

Raman Effect of Molecule Type XY₆

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In each case the contribution due to the multiplicity is of the form

$$F\left(\frac{1}{\rho}\right) - F\left(\frac{1}{m\rho}\right) = F\left(\frac{kT}{hcD}\right) - F\left(\frac{kT}{mhcD}\right). \quad (7)$$

This means that if we plot the multiplet contributions to the thermodynamic functions against temperature, curves with the same m but different values of D will differ only in their scale along the temperature axis.

It is interesting to note that in the case of the specific heat, F is the Einstein function or the specific heat of a single vibration (cf. Einstein's theory of the specific heat of solids). It is easy to show that the curve for C_M has a maximum. The height of this maximum is determined entirely by the multiplicity m , and in no case can the height exceed the gas constant R . For a given m , the location of this maximum is determined entirely by the value of D .

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July 24, 1934.

¹ E. Schrödinger, *Handbuch der Physik*, Bd. X, p. 275.

Raman Effect of Molecule Type XY_6

Yost, Steffens and Gross¹ have given three new valuable examples of the Raman effect of the type XY_6 , first examined experimentally and theoretically by us;² they think, however, our theoretical treatment to be "oversimplified" and think it "necessary to treat the problem more thoroughly."

We have adopted the central force system exactly according to the form suggested by Bjerrum.³ We were, of course, well aware of the fact, that several authors⁴ have introduced the hypothesis, that apart from Bjerrum's forces there are other ones, acting in the equilibrium positions of the atoms; this hypothesis is a reasonable development of Bjerrum's assumption, the latter being a first approximation. We do not know, why Yost, Steffens and Gross take Bjerrum's original system as impossible; probably they assume that the forces present in equilibrium positions have an influence about as great as Bjerrum's

forces. But as those forces can be substituted by forces perpendicular to the line connecting the two respective atoms,⁵ it can be assumed, that they are really considerably smaller than Bjerrum's forces.⁶

In our case we think it perfectly adequate to dispense with those smaller forces; first, because their introduction involves the introduction of additional constants, which cannot be determined by the Raman frequencies; second, because our treatment of the problem gives a perfectly satisfactory interpretation of the experimental results.

In fact, the interpretation of the Raman frequencies given by Yost, Steffens and Gross is essentially identical with ours. That can be said not only of the vibration scheme, but also of the coordination of frequencies and vibrations; especially the relation between the three Raman frequencies given by Yost, Steffens and Gross was used already by us for coordination.

There is no material influence of the different theoretical treatment except in the calculations, leading to the numerical values of Table II, given by Yost, Steffens and Gross. In performing these calculations, however, these authors are forced to introduce not only the new theory of Badger, but also a rather uncertain additional assumption regarding their constant j ; moreover, this assumption seems to be incompatible with their putting the constant k_{24} of the analogous force of Bjerrum equal to zero.

Still, we think our theoretical treatment an adequate interpretation of our experimental results; on the other hand, we regard the calculations performed by Yost, Steffens and Gross, inasmuch as they go further than ours, as a trial of interpretation, very interesting, but necessarily rather uncertain.

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July 25, 1934.

¹ D. M. Yost, C. C. Steffens and S. T. Gross, *J. Chem. Phys.* **2**, 311 (1934).

² O. Redlich, T. Kurz and P. Rosenfeld, *Zeits. f. physik. Chemie* **B19**, 231 (1934).

³ N. Bjerrum, *Verhandl. d. physik. Ges.* **16**, 737 (1914).

⁴ Cf. D. M. Dennison, *Astrophys. J.* **62**, 84 (1925).

⁵ We do not know, whether this substitution has already been made heretofore.

⁶ Cf. an analogous assumption made by R. Mecke, *Zeits. f. physik. Chemie* **B16**, 409 (1932).