The Use of Punched Cards in Molecular Structure Determinations. IV. Approximations to the Temperature Factor

MORTON E. JONES AND VERNEER SCHOMAKER
Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California

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T HE punched-card method 1 which we use for the functions $\Sigma G_i \sin \gamma$ that have to be evaluated in the course of diffraction studies of the molecular structures of randomly oriented molecules requires that the coefficients $G_i$ be constants, independent of $\gamma$. However, in the expression for the intensity of diffraction, in our case,

$$I(\gamma) = \Sigma G_i (\sum Z_i Z_j \exp(-i\gamma \theta_{ij}) \sin \theta_{ij}),$$

(1)

these coefficients often include the so-called temperature factor $\exp(-\theta^2)$, which takes into account the vibrational variation or an effective vibrational variation of the interatomic distance about its mean value $r_i$. The quantity $\theta_{ij}$ is $\langle \delta r_{ij} \rangle$ or, in order to make negligible the variation of some of the coefficients, an effective value $\langle \delta r_{ij} \rangle = \alpha_{ij}$.

On the Polarization of Rayleigh Scattering as an Aid to Determine Molecular Configuration in Liquids

D. H. RANK
Physics Department, Pennsylvania State College, State College, Pennsylvania

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It is well known that from the analysis of the vibration spectra (Raman and infrared absorption) much information can be obtained concerning the arrangement of the atoms in the molecule. In most cases, when these vibrational analyses are coupled with calculations of the entropy, satisfactory and unique solutions of the structure problem can be obtained. It is generally accepted that the determination of the state of polarization of the Raman lines is necessary for any rigorous vibrational analysis.

The purpose of this note is to point out the utility of a much obtainable phenomenon, namely, the polarization of the Rayleigh scattering as an aid to solving the molecular structure problem.

It is well known that certain molecules in the liquid phase form associated complexes. In many cases this association is caused by hydrogen bonding. The phenomenon of association is accompanied, in general, by the observation of a boiling point very much higher than would normally be expected for liquids of the molecular weight in question.

Bhagavantam 2 has assembled a great deal of the data in the literature on the Rayleigh scattering of liquids. Inspection of Bhagavantam’s table brings to light the following empirical regularities which qualitatively would be expected theoretically.

(1) Nonassociated liquids in which the molecular form approaches spherical symmetry show a high degree of polarization of Rayleigh scattering.

(2) Liquids which definitely are associated (the associated complex must certainly approach spherical symmetry) show a high degree of polarization of Rayleigh scattering.

(3) Nonassociated liquids, the molecular form of which is linear or approximately planar, produce highly depolarized Rayleigh scattering.

It should be noted further that, in general, the interaction of the light wave with the scattering entity to a large extent ignores the very light hydrogen atoms, e.g., liquid CCl4 yields a $p=0.06$, while the chloroform molecule CHCl3, which is also of tetrahedral structure, gives a $p=0.24$.

Recently, in this laboratory, the vibrational spectra of methyl hydrazine has been under investigation by Axford, Russell, and Janz. Considering only the heavy atoms, this molecule can be considered to be approximately linear. From various properties of liquid methyl hydrazine it might be supposed that association in the liquid state is present. The author suggested, from the above reasoning, that the Rayleigh scattering would be strongly polarized if association, which is presumably due to hydrogen bonding, was present. The experimental results obtained by Axford, Russell, and Janz, which will be published elsewhere, completely confirm the above contention.

In the case of liquids where association is unlikely, the state of polarization of Rayleigh scattering can be useful in deciding between different geometrical forms when the usual methods do not give a unique answer. This phenomenon might be particularly useful in the case of some of the boranes which exist as liquids, since the approximately planar, pyramidal, or “basket” structures should yield very different values for the polarization of the Rayleigh scattering.

On a punched-card approach to the determination of the state of polarization of the Raman scattering

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Previously, this variation has ordinarily been approximated by constructing the corresponding distribution of the form \( \exp[-(r-r_i)^2/(4a_i)^2] \) and approximating the required integration over the distribution by a sum of equally spaced sinc terms having constant coefficients taken from this curve with suitable normalization. But in the absence of any readily applicable analysis of the situation, the desire for accuracy has usually led to the use of more terms than are actually necessary. Therefore, it was decided to work out to known accuracy several economized representations of this type for general application.

In order to simplify the work, the equal spacing of terms was retained. Then, in terms of appropriate reduced units, the amplitudes and spacings of terms were adjusted so that the approximation differs from the desired value by no more than a fixed maximum amount for \( s \leq s_{\text{max}} \), with \( s_{\text{max}} \) as large as possible. This has been done for 2, 3, 4, and 5 term representations and for maximum errors of \( \pm 2\% \), \( \pm 5\% \), and \( \pm 10\% \) of the ideal initial amplitude, and the results have been arranged in a table. For each of the twelve cases, this table gives directly the \( a \) values that can be achieved with spacings of integral hundredths of an \( A \) (somewhat unhappily, continuous variation of \( a \) is not afforded), the amplitudes of the terms of the representation, and the maximum values of \( a \) for which it is accurate, respectively, to \( s = 20 \) and \( s = 30 \); a simple interpolation gives the maximum \( a \) values for other values of \( s_{\text{max}} \).

Use of the table has simplified the punched-card summation of Eq. (1) by reducing by 50 percent, on the average, the number of terms used to represent temperature factors. It has also reduced to almost nothing the considerable preparatory work which was previously involved in setting up the calculations.

Copies of the table and notes on its use have been prepared and are available upon request.*

* Contribution No. 1536.


‡ R. Spurr and V. Schomaker, J. Am. Chem. Soc. 64, 2693 (1942).

Recent Evidence and Conclusions

The Vibration-Rotation Bands of OH in the Photographic Infrared

George A. Hornbeck and Robert C. Herman

Aplied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland

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Recently, Meinel has obtained in emission some of the vibration-rotation bands of the OH radical in the spectrum of the night sky. These bands lie in the region \( \sim 6800 - \sim 9000 \)A and include the vibrational transitions \( (7-2), (8-3), (9-4), (5-1), (6-2), \) and \( (7-3) \). Benedict, Pyley, and Humphreys have found in emission from the outer cones of the oxy-acetylene and oxy-hydrogen flames numerous lines of the OH vibration-rotation bands \( (2-0), (3-1), \) and \( (4-2) \). We have recently also obtained the \( (4-0), (5-1), \) and \( (6-2) \) bands from the outer cone of the oxy-acetylene flame with a Baird 2-meter grating spectrograph at 8 A/mm using a 25A slit and I-N plates hypersensitized according to the procedure described by Meinel.† Spectrograms of good contrast and density were obtained with exposure times of \( \sim 1 \) hour under the conditions stated. In Fig. 1 is shown a densitometer tracing of a portion of the \( (4-0) \) and \( (5-1) \) bands. In the \( P \)-branch the spin doublets are well resolved as are the \( A \)-doublets for high \( K \) values. The weaker background lines in Fig. 1 are the vibration-rotation lines of the \( \text{H}_2\text{O} \) molecule. At longer wavelengths, the \( \text{H}_2\text{O} \) lines become more intense. However, the \( P \)-branch lines in the \( (4-0) \) band, for example, are readily seen at least as far as \( P(15) \). The \( OH \) bands in this spectral region can also be obtained from the outer cones of methane, ethylene, and hydrogen burning with oxygen. However, in these cases the \( OH \) lines are badly overlapped by the intense \( \text{H}_2\text{O} \) spectrum. Best results have been achieved with the oxy-acetylene flame obtained from an ordinary torch burning at stoichiometric proportions, when viewing the region of the outer cone closest to the tip of the reaction zone.

As yet, we have found no evidence in flame spectra of the vibration-rotation bands of \( OH \) reported by Meinel which originate from the higher vibration levels. Since the outer cone temperature of the oxy-acetylene flame is \( \sim 3000^\circ \)K, this would lend support to Meinel's suggestion of resonance excitation of \( OH \) radicals in the night sky. As to be expected at the higher temperatures in the oxy-acetylene flame, the \( OH \) lines extend to higher \( K \) values and the \( Q \)-branch is relatively low as compared with Meinel's case.

Since the \( OH \) vibration-rotation bands discussed here can be obtained with high dispersion and resolution, an analysis of the bands and a determination of some of the molecular constants is in progress. We hope to report a complete account of this work in the near future.

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Comment on “Gas Bubbles in Solutions”

Frank C. Roessler

Physikalisches Institut, Technische Hochschule Graz, Graz, Austria

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In a recent issue of this Journal, Epstein and Plesset have derived formulas for growth and dissolving of gas bubbles in a liquid phase. Their treatment refers to a bubble at rest and is valid if transport of the dissolved gas takes place by diffusion only.

It seems interesting to consider the opposite limiting case, in which the mechanical motions in the system more than match the diffusion; for many applications (e.g., cavitation bubbles in a strongly turbulent medium or large bubbles of great buoyancy), this case is realized.

As Epstein and Plesset, I shall treat the growth of a single bubble in an infinite volume of fluid. Let us first investigate the influence of a strong transatory motion due to buoyancy. I shall use the notation of Epstein and Plesset except for letters, the meaning of which is especially explained. For laminar flow the velocity of the bubble is proportional to the square of the radius (reference 1, l.c.)

\[ v = KR. \]

Diffusion now comes into play for transport of the gas through the boundary layer only. Outside the boundary layer adhering to the bubble the motion of the fluid outweighs it, and we take