The Effect of Hydrogen Bonding on the Hindered Rotation of the Hydroxyl Group in Alcohols

A. V. Stuart and G. B. B. M. Sutherland

Physics Department, University of Michigan, Ann Arbor, Michigan

(Received September 26, 1953)

It has been shown by Dennison and his co-workers that in gaseous methyl alcohol, the OH group executes a hindered rotation (or libration) about the CO axis and that the height of the potential barrier hindered free rotation is about 380 cm⁻¹ (1.1 kcal/mole). If one regards this motion as a liberation, then the value of the corresponding normal frequency is approximately 225 cm⁻¹ (800 kcal/mole). It seems most probable that this 670 cm⁻¹ band has a broad diffuse shape, very similar in extent to the hindered rotation of the gaseous state. When methyl alcohol is in the liquid state, where it is known that hydrogen bonding exists between the OH groups of neighboring molecules, it is to be expected that the hindered rotation will be completely inhibited and this motion will now more closely resemble the usual type of fundamental vibration. One would also anticipate that the value of the fundamental frequency would be very much greater than 225 cm⁻¹, since the restoring forces will have increased considerably.

Investigation of the infrared spectra of a series of alcohols reveals a broad absorption band stretching about 800 cm⁻¹, reaching a maximum near 670 cm⁻¹ and extending to beyond 500 cm⁻¹. This band is found to shift to lower frequencies, the maximum now being found close to 475 cm⁻¹ in the case of methyl alcohol (Fig. 1).

The effect of hydrogen bonding on theOH stretching frequency near 3250 cm⁻¹ has not yet been possible to determine where this band moves to on dilution, but studies are being continued in the low frequency region. It is interesting and significant that this 670 cm⁻¹ band has a broad diffuse shape, very similar in extent to the well-known hydrogen-bonded OH stretching frequency near 3250 cm⁻¹.

The effect of hydrogen bonding on the in-plane OH deformation vibration has also been studied. The results here are not so straightforward and will be presented in a subsequent publication.

Note on the Free Volume Equation of State for Hard Spheres

Louis H. Lund

Missouri School of Mines and Metallurgy, Rolla, Missouri

(Received October 14, 1952)

In a recent Letter to the Editor, Wood has given an exact solution for a system composed of rigid spheres to the following integral equation derived by Kirkwood in his critique of the free volume theory of the liquid state:

\[ \psi(r) = \exp[-\beta_0 \psi(r)], \]

\[ \psi(r) = \sum_{n=1}^{\infty} p/(n^3) \exp[-\beta_0 \psi(r^2/n^3)], \]

where \( \psi(r) \) is the configurational distribution function for a molecule in its cell, and the terms in \( \beta_0 \), the energy with all molecules at their cell centers, are omitted since it is here zero.

Wood has considered a face-centered cubic lattice and chosen as the cell the dodecahedron \( \Delta \) of Buchler et al. The nearest neighbor distance \( \sigma \) and volume per molecule \( v \) are related by \( \sigma^3 = \sqrt{2}/(\pi) \), and the minimum volume per molecule is \( \sigma^3 = \pi^2/\sqrt{2} \), where \( \sigma \) denotes the diameter of the sphere. His solution for the system of Eq. (1) is

\[ \psi(r) = \begin{cases} 0 & \text{if } r \text{ is in } \Delta', \\ \infty & \text{if } r \text{ not in } \Delta', \end{cases} \]

where \( \Delta' \) is the free volume (\( \sigma^3 - \pi^2/\sqrt{2} \)) per molecule and is a dodeca-
1978 LETTERS TO THE EDITOR

Effect of Opposed Disubstitution on Intensities of Even-Even Electronic Transitions

HARREN MCCONNELL
Shell Development Company, Emeryville, California
(Received October 7, 1952)

The theory of spectroscopic moments devised by Platt has been used by him for the experimental determination of the even-odd \((g-u)\) character of electronic wave functions of excited singlet states of centrally symmetric molecules.\(^1\) One feature of this theory is the prediction that the absorption intensities of "forbidden" even-even \((g-g)\) electronic transitions in centrally symmetric molecules are not affected by opposed dissubstitutions, such as, for example, 2,6-dimethyl substitution in naphthalene. The purpose of this letter is to point out that (a) the above prediction is strictly valid only to within the limits of the Born-Oppenheimer approximation (neglect of perturbations of electronic wave functions by nuclear vibrations) and (b) by opposed dissubstitution. More detailed expressions relating \(E\), the molecular weight of the fractions, which represented

\[\psi(r) = \begin{cases} \frac{1}{\eta} & \text{if } r \text{ inside } \eta \\ 0 & \text{if } r \text{ outside } \eta \end{cases} \]

where \(\psi\) is the mean volume per molecule and \(r_h\) the diameter of the molecule. It is reasonable that Eq. (3) will hold approximately for other kinds of molecular packing with the "\(g\)" replaced by a different constant.

Thus, one might conclude that the solution (2) would hold for many molecular packings of rigid spheres where it is feasible to define a free volume and where one may have

\[\psi(r) = \begin{cases} \frac{1}{\eta} & \text{if } r \text{ inside } \eta \\ 0 & \text{if } r \text{ outside } \eta \end{cases} \]

\[\psi(r) = \begin{cases} \frac{1}{\eta} & \text{if } r \text{ inside } \eta \\ 0 & \text{if } r \text{ outside } \eta \end{cases} \]

\[\psi(r) = \begin{cases} \frac{1}{\eta} & \text{if } r \text{ inside } \eta \\ 0 & \text{if } r \text{ outside } \eta \end{cases} \]


Molecular Weight of Potato Amylopectin as Determined by Light Scattering*

L. P. WITNAUER AND F. R. SENTt
Eastern Regional Research Laboratory, United States Department of Agriculture, Philadelphia, Pennsylvania

AND

M. D. STERN
Department of Chemistry, Temple University, Philadelphia, Pennsylvania
(Received September 22, 1952)

Molecular weights reported for amylopectin range from less than 200,000, as determined by end-group methods,\(^4\) to 230 million by the light-scattering method.\(^5\) We report here the results of light scattering measurements on potato amylopectin in water solutions and on acetylated amylopectin in several organic solvents.

Potato starch (potassium form\(^3\)) was dispersed with vigorous stirring in water at 90°. The amylose was precipitated with pentanol. Amylopectin recovery was 90 percent. Scattering was measured\(^4\) at angles with 135 to 22°. Reliable extrapolation to 0° could be made, proving the absence of large particles of dirt or microgel in the solutions. Concentrations ranged from 10^{-4} to 10^{-4} g/ml. Solutions were centrifuged at 40,000 rpm and then passed through ultrafine sintered glass filters. Three molecular weight determinations averaged 36 million±10 percent. Values at 546 and 436 mu for a series of solutions of varying concentration agreed to ±5 percent. The 90° scattering was unaffected by temperature in the range 25 to 75°. An amylopectin solution 0.5 N in sodium hydroxide was heated two hours at 90°. It showed less than 10 percent decrease in turbidity if oxygen was absent. An amylopectin solution was heated one hour at 120° in a sealed tube free from oxygen without appreciable change in turbidity. These results indicate that if the light-scattering particles are aggregates, they are not broken up by temperature or alkali. In acetone solution the acetate of this amylopectin had a molecular weight (corrected for 40 percent acetyl content) of 38 million.

Nine fractions were obtained by adding ethanol to a water solution of this amylopectin containing 0.1 percent sodium chloride. The molecular weight of the fractions, which represented 93 percent of the amylopectin, ranged from 25 to 52 million. One third had a molecular weight 48 to 52 million. The weight average for the nine fractions was 36 million. The particle diameter ranged from 4300A to 2200A.

Another potato starch (calcium form\(^2\)) was dispersed by autoclaving at pH 6.0, and the amylose was removed by complexing with nitrobenzene and adsorbing on cotton. The molecular weight allowed \(g\rightarrow u\) transition; \(e\) and \(e_0\) in Eq. (1) then apply the intensities of the \(0, 1\) band of the \(g\rightarrow g\) transition.

Equation (1) predicts that on opposed dissubstitution the intensity of a \(g\rightarrow g\) transition will (a) decrease if \(\Delta\omega\) is positive, (b) increase if \(\Delta\omega\) is negative, or (c) remain practically unaltered if \(\Delta\omega\approx 0\). Sufficient experimental data are not available for an adequate test of these predictions. It is noteworthy, however, that the effect of opposed dimethyl substitutions in naphthalene on the intensity of the \(^1A\rightarrow ^1L_0\) transition cannot be accounted for by Eq. (1); this result is consistent with the previously assigned \(u\) symmetry of this \(^1L_0\) excited state.\(^3,4\) Also, 9, 10-dimethyl substitution in anthracene decreases the intensity of the \(^1A\rightarrow ^1L_0\) transition to an extent compatible with Eq. (1); this result is consistent with the previously assigned \(u\) symmetry of the \(^1L_0\) state of anthracene at 45,000 cm^{-1} and the assumption that the \(^1L_0\) state steals intensity from the nearby strongly allowed \(^2B_2\) (\(u\) state at 39,500 cm^{-1}.\(^3,4\) Further discussion of these predictions will be deferred until more data are available.

\[\psi(r) = \begin{cases} \frac{1}{\eta} & \text{if } r \text{ inside } \eta \\ 0 & \text{if } r \text{ outside } \eta \end{cases} \]

\[\psi(r) = \begin{cases} \frac{1}{\eta} & \text{if } r \text{ inside } \eta \\ 0 & \text{if } r \text{ outside } \eta \end{cases} \]

\[\psi(r) = \begin{cases} \frac{1}{\eta} & \text{if } r \text{ inside } \eta \\ 0 & \text{if } r \text{ outside } \eta \end{cases} \]

\[\psi(r) = \begin{cases} \frac{1}{\eta} & \text{if } r \text{ inside } \eta \\ 0 & \text{if } r \text{ outside } \eta \end{cases} \]