Polarization of Raman Lines

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$$\frac{I_a}{I_0} = \left[(I_t{}^0/I_0) - (I_t/I_0) \right]$$

$$\times \frac{(I_t{}^0/I_0)^{\frac{1}{2}}}{(I_t{}^0/I_0) - f\left[1 + \frac{(I_t{}^0/I_0)}{(1-f)^2} \right](I_t/I_0)}. \quad (6)$$

It might be pointed out that a method sometimes used in spectrophotometric work for calculating the absorbed intensity—namely, taking the simple difference between transmitted intensity with the cell empty and filled with gas—can introduce a large error. The factor multiplying $(I_t{}^0/I_0) - (I_t/I_0)$ in Eq. (6), in a typical case (i.e., $I_t{}^0/I_0 = 0.85$, $f = 0.04$), varies from 1.08 for complete absorption by the gas to 1.17 at zero absorption.

We have referred throughout to absorption by a gas. It is clear that a very similar treatment can be given for a liquid solution.

Polarization of Raman Lines

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IN earlier studies of the polarization of Raman lines[1-3] we suggested certain arrangements of polaroid films in front of the slit of the spectrograph. At that time we also employed grids to obtain nearly parallel incident light, in order to measure the depolarization factor. In many experiments on the Raman effect it is, however, sufficient to know which of the Raman lines are depolarized without necessarily determining the depolarization factor numerically. We have therefore evolved another experimental set-up as shown in Fig. 1.

Two Raman tubes (Ra) are supported by two brass tubes (B). These brass tubes carry on the other end two condensing lenses (Le). The bottom of the top Raman tube and the top of the bottom Raman tube are both painted with a strip of optical black $(\frac{1}{8}''$ wide) and parallel to the Raman tube axis. This black strip avoids scattered radiation from each Raman tube interferring with the other. The scattered radiation coming through the windows of the Raman tubes is focused by means of the two lenses (Le) (focal length 12.2 cm) onto the slit of the spectrograph. An appropriate diaphragm is placed in front of the slit and the two scattered beams are separated by a blackened metal foil. The distance between the Raman windows and the lenses is 15.3 cm and the distance from the lenses to the double slit is 17.9 cm.[4] The brass tubes (B) are adjusted by six screws each, until the two scattered light beams from the Raman tubes have the same intensity and shape of image when viewed in the spectrograph. One of the Raman tubes is surrounded by a film of polaroid in which the electric vector lies along the axis of the Raman tube, whereas the second Raman tube is wrapped in a piece of polaroid with its electric vector at right angles to the axis of the Raman tube. We used twelve A. H. 2 General Electric Company mercury vapor lamps arranged horizontally in circular fashion, surrounded by a silvered cylindrical metal reflector. This arrangement is somewhat similar to one described by Edsall and Wilson.[5] Between the Raman tubes and the mercury lamps there is located a water jacket which keeps the heat generated by the lamps from reaching the substance under investigation. The mercury lamps are kept at constant temperature by using a bi-metallic temperature control. Its mercury switch operates the motor of a blower which draws air past the lamps, cooling them. This control is intermittent, but works very satisfactorily. Another blower draws air through the inner region of the water jacket, containing the Raman tubes. By adjusting the speed of this motor, the temperature of the inner region is kept remarkably constant.

We obtain the spectrum of carbon tetrachloride with polaroid films as shown in Fig. 2. With the above-mentioned light sources, the photograph could be taken in four hours' exposure. It is not necessary to use filters. The photographic plates employed were Eastman Kodak 103a-0. By surrounding the two Raman tubes with an appropriate system of metal grids, it should be possible to make the incident light parallel. A numerical measure of the depolarization factor could then be obtained.

An advantage of the new arrangement lies in the fact that current fluctuations affect both Raman tubes in the same way. The qualitative results obtained are sufficient to indicate the depolarized lines.
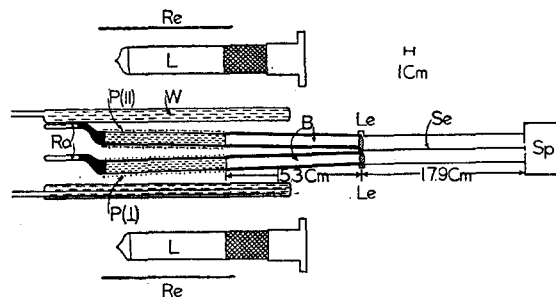

FIG. 1. Raman apparatus. Re = reflector, L = lamps, W = water jacket, Ra = Raman tubes, $P(\|)$, $P(\perp)$ = polaroid films, B = brass tubes, Le = condensing lenses, Se = separating blackened metal sheet, Sp = spectrograph.
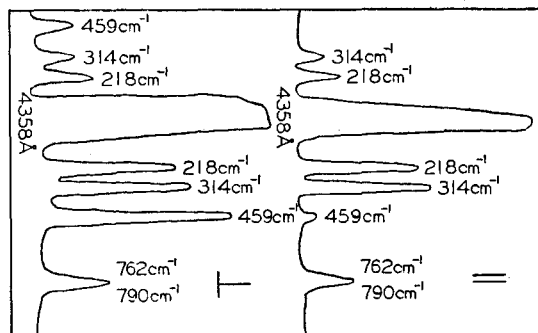

FIG. 2. Microphotograph of CCl_4 spectrum.

We wish to thank Professor B. L. Crawford of the University of Minnesota for the microphotograph (Fig. 2), and the China Institute in America for financial support to one of us (J. Y. T.).

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[3] Geo. Glockler, J. Haskin, and C. P. Patterson, J. Chem. Phys. **12**, 349 (1944).
[4] J. R. Nielsen, J. Opt. Soc. Am. **20**, 701 (1930).
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Note on a Proposed Interpretation of the Zeta-Potential

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January 3, 1947

THE graph of zeta-potential *vs.* concentration in a recent article by this writer[1] should have had the ordinate marked *minus zeta-potential* rather than *zeta-potential* as was shown. It is hoped that this error did not lead to confusion. Examination of the original data would have shown that the zeta-potentials of potassium chloride and barium chloride are negative.

Attention also should be called to another aspect of the new definition of the zeta-potential. Calculations already made by Jones and Wood[2] and Wood and Robinson[3] have shown that Langmuir's theory of the *Jones-Ray Effect* was strikingly substantiated. These calculations were based on the conventional Helmholtz-Perrin values of the ζ-potential. When these corrected surface tensions are recalculated on the basis of the newly defined zeta-potential, no difference in the previous results is obtained (for potassium chloride and barium chloride). The curves given by Jones and Frizzell[4] and Wood and Robinson[3] show that the wetting film thicknesses approach some definite value as the potential increases. The experimental values of the zeta-potential determined in the conventional manner are sufficiently large to be on the part of the curve where further increases in the potential have little or no effect on the thickness of the wetting film. Consequently, the newly defined zeta-potential leaves the corrected values of the surface tension just as they were found from the Helmholtz-Perrin zeta-potentials.

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[3] L. A. Wood and L. B. Robinson, J. Chem. Phys. **14**, 258 (1946).
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On the Equation of State for Gases at Extremely High Pressure*

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December 26, 1946

IN an article bearing the above title, Caldirola[1] has employed the hydrodynamic theory of stationary detonation waves, with experimental values of the detonation velocity, to determine an equation of state valid for the high pressures and temperatures characteristic of the detonation process. The treatment is based upon the Rankine,[2] Hugoniot[3] equations for the continuity of mass, momentum, and energy across the detonation front and the Chapman[4]-Jouget[5] condition for the stable detonation state. The specific-energy increment accompanying the detonation reaction is computed by the thermodynamic relation,

$$E = \bar{C}(T - T_0) - q, \qquad (1)$$

where $\bar{C}$ is the mean specific heat of the detonation products and q the specific heat of reaction at constant volume and at temperature T_0. The equation of state is assumed to be of the form,

$$pv = r(v)T. \qquad (2)$$

We note that Caldirola's calculated values of the detonation temperature increase with increasing density of the explosive.

The writer does not feel that this equation of state is of sufficiently general form for application to the products of detonation of solid explosives, since it implies that the gaseous products are thermodynamically ideal,

$$(\partial E / \partial v)_T = 0.$$

Hirschfelder and his associates[6-7] have pointed out that the internal energy of a gas is a linear function of its density to moderate pressures,

$$E = E_0(T) - \frac{RT^2}{V} \frac{dB(T)}{dT}, \qquad (3)$$

where $B(T)$ is the second virial coefficient, and tables have been provided[7] that permit evaluation of the energy of gas imperfection for substances to which the Lennard-Jones intermolecular potential-energy function applies. The contribution of the second virial coefficient to the energy of gas imperfection is negative at low temperatures and positive for temperatures greater than that for which Em/kT is equal to about 0.04 (Em is the maximum energy of attraction between a pair of molecules). An estimate, based on Eq. (3) and the molecular constants listed by Hirschfelder,[6] leads to a positive value of about 2 kcal./mole for the energy of gas imperfection of CO at 4500°K and density of 1.5. This figure is not negligible in comparison with the temperature-dependent part of the internal energy at zero density and the same temperature, 29 kcal./mole.[8] At the same temperature and density, the second virial coefficient contributes to the internal energies of H_2 and CO_2 of about $+1.2$ kcal./mole and -0.3 kcal./mole, respectively. At high density, terms in higher powers of the density would become significant through the contributions of the third and higher virial coefficients, and one would expect the internal energy to increase exponentially with the density.[6]

From these considerations, it would appear that Eqs. (1) and (2) should be replaced by

$$E = \bar{C}(T - T_0) - q + \int_\infty^v \left[T \left(\frac{\partial p}{\partial T} \right)_V - p \right] dv, \qquad (1')$$

$$pv = r(v, T)T, \qquad (2')$$