Raman Spectrum and Structure of the Metaborate Ion

J. Rud Nielsen and N. E. Ward

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.

Raman Spectrum and Structure of the Metaborate Ion

Ghosh and Das[1] observed two Raman lines scattered by an aqueous solution of sodium metaborate and interpreted them as shifts of 1403 cm^{-1} and 253 cm^{-1} in the 24,705 cm^{-1} and 22,938 cm^{-1} mercury lines, respectively. They ascribed these Raman shifts to the metaborate ion and concluded that it is triatomic, BO_2^-, and nonlinear. This result seems open to serious doubt, since the BO_2^- ion would have sixteen valence electrons and all the triatomic molecules with sixteen valence electrons for which the structure is known are linear.[2]

We have therefore investigated the Raman spectrum of a 5.0 N, or nearly saturated, aqueous solution of sodium metaborate. Although we have made very long exposures, using filters to cut out one or the other of the mercury lines 24,705 cm^{-1} and 22,938 cm^{-1} and also complementary filters,[3] we have failed to observe the lines reported by Ghosh and Das. Instead we have found, besides the water bands, three rather sharp Raman lines corresponding to the single shift of 749±1 cm^{-1} in the 24,705, 24,516 and 22,938 cm^{-1} mercury lines. The two strongest of these, and no other Raman lines, were observed also with a 1.4 N solution of sodium metaborate.

That the observed Raman shift is produced by the metaborate ion seems beyond doubt. It is true that some metaboric acid is formed by hydrolysis, but its molar concentration in the concentrated solution, as calculated from the known ionization constants of HBO_2 and water, is only 0.1 percent of that of the metaborate ion. Since only a single Raman shift occurs, the metaborate ion must be triatomic, linear and symmetrical, and the shift of 749 cm^{-1} must represent the frequency ν_1 of the totally symmetrical vibration. From the values of ν_1 and the atomic masses it is possible to calculate the force constant k_1 and rough values for the frequency ν_3 of the asymmetrical longitudinal vibration. One finds $k_1 = 5.29 \times 10^5$ dynes/cm, $\nu_3 = 1480$ cm^{-1} for a metaborate ion containing the most abundant boron isotope and $\nu_3 = 1530$ cm^{-1} for BO_2^- with boron of atomic mass 10. These frequencies as well as that of the transverse vibration ν_2 should be observable in infrared absorption.

The problem of determining the electronic structure of the metaborate ion now arises. Two formulas suggest themselves, $\overset{-}{O} - \overset{+}{B} - \overset{-}{O}$ and $O = B = O$, the latter corresponding to the structure assumed for carbon dioxide.[4] We have worked out first-order expressions for the energies, but without actually evaluating a number of integrals it does not seem possible to conclude which form is the more stable. However, the low value of the force constant k_1 favors the structure $\overset{-}{O} - \overset{+}{B} - \overset{-}{O}$ which is also indicated by the chemical behavior of borates.

The formula $\overset{-}{O} - \overset{+}{B} - \overset{-}{O}$ does not seem incompatible with the fact that in crystalline borates the boron atoms are generally surrounded by three oxygen atoms.[5] On the basis of his extensive data on the crystal structure of borates, Zachariasen has suggested that the metaborate ion may have a plane ring structure $(B_3O_6)^{-3}$.[6] This possibility seems ruled out by our results.

An investigation of the Raman spectra of solutions of other borates and of crystalline sodium metaborate is under way. This work has been made possible by grants from the American Association for the advancement of Science and the National Research Council.

Department of Physics,
University of Oklahoma,
Norman, Oklahoma,
February 2, 1937.

J. RUD NIELSEN
N. E. WARD

[1] J. C. Ghosh and S. K. Das, J. Phys. Chem. 36, 586 (1932).
[2] Cf. W. G. Penney and G. B. B. M. Sutherland, Proc. Roy. Soc. A156, 654 (1936).
[3] Cf. R. Ananthakrishnan, Nature 138, 803 (1936).
[4] J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. 7, 205 (1935).
[5] W. H. Zachariasen, Proc. Nat. Acad. Sci. 17, 617 (1931); Zeits. f. Krist. 76, 289 (1931); 88, 150 (1934); W. H. Zachariasen and J. E. Ziegler, Zeits. f. Krist. 83, 354 (1932).
[6] This suggestion was made in a letter to one of us. We are indebted to Professor Zachariasen for valuable discussion.

The Internuclear Distance in Te₂

Maxwell and Mosley[1] have recently deduced, from electron diffraction measurements, an internuclear separation in the Te₂ molecule of 2.59±0.02A, in marked disagreement with the value of 2.85A computed from the rotational band spectrum constants.[2] It is perhaps worth noting that the new distance agrees well with the value of 2.61A calculated by the writer's[3] semiempirical equation from the oscillational constants w_e and $w_e x_e$ and a "basic radius" r_1 obtained from the data on I₂. One of the few large discrepancies between experimental r_e values and those calculated in this way is thus removed. Badger's[4] empirical equation leads to $r_e = 2.55A$, also agreeing much better with the electron diffraction value than with the older result.

MAURICE L. HUGGINS

Kodak Research Laboratories,
Rochester, New York,
February 5, 1937.

[1] L. R. Maxwell and V. M. Mosley, Bulletin Am. Phys. Soc. 12, No. 1, Part 1, 9 (1937) (Abstracts for the North Carolina Meeting).
[2] A. Przeborski, Zeits. f. Physik 63, 280 (1930); W. Jevons, Report on Band Spectra of Diatomic Molecules (Physical Society, London, 1932).
[3] M. L. Huggins, J. Chem. Phys. 3, 473 (1935); 4, 308 (1936).
[4] R. M. Badger, J. Chem. Phys. 3, 710 (1935).