

Large Electronic Isotope Effects in Molecular Spectra

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The large electronic isotope effect in the spin coupling of ${}^2\Pi$ -terms, reported by Johnston and Dawson for boron monoxide and for the heads of the OH^2 bands is confirmed by measurements of the fine line structure in the isotopic OH bands. Both for BO and for OH the observed increase in the doublet spacings, in the molecule with the heavier isotope, agrees closely with the results to be expected from Hill and Van Vleck's theoretical treatment of spin coupling energy, although their equations do not so well reproduce the separate doublets. This isotope effect is zero at the band origins, increases to a maximum (which amounts to 20

cm^{-1} in the $0''$ vibrational level of OH) and approaches zero asymptotically at high rotational quantum numbers. A large electronic isotope effect in Λ -doubling is also observed for OH. This effect, which is zero at the band origin and increases with increasing rotation, amounts to 17 cm^{-1} at $K=25$. It is not correctly accounted for by Van Vleck's equations for Λ -doubling although ratios of the Λ -doublets in OH^1 and OH^2 are correctly given, for a case b molecule. No noticeable effect was observed on the spacings of the ${}^2\Sigma$ -doublets in the excited state of OH.

IN the conventional treatment of the isotope effect in molecular spectra only vibrational and rotational effects are regarded as significant. Electronic effects have been sought in shifts in the origins of band systems but in the few instances in which some evidence of such a shift has been found the effect has usually amounted to only a few hundredths of a wave number and has been scarcely beyond the limits of experimental error.

Some time ago Johnston and Dawson¹ reported the presence of a large electronic shift (amounting to approximately 10 cm^{-1} in the lines at the head of the (1,0) band) in the spectrum of O^{16}H^2 and mentioned that the effect may also be observed, although to a lesser degree, in the spectrum of boron monoxide. This effect results from the influence of atomic mass on the energy of coupling in the ${}^2\Pi$ -terms of these molecules. The spacings of these spin doublets are *wider* for the *heavier* molecules in contrast to the usual isotopic influence on the vibrational and rotational spacings.

We now wish to present this more fully with the additional evidence gained from the analysis

of the fine structure² of the individual bands of O^{16}H^2 . We also find a large electronic isotope effect (amounting to 17 cm^{-1} at $K=25$) associated with the separation of the components of the Λ -doublets in the normal state of OH.

The isotopic effects on the spacings of the spin components associated with the ${}^2\Pi$ -electronic terms for BO and for OH, respectively, are plotted in Figs. 1 and 2. The experimental values

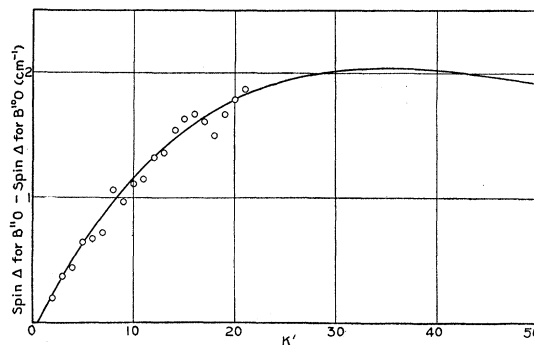


FIG. 1. Isotope effect in the width of the ${}^2\Pi$ -components of BO. Full line, theoretical curve; circles, observed values (computed from the data of Jenkins and McKellar).

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

² Unpublished work of Johnston and Dawson, based on photographs obtained by Dawson with water containing 35 percent heavy hydrogen furnished by Professor G. N. Lewis.

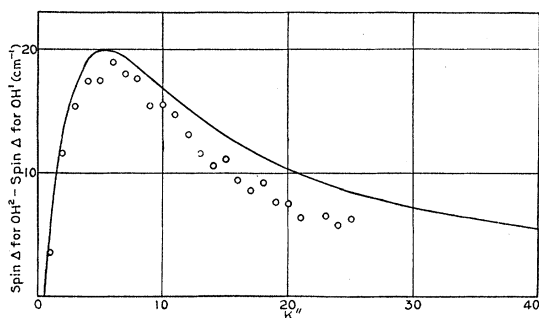


FIG. 2. Isotope effect in the width of the ${}^2\Pi$ -components of OH. Full line, theoretical curve; circles, observed values (unpublished data of Johnston and Dawson).

of the isotope effect, plotted as circles, are calculated from the data of Jenkins and McKellar,³ for BO, and from the unpublished data of Johnston and Dawson, for $O^{16}H^2$.⁴ The continuous curves in Figs. 1 and 2 are the theoretical values for the isotope effect and were constructed through the use of Eq. (9) of Dawson and Johnston,⁵ which is a convenient way of expressing the Hill and Van Vleck relationship.⁶ Attention is called to the fact that this equation does not accurately reproduce the spin doublet spacing of either isotopic molecule, for either BO or OH, although the disagreement in this respect is much less for BO. Hence the perfect agreement with the experimental values for BO and the near agreement with OH is more than we could have expected. As the curves (together with the theoretical equation) show, the spin doublet isotope effect is zero at the band origin, rises rapidly to a maximum and again approaches zero asymptotically at high quantum numbers.

Figs. 3 and 4 show the presence of the large Λ -coupling electronic isotope effect, in the ${}^2\Pi_{3/2}$ -state (Fig. 3) and in the ${}^2\Pi_{1/2}$ -state (Fig. 4). In these figures the upper curves, with the black circles to represent the experimental data, give the full Λ -widths for $O^{16}H^1$ while the white circles represent the experimental data for $O^{16}H^2$.

³ Jenkins and McKellar, Phys. Rev. **42**, 464 (1932).

⁴ We employ the data of the (1, 0) band, of OH, because the lines of that band fall in a good region for measurement and are not often obliterated. We have similar data from several other bands which agree well with that from the (1, 0) band.

⁵ Dawson and Johnston, Phys. Rev. **43**, 980 (1933).

⁶ Hill and Van Vleck, Phys. Rev. **32**, 250 (1928).

The experimental points along the upper curves are average values for the (2,0), (1,0) and (0,0) levels while the white circles, as in Fig. 2, are based on the (1,0) band.

Van Vleck⁷ gives a theoretical expression for Λ -doubling but his equation fails to fit, for OH, by quite a large factor.⁵ It also fails to give the proper *differences* between the Λ -doublets of $O^{16}H^1$ and $O^{16}H^2$. However, we find that Van Vleck's equation for a case "b" molecule will give nearly the correct *ratios* of the Λ -doublets, for a common value of the rotational quantum number. This ratio, which reduces to the inverse square of the ratio of the moments of inertia of the isotopic molecules, is about 0.284 for OH.

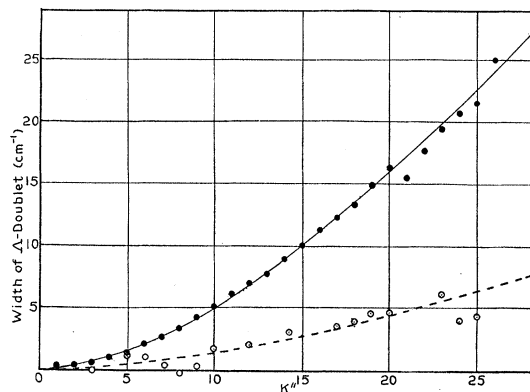


FIG. 3. Isotope effect in the Λ -doublets of the ${}^2\Pi_{3/2}$ -level of OH. Black circles, observed Λ -doublets in $O^{16}H^1$ [averages of the (2,0), (1,0) and (0,0) bands]; full line, smooth curve through the data; open circles, observed Λ -doublets in $O^{16}H^2$ [from the (1,0) band]; dotted line, constructed from the data for $O^{16}H^1$ by using the B_0^2 ratio.

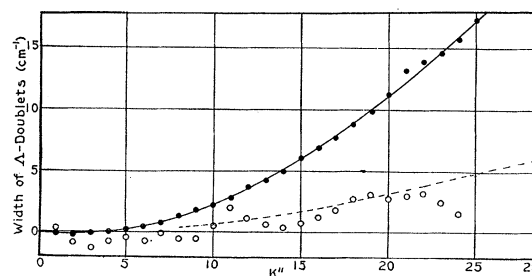


FIG. 4. Isotope effect in the Λ -doublets of the ${}^2\Pi_{1/2}$ -level of OH. Black circles, observed Λ -doublets in $O^{16}H^1$ (averages); full line, smooth curve through the data; open circles, observed Λ -doublets in $O^{16}H^2$ ($1',0''$) band; dotted line, constructed from the data for $O^{16}H^1$ by means of the B ratios.

⁷ Van Vleck, Phys. Rev. **33**, 467 (1929).

The curves with broken lines were constructed from the smoothed data for $O^{16}H^1$ (represented in the continuous curves) by reducing the latter by the factor 0.284.

The isotope shifts in the spectrum lines are one-half of the isotope effects on the doublets width since the separate components of the

doublets are each shifted nearly symmetrically from their common center of gravity. The shifts in the spectrum lines may be either positive or negative in sign, depending upon the arrangement of the levels involved in the transition.

No appreciable isotope effect was observed in the separation of the components of the $^2\Sigma$ -level.