The Raman Spectra of Some Isomeric Octanes

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LETTERS TO THE EDITOR

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The Raman Spectra of Some Isomeric Octanes

The Raman spectra of 3,4-dimethylhexane and 2,5-dimethylhexane have been examined using the technique described by Murray and Andrews.[1] The samples studied were synthesized in this laboratory for experiments on motor fuels by C.W.A. workers in an investigation of carbon monoxide elimination. They are believed to be of satisfactory purity having boiling ranges not greater than 0.2°. Spectra were excited by the violet and blue lines of the mercury arc separately, using appropriate filters. The following lines were observed.

3,4-dimethylhexane: 338(5b), 436(5), 462(1), 489(0), 558(1), 583(0), 733(5), 754(5), 801(3b), 840(4), 897(5), 955(4), 984(5), 1034(5), 1054(4), 1123(1), 1163(4), 1182(2), 1286(4b), 1355(2b), 1455(20b), 1658(1), 2732(2br), 2860(10), 2875(20), 2907(8), 2934(10), 2967(20).

2,5-dimethylhexane: 265(3), 313(2), 444(4b), 553(0) 778(2), 839(6), 962(3br), 1048(1), 1150(3), 1176(4), 1233(1/2), 1302(2b), 1338(4), 1453(10b), 2650(0), 2720(2), 2763(1), 2871(10), 2921(3), 2962(10). Estimated relative intensities are given in parentheses following the displacements of the Raman lines together with symbols to indicate the character of the lines; *b* meaning broad, and *r* shaded toward the red.

Whereas the molecules in question are too complex to permit detailed assignments of frequencies to types of motion, a few features of these spectra appear worthy of comment. It is to be expected that 2,5-dimethylhexane should have lower frequencies than the 3,4- isomer as the methyl groups are situated nearer the ends of the vibrating hydrocarbon chain. This is in accordance with the observed spectra. The 3,4-dimethylhexane has two asymmetric carbon atoms and hence should occur in three stereoisomeric forms. The synthesized product should be a mixture of all three and hence the spectrum should consist of two superimposed spectra as the *d* and *l* forms should have identical spectra. The fact that several more lines are found for this compound than for the 2,5- isomer is in accord with this expectation although the greater symmetry of the latter compound would also tend to produce this effect.

JOHN W. MURRAY

Johns Hopkins University,
    July 17, 1934.

[1] J. W. Murray, and D. H. Andrews, J. Chem. Phys. 1, 406 (1933).

The Thermodynamic Functions of a Diatomic Gas Whose Molecules Have a Multiplet Normal Electronic State Belonging to Hund's Case (a)

In Hund's case (a), which occurs only when $\Lambda \neq 0$, the energy levels of the multiplet are given in cm^{-1} by the formula

$$F_s(v,J) = B_s(v)[(J+\tfrac{1}{2})^2 - \Omega_s{}^2] + (s-1)D + E_s(v). \qquad (1)$$

Here s numbers the components of the multiplet from 1 to m, m being the multiplicity; D is the separation between the successive components of the multiplet. In any given component of the multiplet J takes on the values Ω_s, Ω_s+1, etc. $E_s(v)$ is the vibrational energy in terms of the new quantum theory.

The partition sum is then

$$P_1 = \sum_{s,v,J} 2(2J+1)e^{-\sigma_s(v,J)+\sigma_0}, \qquad (2)$$

where

$$\sigma_s(v,J) = hcF_s(v,J)/kT, \qquad \sigma_0 = \sigma_1(0,\Omega_1)$$

and $2(2J+1)$ is the statistical weight of the state $F_s(v,J)$, the factor 2 coming from Λ-type doubling.

Inserting the expression (1) in (2) and making the usual approximations,[1] it can be shown that the partition sum splits into a product of four factors, one due to rotation, one to vibration, one due to the multiplicity, and the factor e^{σ_0}. Designating by a subscript M the factor due to the multiplicity,

$$P_{1M} = (1-e^{-m\rho})/(1-e^{-\rho}), \qquad (3)$$

where $\qquad \rho = hcD/kT.$ $\qquad (3a)$

As a consequence the specific heat, entropy and free energy will each have an extra additive term due to the multiplicity. These terms are, respectively,

$$\frac{C_M}{R} = \frac{\rho^2 e^{-\rho}}{(1-e^{-\rho})^2} - \frac{m^2\rho^2 e^{-m\rho}}{(1-e^{-m\rho})^2}, \qquad (4)$$

$$\frac{S_M}{R} = \frac{\rho e^{-\rho}}{1-e^{-\rho}} - \log(1-e^{-\rho})$$
$$\qquad\qquad - \left[\frac{m\rho e^{-m\rho}}{1-e^{-m\rho}} - \log(1-e^{-m\rho})\right], \qquad (5)$$

$$\left(-\frac{F-E_0{}^0}{RT}\right)_M = \log(1-e^{-m\rho}) - \log(1-e^{-\rho}). \qquad (6)$$

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 XY₆

Yost, Steffens and Gross[1] 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 "over-simplified" 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 authors[4] 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).