Spectrum of $O^{16}H^2$

Intermittently, for some months, we have been working on the analysis of the spectrum of OH produced in water vapor containing 35 percent of the hydrogen as H^2, from which we have obtained good photographs.[1]

We have been successful in identifying and assigning nearly 500 new lines, in the OH^2 spectrum, which are distributed through eight bands, including the (3,1) and (3,2) bands. Assignments extend beyond $K=30$ in the (0,0) band.

In order to calculate isotope *shifts* between corresponding lines of $O^{16}H^1$ and $O^{16}H^2$ we find that it is necessary to introduce corrections for isotope effects in spin coupling[1] and in Λ-doubling in the ground $^2\Pi$ level and to include γ_e terms in the expansion of the rotational constant B_v in both the upper and the lower levels. The latter is easily accomplished from the rotational constants now in the literature[2] which give:

$$B_e'=17.375 \qquad \alpha_e'=0.838 \qquad \gamma_e'=-0.0075$$
$$B_e''=19.009 \qquad \alpha_e''=0.686 \qquad \gamma_e''=-0.0125$$

The results of the empirical analysis will be published in the near future.

We wish to acknowledge our indebtedness to Professor G. N. Lewis, who generously placed the sample of "heavy water" at our disposal.

Herrick L. Johnston[3]
David H. Dawson[4]

The Ohio State University,
Columbus, Ohio,
November 29, 1933.

---

[1] Cf. Johnston and Dawson, Naturwiss. **21**, 495 (1933).

[2] Johnston, Dawson and Walker, Phys. Rev. **43**, 473 (1933).

[3] Fellow of the John Simon Guggenheim Memorial Foundation while this work was carried out.

[4] DuPont Fellow in Chemistry 1932–3.

On the Breakdown of the Coulomb Law for the Hydrogen Atom

The well-known measurements of the doublet separations in the Balmer series by Kent, Taylor and Pearson,[1] and by W. V. Houston[2] indicate that $H\beta$ is about three percent narrower than predicted by the relativistic fine structure theory, whereas the separations for $H\alpha$ and $H\gamma$ agree with the theory within the limits of experimental error. The more recent observations of Spedding, Shane and Grace[3] indicate, if we interpret their preliminary report correctly, that the $H^1\alpha$ and $H^2\alpha$ doublets are both somewhat less than one percent narrower than expected from the theory. Finally, the new interferometer measurements of Houston and Hsieh[4] increase the discrepancy to about three percent for all the doublets of light hydrogen (H^1). These last experiments were conducted under such conditions that the intensity ratios of the components were those expected theoretically, and the discrepancy is accordingly attributed to a deficiency in the theory. A simple computation shows that this discrepancy can be accounted for by a deviation from the Coulomb law at small distances from the nucleus. Such a deviation is known to occur for heavier nuclei and there exists evidence pointing to the same conclusion for hydrogen.[5] It might be due in the present case to the finite size of the electron and proton suggested by Born,[6] or to an eventual composite structure of the proton (neutron plus positron).

We suppose that the field is Coulomb down to a radius a where a change occurs into some other type of law. A potential attractive as $1/r^n$, where n is greater than or equal to 2, must be rejected on the basis of mathematical considerations.[7] Since the exact shape of the potential curve is not important for such very small distances, we have represented the case where the potential approaches a finite limit by the constant potential e^2/a and the case where the potential becomes positively infinite by a law repulsive as e^2/r. As both types were found to give approximately the same result, we shall discuss only the first, which, according to Born's new theory,[6] should be more nearly correct than an exact Coulomb field. A first order perturbation method, by using the Dirac wave functions, was applied to the $n=l$ level and yielded appreciably the same results as the ordinary Schrödinger functions. The latter were then used to compute the displacements of the energy levels as functions of a. It was readily seen that the s levels were raised by an amount $2a^2e^2/3n^3r_0^3$ equivalent to the introduction of a quantum defect $n-n^*=a^2e^2/3Rhr_0^3$. Here R is the Rydberg constant and r_0 is the radius of the innermost Bohr orbit. This results in a narrowing of the doublets in agreement with experiment. The converse effect of a broadening of the doublets would be difficult to account for, but fortunately does not occur. Combining the relative shifts of the fine structure components of $H\alpha$ in accordance with the Sommerfeld-Unsöld intensity ratios, new centers of gravity were obtained for the doublet humps. One remains almost fixed and the other moves in by about 40 percent of the computed displacement of the $2s$ energy level, or about $a^2e^2/30r_0^3$. All the doublets are narrowed by approximately this amount in agreement with the results

---

[1] Kent, Taylor and Pearson, Phys. Rev. **30**, 266 (1927).

[2] W. V. Houston, Astrophys. J. **64**, 81 (1926).

[3] Spedding, Shane and Grace, Phys. Rev. **44**, 58 (1933).

[4] Houston and Hsieh, Bull. Am. Phys. Soc. **8**, No. 6, p. 5, Nov. 24, 1933.

[5] Cf., e.g., Ruark and Urey, *Atoms, Molecules, and Quanta*, p. 49; H. Jensen, Zeits. f. Physik **82**, 794 (1933).

[6] M. Born, Nature **132**, 282 (1933).

[7] G. H. Shortley, Phys. Rev. **38**, 120 (1931).

of Houston and Hsieh. The value of a determined by this method using the estimate of 3 percent for the displacements to be accounted for, is about 5×10^{-12} cm. The hypothesis of a positively infinite potential decreases a to about 4×10^{-12} cm.

The values of a are surprisingly large but could not be reduced to the classical electron radius of 2×10^{-13} cm by any modification of the experimental results which did not affect the order of magnitude of the recently discovered discrepancies.

E. C. Kemble
R. D. Present

Harvard University,
December 2, 1933.

The Infrared Spectrum of Heavy Ammonia—ND_3

The writers have made an investigation of the infrared absorption spectrum of ND_3, using a rocksalt prism spectrometer. The sample used was very kindly supplied to us by Professor H. S. Taylor, and was prepared from heavy water estimated to be 99 percent pure. The ammonia sample was estimated to be more than 90 percent ND_3, and the absorption spectrum gave no bands characteristic of ordinary ammonia. By following the procedure of Dennison[1, 2] it is possible to calculate the positions of the fundamental vibrations of this molecule, assuming that the force fields are similar, and that the interatomic distances are the same for the two isotopes. The agreement between observed and calculated values is about as good for the ND_3 as for the values calculated and observed in the literature for the NH_3.[3] These are given in Table I. The spectrum should consist of four bands (of the six possible modes of vibration, two are doubly degenerate), in two of which the change in moment should be perpendicular to the symmetry axis. In the NH_3, the bands at 950 cm^{-1} and 3336 cm^{-1} have been assigned to the parallel vibrations, and the bands at 1631 cm^{-1} and 4417 cm^{-1} are the two fundamental perpendicular vibrations. Of the four bands observed for ND_3, the similarity in the structure of the envelopes of the bands to the corresponding frequencies of NH_3 holds extremely well, and in each case indicates the predicted type of vibration.

Table I.

Light ammonia NH_3				Heavy ammonia ND_3			
ν	Calc.	Obs.	Type	ν'	Calc.	Obs.	Type
ν_3	938	950	$\parallel$	$\nu_3'=0.762$	$\nu_3=715$	770	$\parallel$
ν_2	1679	1631	$\perp$	$\nu_2'=0.708$	$\nu_2=1189$	1158	$\perp$
ν_1	3336	3336	$\parallel$	$\nu_1'=0.715$	$\nu_1=2385$	2421	$\parallel$
ν_4	4466	4417	$\perp$	$\nu_4'=0.742$	$\nu_4=3334$	3287	$\perp$

The writers are continuing this investigation with a grating spectrometer of higher resolution and further details concerning the rotational structure of the bands will be presented in the future.

The writers are much indebted to Professor H. S. Taylor and Dr. H. Eyring and their co-workers at Princeton University for their kindness in supplying the compound.

S. Silverman
J. A. Sanderson

Physical Laboratory,
The Johns Hopkins University,
December 2, 1933.

---

[1] Dennison, Phil. Mag. **1**, 195 (1926).

[2] Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[3] Schaefer and Matossi, *Dasultrarote Spektrum*, p. 251.