

Raman Spectra of Fused Salts

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The Structure of Cyanuric Triazide

Mr. E. W. Hughes has recently described a structure for cyanuric triazide,¹ which in general outline is similar to one which I found some time ago and which was briefly described by Sir William Bragg in *Nature* of last July.² It differs, however, from mine in certain important details. The atomic distances in the cyanuric ring are given as 1.33Å and all equal, thus indicating an oscillating double bond as in benzene. I find two distances 1.38Å and 1.31Å, corresponding to fixed single and double bonds alternating in the ring. In Mr. Hughes' structure the azide group departs considerably from linearity, being bent 15° at the middle nitrogen atom, while in my structure the group is straight or very nearly so. In the azide group, the nitrogen atom, which is directly linked to the cyanuric ring is unfortunately not completely resolvable in the Fourier projection on the (0001) plane because of a similar nitrogen atom of the second molecule of the unit cell being separated from it in the plane of projection by only 0.92Å, so that there is rather less precision in locating its center than is the case with the rest of the atoms. For this reason, it is not possible to be certain of the exact linearity of the azide group, but even so I estimate that any departure from it could not exceed 3° or 4°.

It is not possible to follow Mr. Hughes' work very closely, since he has not published the figures which he used for the intensities in his Fourier analysis nor the numerical values which he obtained from the summations, nor does he give any indication of the closeness of the points in the (0001) plane at which he carried out his summations.

I may point out, however, that Mr. Hughes' estimates of intensity were visual only. My intensity measurements were made on a Robinson photometer³ and in my analysis I used the intensities from 99 planes of the (0001) zone, whereas Mr. Hughes only used 66 values. The intensities, which he has omitted are not in all cases the weakest. Many correspond to quite strong reflections, some of them having intensities which I found equal to one-half of the highest value I obtained for any plane in the zone. The Fourier series, which he used, must therefore be very far from convergent and it has been our experience in this laboratory that unless the series is very nearly convergent, that is, unless none but the very weakest reflections have been omitted, we do not obtain well-defined or correct positions for the atoms, nor do contour lines which follow faithfully the results of the calculations, these having been carried out at a sufficient number of points, appear smooth or circular round the atom centers.

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My intensity measurements have recently been put on an absolute scale by a few accurate determinations using the ionization method and molybdenum rays, to eliminate absorption. This has revealed an interesting feature of the structure, namely, that the electron density at the centers of the atoms is unusually high, rising to above 8 and 10 electrons per square Angstrom unit for carbon and nitrogen, respectively. Now that the work is quite complete, I hope that it will soon be published in detail.

I. ELLIE KNAGGS

Davy Faraday Laboratory,
The Royal Institution,
Albemarle, St.,
London, W. 1, England,
February 8, 1935.

¹ Hughes, J. Chem. Phys. **3**, 1 (1935).

² Bragg, *Nature* **134**, 138 (1934).

³ Robinson, Proc. Roy. Soc. **A130**, 120 (1930).

Raman Spectra of Fused Salts

In order to assist in the interpretation of results obtained from a series of thermodynamic studies of fused salts, we have begun a search for Raman spectra in a number of salts in the fused condition.

We report some preliminary measurements of carefully purified salts made with a spectrograph of comparatively low dispersion. The mercury arc radiation was filtered with either an aqueous solution of sodium nitrite or a solution of iodine in carbon tetrachloride. No photochemical decomposition of the fused zinc chloride was observed after continued illumination using either filter. In the pure state these salts did not etch the Pyrex Raman cells even after being confined at over 500°C for several weeks. Exposure times varied from four to twenty-four hours.

The 100 cm⁻¹ anti-Stokes line from the 4358Å exciting line was not observed since it would lie too close to the 4339Å mercury line for resolution. The 285 cm⁻¹ frequency value is the least exact, only one comparatively poor plate being available for this frequency. The Stokes and anti-Stokes lines are of comparable intensity as might be expected for the temperature used.

Substance	Temperatures	Exciting line	Displaced frequencies (cm ⁻¹)
ZnCl ₂	(400°, 430° and 500°C)	4358Å	230 ± 9; 98 ± 5 (Stokes)
			233 ± 8 (anti-Stokes)
		4046Å	285 (broad); 101 ± 8 (Stokes)
ZnBr ₂	(440°C)	4358Å	231 ± 5; 15 ± 5 (anti-Stokes)
			155 ± 8; 79 ± 10 (Stokes)
			137 ± 20 (anti-Stokes)

Krishnamurti¹ investigated the Raman spectra of a number of inorganic halides in the solid state at room temperature. Those substances with heteropolar binding showed no Raman spectra whereas homopolar substances such as the mercuric halides showed strong Raman lines. Zinc chloride and cadmium iodide, substances of intermediate polarity, whose crystal structure is of the layer lattice type showed weak Raman lines. Our data would classify zinc bromide in the intermediate group with zinc chloride and cadmium iodide, the higher electrical conductivity of the zinc bromide being offset by its lower melting point.

Krishnamurti¹ found a frequency shift for zinc chloride of 234 cm^{-1} , which is in satisfactory agreement with the higher frequency line found by us. The frequency shifts of 297 and 396 cm^{-1} found from concentrated aqueous solutions of zinc chloride by Hibben² are probably due to complex ions or molecules.^{3, 4} Furthermore, Braune and Engelbrecht⁵ have shown that the displaced frequencies of the mercuric halides are nearly the same for the fused salt as for the salt at room temperature. Grassman⁶ and Thatte and Ganesan⁷ obtained similar results for a number of nitrates. The fact that the Raman frequencies persist some hundred degrees above the melting point indicates that the frequencies found here are not due to vibrations in the crystal lattice but are rather due to oscillations in the zinc halide grouping.

The results for both zinc chloride and zinc bromide do not indicate a linear type of molecule. The determination of the angle between the valence bonds and strength of bonds awaits additional data.

We failed to observe Raman lines from fused LiBr , PbCl_2 , PbBr_2 and CdCl_2 , but the experimental conditions for obtaining these lines were not as satisfactory as with the zinc salts.

EDWARD J. SALSTROM
LOUIS HARRIS

Research Laboratory of Physical Chemistry,
Massachusetts Institute of Technology,
February, 27, 1935.

¹ Krishnamurti, *Ind. J. Phys.* **5**, 113 (1930).

² Hibben, *Proc. Nat. Acad. Sci.* **18**, 532 (1932).

³ Damaschun, *Zeits. f. physik. Chemie* **B16**, 92 (1932).

⁴ Braune and Engelbrecht, *Zeits. f. physik. Chemie* **B11**, 416 (1931).

⁵ Braune and Engelbrecht, *Zeits. f. physik. Chemie* **B19**, 303 (1932).

⁶ Grassman, *Zeits. f. Physik* **77**, 616 (1932).

⁷ Thatte and Ganesan, *Ind. J. Phys.* **8**, 341 (1934).

The Absolute Rate of a Chemical Reaction

Various writers^{1, 2, 3} have attempted to formulate the factors determining the absolute rate of a chemical reaction. To a first approximation the task is not difficult. There are two methods of approach. One method is to calculate the number of favorable collisions from kinetic theory. The other is to treat the colliding molecule as a complex and apply the laws of statistical mechanics and chemical equilibrium for what they are worth. The two methods correspond at every point. Thus, the heat of activation in the latter treatment becomes the factor which determines the number of collisions of sufficient violence in the former method. The collision radius in the kinetic theory deter-

mines the moment of inertia and rotational entropy of the complex in the thermodynamic treatment. The greater the entropy of the complex, the greater must be the probability of reaction. By an arbitrary choice of collision radii, the "steric" factor may often be made unity, but this does not really give us any more information than we had before. Both methods involve uncertainties due to the lack of exact knowledge of force constants, collision radii, etc.

Recently Eyring⁴ has proposed to treat the subject by a method which is essentially the second method mentioned above. His method is not, therefore, novel, nor does it produce any results new to statistical mechanics. What he does propose that is new is to calculate the contours of the potential surface by wave mechanics so that the various uncertainties mentioned above may disappear. It may even be possible to calculate the rate of reflection at a barrier. This latter quantity may be described as a true steric factor.

One may await results to see how well it will succeed. Presumably no one would claim that it is now possible to calculate the energy of any but the simplest chemical bonds with any precision by wave mechanics. Certainly a survey of the amount of work required to reach a satisfactory value for the heat of dissociation of the hydrogen molecule does not inspire one with confidence. The method of Heitler and London may be a better approximation in the case of a reactive complex than a stable molecule; it would be very fortunate if this is the case. It is, of course, possible to adapt calculations to experimental data, but in doing this one may produce agreement by changing one factor when some other factor is really at fault.

Nevertheless, the writer has believed for a long time that it should be possible to determine all the constants of a reaction rate from measurements at a single temperature.

W. H. RODEBUSH

University of Illinois,
February 27, 1935.

¹ W. H. Rodebush, *J. Am. Chem. Soc.* **45**, 606 (1923); *J. Chem. Phys.* **1**, 440 (1933).

² M. Polanyi and E. Wigner, *Zeits. f. physik. Chemie (Haber band)*, 439 (1928).

³ O. K. Rice and H. Gershinowitz, *J. Chem. Phys.* **2**, 853 (1934).

⁴ Eyring, *J. Chem. Phys.* **3**, 107 (1935).

The Raman Spectrum of Deuterium

A number of observers have studied the emission spectra of mixtures of hydrogen and deuterium. The Fulcher bands for HD and D₂ have been photographed.¹ In the extreme ultraviolet Jeppesen,² and Beutler and Mie,³ have obtained emission spectra from hydrogen-deuterium mixtures and have ascribed several bands to HD. From these data on HD, Urey and Teal⁴ have calculated molecular constants for the molecule D₂ in the ground state. No experimental data for this molecule in this state appear to have been obtained.

We have obtained Raman spectra of gaseous deuterium (99.5 percent D₂) at a pressure of 2.5 atmos., using Hg 2537 as an exciting line. 24- to 48-hour exposures were made. Two rotation lines and the Q branch of the vibration line were obtained. Their frequencies and mean deviations from