

Letters to the Editor

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Situation of the A ($^3\Sigma$) Level in the Nitrogen Molecule

IN a recent communication in NATURE, Appleyard, Thompson and Williams¹ have discussed the question as to the height of the A level of the nitrogen molecule, which is the bottom state of the first positive group.

Using the electron collision method, they find for the excitation potential of the first positive group the value 8.34 volts, in good agreement with previous measurements of Sponer. This result they take to indicate that the height of the A level or the level difference ($X-A$) should be considerably higher than the value derived from the bands recently observed by Kaplan. They express the opinion that the bands observed by Kaplan are too limited in number for a determination of the vibrational terms with such an accuracy as to prove their identity with the vibrational terms of the A and X level.

If the interpretation of the Kaplan bands and the calculation of vibrational terms were merely based on the few bands observed by him, Appleyard, Thompson and Williams would be justified in expressing some doubt as to the validity of his interpretation; but in this connexion I wish to direct attention to the fact that the Kaplan bands—as clearly pointed out by Kaplan himself—are identical with the bands of the so-called ϵ -system, which I discovered nine years ago in the luminescence from solid nitrogen.

This ϵ -system appears with great intensity and up to the present no less than 111 vibrational bands belonging to this system have been observed. In the lower level of the ϵ -system, 22 vibrational states have been measured, and in the upper electronic level 7 vibrational states are concerned in the formation of the observed bands.

In a paper published in 1930² it was shown that the bottom level of the ϵ -system was identical with the normal state of the nitrogen molecule, which forms the bottom level of the Lyman and the Birge-Hopfield bands. As a consequence, an electronic level of the N_2 -molecule had to be placed about 6 volts above the normal state. In a paper published in January 1932³, I showed that this upper ϵ -level was no doubt identical with the bottom level (A) of the first positive group, and this would have the effect of lowering the A level about 2 volts from the height then accepted.

During the past year, Mr. S. Stensholt and I have obtained spectrograms of the ϵ -bands in the region from red to far in the ultra-violet with a 1-metre grating spectrograph giving dispersion of 17 Å./mm. and a corresponding accuracy of the wave-length measurements (probable error about 0.02 Å.).

A more complete account of our results relating to the ϵ -system will be given in a subsequent paper. In this connexion I merely wish to mention that on the basis of the new measurements, we have found the following more accurate and slightly modified formula for the ϵ -band system:

$$= 49617.5 + (1444.6v_1 - 13.7v_1^2) - (2344.2v_2 - 14.6v_2^2).$$

The vibrational term of the A level derived from the first positive group is:

$$1446.46v - 13.93v^2,$$

and the vibrational term of the normal (X) state derived from the Lyman and the Birge-Hopfield bands is:

$$2345.16v - 14.445v^2.$$

Within the limit of error, these terms are seen to be identical with those of the upper and lower level of the ϵ -system respectively.

From the formula of the ϵ -system, we find that the difference in height between the vibrational zero levels corresponds to 6.12 volts, or the electronic levels corrected for vibrational influence should be situated 6.18 volts apart. In other words, the electric (A) level forming the bottom level of the first positive group is situated 6.18 volts above the normal state (X).

This result is in good agreement with the results of Smyth, Levesly, Rudberg and Brindley, who by electron bombardment found signs of an electronic state between 6 and 7 volts. In view of the results derived from the study of the ϵ -system, this level is no doubt identical with that of the upper ϵ -state, which again is identical with the A ($^3\Sigma$) state.

The excitation potential of 8.34 volts found by Appleyard, Thompson and Williams then must mean that for some reason a potential considerably higher than ($A-X=6.18$ volts) is necessary to excite the first positive group.

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¹ NATURE, 134, 322, Sept. 1, 1934.

² Ann. Phys., 6, 487, 1930.

³ Z. Phys., 75, 30; 1932. Compare also Z. Phys., 79, 471; 1932.

Isotope Effect in the Band Spectrum of Sodium Hydride

As has been pointed out by Holst and Hulthén¹, the elementary theory of isotopy in band spectra cannot account for shifts and the constants of deuterides, determined with the highest precision. They find it necessary, in calculating the reduced mass of the molecule, to add a correction for the electronic masses, which are supposed to partake fully in rotation and vibration. Since this correction is quite general, one would expect it in all deuterides determined with sufficient precision. The only reported cases which fulfil this prescription are:

AlH/AlD², calculated ratio of the reduced masses

$$= \frac{Al \cdot H}{Al + H} : \frac{Al \cdot D}{Al + D} = \rho^2 = 0.51848,$$

$$\text{observed, } \rho^2 = \frac{B_e(\text{AlD})}{B_e(\text{AlH})} = 0.51889.$$

CaH/CaD³, calc. $\rho^2 = 0.51276$, observed $\rho^2 = 0.51337$, and from an investigation of NaD by the present author,

$$\text{calc. } \rho^2 = 0.52147,$$

observed in the normal state, $\rho^2 = 0.5222 \pm 0.0003$.

In all these cases the agreement between calculated and observed values is complete, if one adds the small correction proposed by Holst and Hulthén.