra-red absorption spectra of a number of hydrocarbons at different temperatures through much of the liquid and solid range. Our investigation was concerned chiefly with the occurrence of rotational isomers and not in a discussion of band breadth. However, in the case of all the spectra which we have investigated, one of the most prominent features was the distinct sharpening of the bands as the temperature was reduced.

Reduction of band width with decreasing temperature in the liquid phase was immediately apparent since in many cases double bands were merely resolved as shoulders at room temperature while at low temperature clean resolution of these doublets was achieved. In addition, the narrowing of the bands was considerably greater than mere appearance of the curves would indicate. (Since the cell thickness is sensibly constant and the density of the liquid increases with decrease of temperature, more molecules are in the absorbing beam at low temperature than at high temperatures. The effect of increased absorbing path would be to decrease the transmission and make the bands appear wider from this cause alone. For quantitative measurements it is of course necessary to compare band widths at the same percentage transmission as Avery and Ellis¹ have done.)

The curves shown in our paper,⁴ Figs. 1 to 5, for *n*-pentane, *n*-hexane, *n*-heptane, 2 methylbutane and 2:3 dimethylbutane are reproduced on too small a scale to show clearly the large effect of temperature on narrowing of these absorption bands.

We wish to point out further that the narrowing of Raman lines at low temperatures in liquids can be easily and unequivocally observed for a number of the hydrocarbons. Microphotometer curves of the Raman spectrum of liquid *n*-butane at 300°K and 147°K obtained by one of us⁵ clearly show the effect of temperature in narrowing these bands.

We are not aware of any incontrovertible evidence in the literature where distinct rotational fine structure has been found in the infra-red absorption spectrum of a liquid. The situation with respect to solids is similar.⁶ In spite of the lack of direct spectroscopic evidence for the existence of discrete rotational and rotational vibrational states in a liquid, the breadth and temperature behavior of many infra-red bands yields indirect spectroscopic evidence for rotation. It seems plausible that discrete rotational structure is not to be expected in a liquid since the pressure broadening of the lines would be extremely large.

The observation of Avery and his co-workers^{1,2} that quantitatively certain infra-red bands in liquids and solids follow Bjerrum's formula with regard to their breadth as a function of temperature can only be considered to be fortuitous in its strict quantitative aspect. It is certain that at the present time our