Mass Ratio of Hydrogen and Deuterium from Band Spectra

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The size of the several corrections to the observed, apparent B_e constants of the usual rotational energy expression in order to obtain "true" B_e values is calculated for some diatomic hydride and deuteride molecules. It is shown that the corrections arising from the uncoupling terms due to the interaction of certain electronic levels (Van Vleck, Mulliken) and from the inclusion of the interactions between nuclear and electronic motions (Kronig) are by far the most important for the molecules considered. The calculations also show that, assuming 1.0081 to be the mass of the hydrogen atom, the mass of deuterium has to be greater than the 2.01423 value given in a number of recent articles. A value close to Aston's latest, 2.0148, is indicated.

THE investigation of the hydrogen isotope effect in the spectra of several diatomic hydride molecules[1–8] has shown that the constants B_e of the usual rotational energy expressions for the two isotopic molecules are never exactly in the ratio of their reduced masses. To explain this failure of the simple isotope theory one or more of the following effects have been mentioned with varying emphasis in each case:

(a) Quantum-mechanical interaction of the electronic level in question with other electronic levels of the molecule gives rise to uncoupling terms[9] which make the apparent B (Mulliken's B^*) different from the real B.[10]

(b) Inclusion of the usually neglected interactions between nuclear and electronic motions in the calculation of the effective potential function makes the equilibrium distance between the nuclei depend slightly upon the reduced mass of the molecule under certain conditions.[11]

(c) Small corrections to the observed B_e^* come from the higher order anharmonic terms because of the interaction of vibration and rotation.[12]

(d) The rotation of a few of the outermost electrons may have to be treated independently of the nuclear rotation, thereby causing an additional contribution to the moment of inertia of the molecule.[1, 13]

These corrections may be considered to be effectively independent of each other. We list them in the order of decreasing importance for most of the molecules. To support this statement and to aid in clearing up the confusion in the literature as to the relative magnitude of these reasons for the discrepancy between the B_e ratios and the ratios of the reduced masses, we shall discuss briefly the size of the corrections for some of these hydride and deuteride molecules. Of some interest also is the indicated maximum value for the ratio of the masses of the H and D atoms.

For the normal $^2\Sigma$ state of BeD, which has negligible spin doubling, the observed, apparent B_e ($=Y_{01}$ in Dunham's notation) is 5.6807, the corresponding quantity for BeH being 10.308. The ratio of these B's is 0.55110, whereas ρ^2, the ratio of the two reduced masses, is 0.55062. In calculating this ρ^2 we use the atomic weights 9.011, 1.0081 and 2.0148 for Be, H and D, respectively, the values for H and D being those recently obtained by Aston.[14] Application of the anharmonic corrections (c) (Dunham's Eqs. (15) and (19)) changes these B values to 5.6812 and 10.3095 which have the ratio 0.55106. This is but a small reduction of the total discrepancy. A considerably larger correction comes from effect (a), for which the q coefficient for the Λ-doubling of the interacting Π state is to be added to the observed B^* to give the "true" B.[10] For BeD $q_0=0.0043$, while for BeH $q_0=0.0142$. Addition of these quantities raises the B values to 5.6855 and 10.3237 giving a ratio 0.55072.

The difference between this ratio and that of

[1] W. Holst and E. Hulthén, Zeits. f. Physik **90**, 712 (1934). (AlH)
[2] W. W. Watson, Phys. Rev. **47**, 27 (1935). (CaH)
[3] E. Olsson, Zeits. f. Physik **93**, 206 (1935). (NaH)
[4] E. Svensson, *Die Bandenspektren des CdH und CdD* (Stockholm, 1935).
[5] F. H. Crawford and T. Jorgensen, Jr., Phys. Rev. **47**, 358, 932 (1935). (LiH)
[6] P. G. Koontz, Phys. Rev. **48**, 138 (1935). (AgH)
[7] E. Hulthén and E. Knave, Zeeman Jubilee Volume of Physica (1935). (AgH)
[8] P. G. Koontz, Phys. Rev. **48**, 707 (1935). (BeH)
[9] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).
[10] R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87 (1931).
[11] R. de L. Kronig, Physica **1**, 617 (1934).
[12] J. L. Dunham, Phys. Rev. **41**, 721 (1932).
[13] L. Hulthén, Nature **135**, 543 (1935).
[14] F. W. Aston, Nature **135**, 541 (1935).

the reduced masses may be further decreased by consideration of effect (b). Incidentally, both (a) and (b) involve the perpendicular components of the angular momentum of the electrons, but they are not the same. Kronig[11] shows that (b) introduces a correction term $\bar{U}(r)$ to the potential function given by

$$\bar{U}=\frac{h^2}{8\pi^2\mu}\left[\frac{L(L+1)}{r^2}+\Sigma\int\left(\frac{\partial\Phi}{\partial r}\right)^2 d\tau\right], \quad (1)$$

where L is the orbital angular momentum for the atom imagined to be formed by uniting the two atoms, r is the internuclear distance and Φ the electronic part of the wave function. The first term in (1) produces a difference in the equilibrium distance between the nuclei for the two isotopic molecules given by the difference Δr_1 in the correction

$$r_1=(h^2/8\pi^2\mu)2L(L+1)/fr_0^3 \quad (2)$$

for the two. In (2) f is the force constant for the vibrations. Computation of r_1 for BeD as against BeH (L for the "united atom" has the value 1) yields $\Delta r_1=0.63\times10^{-12}$ cm, r_1 being less for the heavier molecule. A difference in the equilibrium internuclear distance for the two molecules of 1.22×10^{-12} cm in this same sense would account for the whole of the discrepancy between the ratio 0.55072 and the mass ratio 0.55062. The first term of (1) thus accounts for half of this difference. The small remainder might well represent the effect of the second term in (1) which involves the perturbation of this state of BeH by other near-lying states and is of the same sign as the first term.

There is then at the most but very slight discrepancy between this legitimately corrected B_e ratio and the ratio of the reduced masses to be explained by any such effect as (d). Furthermore, if (d) were important, about the same discrepancies should exist for all the hydrides, whereas Koontz finds[6, 8] for BeH^+/BeD^+ and AgH/AgD considerably smaller deviations from mass ratios. This would follow from (b), since for both of these molecules $L=0$. These observed small differences would certainly also be reduced by consideration of (a), the second term in (1) and, in the case of BeH^+, effect (c). It should be emphasized that the observed B_e's are always B_e*'s, for the uncoupling terms are always at least incipiently present.

In the calculation of the reduced mass Casimir[15] has shown that it is proper to include the masses of the electrons in closed shells with the mass of the nucleus. The hydrogen electron, however, will be somewhat shared with the heavier atom. If BeH in its lowest state has a dipole moment as large as that of HCl, something like one-fifth of the H electron[16] may be considered to be associated with the Be atom. Adding one-fifth of the mass of an electron to that of the Be atom and subtracting it from that of the H or D atoms merely reduces ρ^2 to the value 0.55059, which would not affect our conclusions appreciably.

Accepting the value 1.0081 for the mass of the hydrogen atom, that of deuterium should be 2.01423 according to the mass-spectrograph measurements of Bainbridge.[17] These masses together with the value 9.011 for Be make $\rho^2=0.55075$. This mass ratio is so much higher than the ratio of the corrected B constants as to seem quite impossible. The corrected B ratio is consistent with the higher value 2.0148 for the deuterium mass, as outlined above, but of course cannot be used to indicate any exact value for this quantity.

Similar calculations on these ratios may be made for AlH/AlD. The observed B_e* values[1] for the normal $^1\Sigma$ state are 6.3962 and 3.3185. Correcting for effect (a) from the known Λ-doubling raises these to 6.4040 and 3.3208, which have the ratio 0.51855. The anharmonic corrections only drop this ratio to 0.51854. Taking the mass of the Al atom to be 26.97 and the masses of H and D as 1.0081 and 2.0148, respectively, as before, $\rho^2=0.51835$. The discrepancy between this mass ratio and the ratio 0.51854 for the B_e constants could be accounted for if the equilibrium internuclear distance for AlD were 3.0×10^{-12} cm smaller than for AlH. Now the difference between r_1 for the two molecules as calculated from (2) is 2.6×10^{-12} cm, AlD having the smaller r_e. The effect of the second term in (1) could well account for the

[15] H. Casimir, Physica **1**, 1073 (1934).
[16] J. D. Hardy, E. F. Barker and D. M. Dennison, Phys. Rev. **42**, 279 (1932).
[17] K. T. Bainbridge, Phys. Rev. **44**, 56 (1933).

remainder of the discrepancy, and so (d) would seem to have little validity. If the mass of deuterium is taken as 2.01423 and the other masses as before, the reduced mass ratio is 0.51849. Again this is considerably higher than the B_e ratio when the corrections (a), (b) and (c) have all been made to the observed B_e^* values.

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Mass Ratio of the Lithium Isotopes from the Spectrum of Li_2

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It is shown from a study of the $^1\Sigma \rightarrow {}^1\Sigma$ Li_2 band system that the relative masses of the two isotopes of Li as calculated from the observed isotope effect in each of the two lowest states of Li_2 is in excellent agreement with the mass ratio obtained by other precise methods. Various methods of treating the data lead consistently to the conclusion that the mass-coefficient ρ is 1.04077 ± 0.00004 and that the mass ratio is 1.16640 ± 0.00016. This result disagrees with that of McKellar and Jenkins who, from a less extensive study of the $^1\Pi \rightarrow {}^1\Sigma$ system of Li_2, concluded that the mass ratio was 1.1678 ± 0.0008, a result which cast suspicion upon the band spectrum method of determining relative atomic masses. There has also been found a small but definite electronic isotope shift: $\nu_e{}^i - \nu_e = -0.064 \pm 0.010$ cm^{-1}.

THE accuracy of the band spectrum method of determining the mass ratio of isotopes has been called in question by two series of investigations. First, a consistent ratio of the masses of H^2 and H^1 has not been obtained when the simple theory of the isotope shift has been applied to measurements on various hydrogen and hydride band systems. On account of the large change of reduced mass in these instances, they form a rather special case. Although this problem is not yet completely solved, sufficient reasons for the discrepancies have been advanced from various quarters, by Kronig,[1] by Dieke[2] and by Holst and Hulthén.[3] Second, McKellar and Jenkins[4] have found from measurements on the blue-green system of Li_2 bands ($^1\Pi \rightarrow {}^1\Sigma$) that the mass coefficient $\rho (= (\mu/\mu^i)^{\frac{1}{2}}$, where μ is the reduced mass of $Li^7\,Li^7$ and μ^i that of $Li^7\,Li^6$) and, therefore, the mass ratio of Li^7 to Li^6 are greater by several times the estimated probable errors than the corresponding quantities as determined by Bainbridge[5] who used the mass spectrograph. The latter have been corroborated by the recent extremely precise determinations of Oliphant, Kempton and Rutherford[6] who used the data from certain nuclear transformations. The comparison is given in Table IV. Since in some cases, notably that of oxygen, the mass ratio of the isotopes has been determined only from the band spectrum, it is worth while to examine the apparent discrepancy in the case of lithium, by determining spectroscopically the mass ratio of Li^7 to Li^6 under the more favorable conditions existing in the red band system of Li_2. This system has been analyzed by Wurm,[7] but the constants of $Li^7\,Li^7$ were not determined with great precision, and the constants of $Li^7\,Li^6$ not at all.

In a recent Letter to the Editor of this journal[8] we showed that the mass ratio of the Li isotopes calculated from the molecular constants obtained from a study of the $(v',0)$ progression of the red $^1\Sigma \rightarrow {}^1\Sigma$ system of Li_2 was in good agreement with the mass ratio obtained by other methods. Since the most accurate value of ρ came from the vibrational constant ω_e of the

[1] R. de L. Kronig, Physica **1**, 617 (1934).
[2] G. H. Dieke, Phys. Rev. **47**, 661 (1935).
[3] Holst and Hulthèn, Zeits. f. Physik **90**, 712 (1934).
[4] F. A. Jenkins and A. McKellar, Phys. Rev. **44**, 325 (1933); A. McKellar, Phys. Rev. **44**, 155 (1933).
[5] K. T. Bainbridge, Phys. Rev. **44**, 56 (1933).
[6] M. L. E. Oliphant, A. E. Kempton and Lord Rutherford, Proc. Roy. Soc. **A149**, 406 (1935).
[7] K. Wurm, Zeits. f. Physik **59**, 35 (1929).
[8] G. M. Almy and G. R. Irwin, Phys. Rev. **48**, 104 (1935).