

## The Influence of an Electric Field on the Depolarization Factors of Raman Lines

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C<sup>+</sup> from CO). They are not to be confused with, or treated on an equal footing with results obtained with the mass spectrometer alone (O<sup>+</sup> from O<sub>2</sub>), or for which the ion peak shape is anomalous (O<sup>+</sup> from CO and NO).<sup>5</sup> The N<sup>+</sup> onset potentials in NO are not confused by the fact that there are two processes for the formation of N<sup>+</sup> ions as Gaydon suggests. The situation is entirely analogous to that found for C<sup>+</sup> ions from CO.

It is the opinion of this writer that the electron impact experiments should carry considerably more weight than the series comparisons presented by Glockler. It is also difficult to see the justification for the rigorous use of the non-crossing rule in view of the theoretical limitations on its applicability and evidences in band spectra of its violation. Glockler, although careful to point out that the rule is not violated for NO if  $D(\text{NO}) \approx 6.49$  ev, is apparently willing to accept values of  $D(\text{CO})$  which involve violations for CO. Considerations relating to  $D(\text{CN})$  and  $D(\text{CN} - \text{CN})$  are based on experiments which are more readily re-interpreted than the electron impact experiments. Thus the diffuse spectra observed by Hogness and Liu-Sheng<sup>8</sup> in cyanogen might be interpreted differently as suggested by themselves and by Gaydon, and the result of Robertson and Pease<sup>9</sup> depends on the acceptance of a rather involved chain mechanism for the thermal reaction of hydrogen and cyanogen. Similarly, the Born-Haber cycle given by Glockler involves a number of questionable energetic quantities.

The occasion of this letter will also be taken to discuss interpretations of electron impact work to be found in Gaydon's book<sup>4</sup> which appear to this writer to be in error or concerning which new evidence is now available. The appearance potential for C<sup>+</sup> ions from CO at 22.8 ev has been determined for ions of zero initial kinetic energy so that one cannot attribute a part of this potential to undetected kinetic energy of the products.<sup>10</sup> The appearance potential for O<sup>+</sup> ions at the maximum of its kinetic energy distribution (27 ev) is not to be compared with the value for ions of zero initial kinetic energy  $\left(23.5 \begin{smallmatrix} +0.0 \\ -0.4 \end{smallmatrix} \text{ ev}\right)$ . The values 23.1 and 23.5 ev are not two independent appearance potentials but the experimental limits for a single one. C<sup>-</sup> cannot be the other product in the process yielding O<sup>+</sup> from CO because C<sup>-</sup> was looked for and not found.<sup>5</sup>

Concerning Gaydon's remarks about O<sub>2</sub> it may be pointed out that only the mass spectrometric result is available for the O<sup>+</sup> ion and there appears to exist no valid objection to the interpretation which has been given for the O<sup>+</sup> onset potential. The potential curve of O<sub>2</sub><sup>+</sup> involved in the dissociation process cannot be that of the ground state of the molecular ion as Gaydon assumes because the known  $r_e$  values of this state and the ground state of O<sub>2</sub> are nearly identical.

In connection with these discussions it is of interest to note the excellent agreement now obtained for the electron affinity of the oxygen atom by the method of ionization at a heated filament<sup>11</sup> with the electron impact result.<sup>5,6</sup> The present writer has had the opportunity to look at the original electron impact data for HCl,<sup>12</sup> referred to by Gaydon, and has found that if the data are evaluated by

the vanishing current method rather than the now discredited linear extrapolation method used by Nier and Hanson, good agreement with the band spectroscopy of HCl is obtained.

<sup>1</sup> G. Glockler, J. Chem. Phys. **16**, 600 (1948).

<sup>2</sup> G. Glockler, J. Chem. Phys. **16**, 602 (1948).

<sup>3</sup> G. Glockler, J. Chem. Phys. **16**, 604 (1948).

<sup>4</sup> A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (John Wiley and Sons, Inc., New York, 1947).

<sup>5</sup> H. D. Hagstrum and J. T. Tate, Phys. Rev. **59**, 354 (1941).

<sup>6</sup> W. W. Lozier, Phys. Rev. **44**, 575 (1933); *ibid.* **45**, 850 (1934); *ibid.* **46**, 268 (1934).

<sup>7</sup> E. E. Hanson, Phys. Rev. **51**, 86 (1937).

<sup>8</sup> T. R. Hogness and Liu-Sheng T'sai, J. Am. Chem. Soc. **54**, 123 (1932).

<sup>9</sup> N. C. Robertson and R. N. Pease, J. Chem. Phys. **10**, 490 (1942).

<sup>10</sup> H. D. Hagstrum, Phys. Rev. **72**, 947 (1947).

<sup>11</sup> M. Metlay and G. E. Kimball, J. Chem. Phys. **16**, 779 (1948).

<sup>12</sup> A. O. Nier and E. E. Hanson, Phys. Rev. **50**, 722 (1936).

### The Influence of an Electric Field on the Depolarization Factors of Raman Lines\*

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(May 20, 1948)

IT has been reported that the depolarization factors of some of the Raman lines of liquids are altered by an electric field.<sup>1</sup> It would seem that valuable information could be obtained by a detailed and quantitative investigation of this phenomena.

In order to investigate this effect two sample tubes containing flat brass electrodes were made. The space between the electrodes was 5 mm in one tube, and 2 mm in the other. The electric field was applied to the electrodes by means of tungsten wires sealed through the glass. The depolarization factors of the Raman lines of the sample were determined by means of a photoelectric recording spectrograph by a method which has been described previously.<sup>2</sup> To determine the effect of the electric field, the spectrograph was set at the Raman line under investigation and the change in intensity when the electric field was applied was measured directly by the galvanometer deflection. The effect of the field on both the strong and weak component was determined.

Measurements were made on the most highly polarized lines of benzene; cyclohexane; carbon tetrachloride and chlorobenzene and also on some of the less highly polarized lines. The field strength varied somewhat but most of the trials were made with a direct field of 20,000 volts per cm and then repeated with an alternating field of 70,000 volts per cm.

In no case did the applied field produce any noticeable change. Certainly, in no case did it change the depolarization factor of the highly polarized lines by more than 0.01. It is recognized that this result is in direct contradiction to the results published previously which lead one to expect a change in the depolarization factor of the order of 0.1. However, the method of measurement used here is direct and accurate and not subject to the many errors of the photographic method.

There still exists the possibility that measurable changes in the depolarization factor may occur at higher field

strengths. Such high fields can be applied to very few liquids and even in these cases, only under special conditions. Therefore it appears unlikely that the Raman spectrum of liquids in electric fields will yield much additional information.

\* This research was carried out on Contract N60nr-269 Task V of the Office of Naval Research.

<sup>1</sup> S. C. Sirkar, *Ind. J. Phys.* **8**, 337 (1933).

<sup>2</sup> D. H. Rank, *J. Opt. Soc. Am.* **37**, 798 (1947).

### Note on the Correlation through Anharmonic Force Theory of the Compressibility Modulus and Thermal Expansion Coefficient of KBr at Low Temperatures

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June 7, 1948

THE purpose of this note is to show that the temperature dependence of the compressibility modulus and volume of KBr at low temperatures may be understood approximately in terms of the theory of anharmonic lattice dynamics as formulated by Debye.<sup>1</sup>

Galt<sup>2</sup> has measured the elastic modulus  $c_{11}$  of KBr down to liquid helium temperatures, and he has also measured  $c_{12}$  down to 140°K. The modulus  $c_{12}$  was found to be approximately independent of temperature, and if we suppose that this independence continues down to 0°K we may deduce values of the compressibility modulus  $K = (c_{11} + 2c_{12})/3$  over the temperature range from the liquid helium region to room temperature, at which point the values join on to the earlier measurements of Slater<sup>3</sup> over the range 30°–75°C.

Since Galt's measurements appear to be the first which go down to temperatures such that  $dK/dT \rightarrow 0$ , it is of interest to see whether his results are intelligible in terms of anharmonic lattice interactions; as a check on the anharmonic constants one may also examine the thermal expansion data. The existence of a relation between the change  $\delta K$  in compressibility modulus and the change in volume, with increasing temperature, may be made plausible by the following very crude consideration. As a result of anharmonic terms, the compressibility modulus will be a function of the volume:

$$K = K_0 + \delta K = K_0 + K_1 \Delta + \dots,$$

where  $\Delta$  is the fractional change of volume; now even if  $\Delta$  is due to thermal expansion, we may expect that  $\delta K/\Delta$  will be approximately constant.

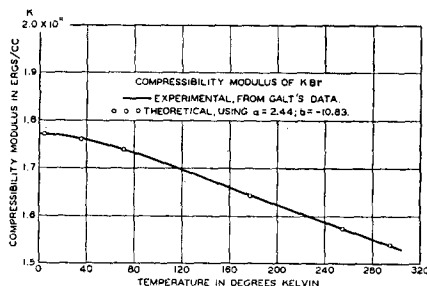


FIG. 1. Variation of compressibility modulus with temperature in KBr.

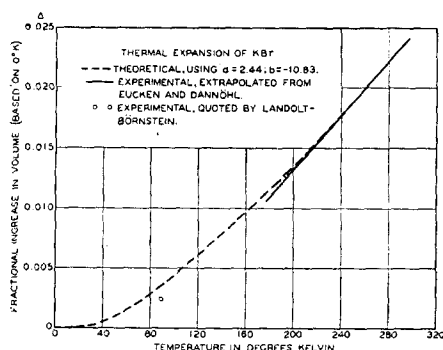


FIG. 2. Fractional increase in volume with temperature.

Debye expresses the effect of the anharmonic terms in the lattice interactions by supposing that the characteristic temperature  $\Theta$  may be expressed as a power series in the fractional volume change

$$\Theta = \Theta_0 [1 - a\Delta + (b/2)\Delta^2 + \dots]$$

where  $\Delta = (V - V_0)/V_0$ . Debye then goes on to derive by straightforward methods certain approximate expressions for the compressibility modulus and for the thermal expansion coefficient as functions of the temperature and of the anharmonicity constants  $a$  and  $b$ . The expressions are too complicated to reproduce here.

Figure 1 shows an experimental curve for the compressibility modulus *vs.*  $T$ , derived from Galt's data, and the "best fit" theoretical values calculated from Debye's results using  $a = 2.44$ ,  $b = -10.83$ . For KBr,  $\Theta_0 = 177^\circ\text{K}$ . The algebraic signs of  $a$  and  $b$  are physically plausible.

Figure 2 shows experimental values of the fractional volume increase *vs.*  $T$  and a theoretical curve calculated from Debye's results with the same values of  $a$  and  $b$  which gave the best fit to the compressibility data. The experimental data are taken from the Landolt-Börnstein tables and from an extrapolation to low temperatures of the high temperature measurements of Eucken and Dannöhl.<sup>4</sup> The volume was normalized so that the theoretical and experimental values of  $\Delta$  were equal at 0°C.

The following conclusions may be drawn from this work:

(a) The Debye theory with anharmonic terms gives a satisfactory representation of the temperature variation of the compressibility modulus.

(b) Using the values of the anharmonicity constants determined by (a), the Debye theory gives correctly the slope of the curve of  $\Delta$  *vs.*  $T$ : that is, it gives the thermal expansion coefficient.

I wish to express my thanks to Miss C. L. Froelich for computational assistance.

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<sup>3</sup> J. C. Slater, *Phys. Rev.* **23**, 488 (1924).

<sup>4</sup> A. Eucken and W. Dannöhl, *Zeits. Elektroch.* **40**, 814–821 (1934).