

The Structure of Cyanuric Triazide

Edward W. Hughes

Citation: [The Journal of Chemical Physics](#) **3**, 650 (1935); doi: 10.1063/1.1749569

View online: <http://dx.doi.org/10.1063/1.1749569>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/3/10?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Vibrational Spectra of Cyanuric Triazide](#)

J. Chem. Phys. **48**, 1138 (1968); 10.1063/1.1668774

[Zeeman Quadrupole Spectrum of Cyanuric Chloride](#)

J. Chem. Phys. **29**, 1381 (1958); 10.1063/1.1744727

[Pure Quadrupole Spectrum of Cyanuric Chloride](#)

J. Chem. Phys. **27**, 602 (1957); 10.1063/1.1743791

[The Structure of Cyanuric Triazide](#)

J. Chem. Phys. **3**, 241 (1935); 10.1063/1.1749642

[The Crystal Structure of Cyanuric Triazide](#)

J. Chem. Phys. **3**, 1 (1935); 10.1063/1.1749546



LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor

not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

The Structure of Cyanuric Triazide

Some months ago I published in this Journal¹ a description of a crystal structure for cyanuric triazide which was based upon visual estimates of the x-ray reflection intensities. Since there were ten parameters to evaluate, a Fourier method was used although such a procedure is not customary when quantitative measurements are not available. Approximations and graphical methods were introduced to reduce the labor of the method to a level warranted by the accuracy of the data. The limit of error placed upon the resulting parameters was consequently large compared with that usually ascribed to Fourier analyses. It was estimated from the agreement between calculated and estimated structure factors that the average error would not exceed one-one hundredth of the edge of the unit cell a .

Miss I. E. Knaggs has now published² details of her very careful examination of the same crystal, including a Fourier analysis based upon absolute quantitative measurements. In recent letters³ Miss Knaggs has pointed out the differences between our structures. I should like to point out that my parameters agree with Miss Knaggs' more accurate ones within the limits cited in my paper, as is shown by Table I. Column 1 indicates the parameters using Miss Knaggs' atomic designations. The second column gives her parameters reduced to fractions of the cell edge while the third gives my corresponding values. The final column records the differences. It will be observed that the average value is considerably less than 0.010 and that only one difference is notably greater than 0.010.

It would seem that my structure was sufficiently accurate for the purpose at hand, which was to confirm the chain

form found for the azide group by Brockway and Pauling.

Comparison of my estimated structure factors with the quantitative measurements shows that as relative values they are not excessively bad. The average difference for seventy-five reflections was found to be about 16 percent. It is my opinion that the differences in results are due more to my omission of less important Fourier amplitudes than to errors in estimating the amplitudes and that my data really warranted more careful analysis than I thought appropriate at the time. If all observed reflections had been included in the Fourier series it is probable that the accuracy obtained would have been sufficient for most purposes and I feel that one would be justified in repeating this qualitative method for similar structures if quantitative measurements could not be made. I am not so certain however how valuable such an analysis would be in locating atoms of low atomic number in crystals containing heavy atoms or in locating the centers of atoms which "overlap" badly in the projection.

EDWARD W. HUGHES

Cornell University,
Ithaca, N. Y.,
August 21, 1935.

¹ Hughes, J. Chem. Phys. 3, 1 (1935).

² Knaggs, Proc. Roy. Soc. A150, 576 (1935).

³ Knaggs, Nature 135, 268 (1935); J. Chem. Phys. 3, 241 (1935).

Raman Spectrum of Methyl Deuteride

We report on the vibrational frequencies of CH_3D observed in the Raman effect. A theory of the isotope effect for such pentatomic molecules has been developed by Rosenthal¹ in terms of a five constant potential energy function. Dennison and Johnston² using the observed frequencies of CH_4 ^{3,4} and the value of the rotational-vibrational interaction⁵ have calculated the five force constants of the Rosenthal development, and the normal frequencies of the four deuterio-methanes. Barker and Ginsburg⁶ have observed the infrared absorption spectrum of CH_3D .

The methyl deuteride was prepared from methyl iodide and pure deuterium oxide with an aluminum-mercury couple. CH_3I and D_2O were vacuum distilled on to dry aluminum-mercury couple. The mixture was then allowed

TABLE I.

Atom	K	H	Δ
A	0.214	0.208	0.006
B	.386	.385	.001
C	.458	.455	.003
D	.342	.325	.017
E	.242	.240	.002
		.480	.005
		.560	.008
		.433	.009
		.270	.011
		.125	.012
		Mean	.0074

TABLE I.

Molecule	Vibration ^a	Calculated	Observed	Intensity	Differences
CH ₄	ω_1	2914.8 ⁴	2914.2	4	- 0.6
CH ₃ D	ω_{4ab}	1300	1330.1	2	+30.1
	ω_{5ab}	2183	2199.0	2	+16.0
	$2\omega_{5ab}$	2302	2314.8	10	+12.8
	$2\omega_2$	2920	2921.7	4	+ 1.7

to heat up and react until the pressure was atmospheric. At this point, the gas was bled off and collected over mercury. This method produces 10–15 percent D₂. The small amount of CH₄ evidently present may come from exchange or adsorbed H₂ on the couple. The Raman spectrum was obtained at a pressure of three atmospheres using Hg2537

as the exciting line.⁷ Exposure time was 120 hours. Four vibrational lines of CH₃D and one of CH₄ were obtained. Their values in cm⁻¹ in vacuum and a comparison with the calculated values of Dennison and Johnston² are given in Table I. No rotational structure was observed.

GEORGE E. MACWOOD
H. C. UREY

Department of Chemistry,
Columbia University,
August 29, 1935.

¹ J. Rosenthal, Phys. Rev. **45**, 538 (1934).

² D. Dennison and M. Johnston, Phys. Rev. **47**, 93 (1935).

³ J. Cooley, Astrophys. J. **62**, 73 (1925).

⁴ Dickinson, Dillon and Rasetti, Phys. Rev. **34**, 582 (1929).

⁵ E. Teller, Hand- und Jahrbuch d. Chem. Physik **9**, 125 (1934).

⁶ E. Barker and N. Ginsburg, J. Chem. Phys. **2**, 299 (1934).

⁷ Spectrograph and accessories are completely described in a paper by G. Teal and G. MacWood to appear shortly.

⁸ J. Rosenthal, Phys. Rev. **46**, 730 (1934).