FIG. 3. Schematic representation of the pure rotation spectra of NH_3 and ND_3. Intensities as shown are only approximate.

applicable to the symmetric rotator type. Dr. W. S. Benedict has shown that additional terms in the cubic formula are necessary, and are particularly important in ND_3. Since the present experimental results are not accurate enough to test this point, details will be reserved for a later time. For the present, the simple formula is taken, with $D_{ND_3} = \frac{1}{4}D_{NH_3}$; the resulting value of $B_{ND_3} = 5.13$. From this and $B_{NH_3} = 9.94$, the height of the pyramid may be calculated, since $1/B \sim I$ and

$$I_{NH_3} = (3/2)m_H a^2 + \frac{3m_H m_N}{m_N + 3m_H}q^2$$

and

$$I_{ND_3} = (3/2)m_D a^2 + \frac{3m_D m_N}{m_N + 3m_D}q^2,$$

where a is the distance from the symmetry axis to an H or D atom, and q is the height. Solving, we find $q = 0.36A$, $r_{N-H} = a^2 + q^2 = 1.02A$. The accuracy of this result is not high, but the agreement with the value calculated indirectly, $0.37A$, is good.[6]

Fig. 3 shows schematically the relative positions of the rotation lines of the two symmetrical ammonias.

The author wishes to express his appreciation to Drs. C. M. Lewis and W. S. Benedict who aided greatly in making these measurements, and to Professor Taylor and Dr. J. C. Jungers who prepared the heavy ammonia.

[6] Manning, J. Chem. Phys. 3, 136 (1935).

On Isotopic Shifts in the Spectra of Diatomic Molecules

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An inspection of the theory of diatomic molecules shows that the elementary theory of the dependence of the energy of diatomic molecules on the mass of the nuclei must be supplemented in two ways. In the first place the reaction of the nuclei to the precession of the electronic angular momentum about the internuclear axis gives a term

$$[B_e - \alpha(V + \tfrac{1}{2})][L(L+1) - \Lambda^2].$$

Furthermore there is a second positive term of uncertain magnitude. Both these terms are of importance only for very light molecules especially for the hydrogen molecule. The large electronic shifts observed for some band systems of H_2, HD and D_2 are well accounted for by this theory. A very accurate comparison of the constants of very light isotopic molecules necessitates also taking into account small corrections which appear in the higher order approximations of the energy values for a rotating anharmonic oscillator.

THE study of the spectra of molecules in which one or more of their atoms are substituted by the corresponding isotope can often furnish information about the structure of the molecule which cannot at all, or only with difficulty, be obtained in any other way. This is especially true for those molecules in which a hydrogen atom is replaced by its heavy isotope deuterium, because for this substitution the relative change in the masses is so much greater than for all other isotopic substitutions. In order to make full use of the material which can be obtained in this way it is necessary to know

exactly the changes which must be expected in the structure of the corresponding energy levels and wave functions. The approximate theory which was hitherto quite adequate to give a satisfactory account of all the changes as long as only heavy atoms were concerned is not able to explain all the details for proton deuteron substitutions. Kronig[1] called attention to the fact that if certain terms in the Hamiltonian of a diatomic molecule which are usually omitted are taken into account, there is for many states a slight difference in the equilibrium distance even for the

[1] R. de L. Kronig, Physica 1, 617 (1934).

nonvibrating and nonrotating molecule. It is very difficult to prove such a difference experimentally, and it is very doubtful whether the effect discussed by Kronig is the cause for the discrepancies found by Holst and Hulthén[2] in the spectrum of AlH and AlD.

An investigation of the spectra of H_2, HD and D_2 must be expected to give the most detailed empirical information about the deviations from the elementary theory, as these deviations are all inversely proportional to the mass and therefore especially large for these light molecules. It is found that there are large electronic isotope shifts up to 25.6 cm^{-1}. The electronic isotope effect usually is understood to be the shift in the electronic frequency of a band system when one isotope is substituted for another. The electronic frequency is the frequency which the nonrotating and nonvibrating molecule would emit. It does not correspond to an actual line but can be obtained by extrapolation from the observed band lines of the system. In the following it is shown that shifts of this magnitude are demanded by theory. Furthermore, it is shown which terms have to be considered in order to find out a more accurate expression for the dependence on the molecular mass of the vibrational frequency and other constants.

§1.

We shall restrict ourselves to the nonrotating molecule. The vibrational energy is then determined by

$$\left[\frac{h^2}{8\pi^2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - V_e(r) + W^0\right]R(r) = 0, \quad (1)$$

in which $R(r)$ is the vibrational eigenfunction and $V_e(r)$ the potential energy for fixed nuclei. If the electronic wave function for fixed nuclei is Φ, the total wave function for the nonrotating molecule is

$$\psi = \Phi \cdot R. \quad (2)$$

(1) and (2) are valid only approximately, as certain terms of the complete Hamiltonian have been neglected.[3] We can introduce these terms

now as perturbations with the perturbation function H' such that

$$H'\psi = \frac{h^2}{8\pi^2\mu r^2}\left[(\mathbf{M}_\xi^2 + \mathbf{M}_\eta^2)\Phi - r^2\frac{\partial^2\Phi}{\partial r^2}\right]R; \quad (3)$$

$\mathbf{M}_\xi$, $\mathbf{M}_\eta$, $\mathbf{M}_\zeta$ are the components of the orbital angular momentum[4] with respect to axes fixed to the molecule. (The ζ axis is the internuclear axis.) We shall consider in this paper only the first term in this expression. For an evaluation of the influence of the second term a knowledge of the Φ would be necessary. The empirical data seem to show that its influence for the two levels for which sufficiently accurate data are available is small compared to that of the first term.

The influence of (3) on the energy is in the first approximation

$$W_1' = \int \bar{\psi}H'\psi dv = \int \bar{R}Rdr\int \bar{\Phi}H'\Phi dv'. \quad (4)$$

We have

$$(\mathbf{M}_\xi^2 + \mathbf{M}_\eta^2)\Phi = (\mathbf{M}^2 - \mathbf{M}_\zeta^2)\Phi$$

$$= [L(L+1) - \Lambda^2]\Phi, \quad (5)$$

in which $\mathbf{M}$ is the operator corresponding to the total orbital momentum. L is the quantum number corresponding to this operator and Λ that corresponding to $\mathbf{M}_\zeta$. (5) is correct only if the angular momentum is constant. This will be the case especially for higher levels of light molecules, but (5) can be expected to be a fairly good approximation also for most other molecular levels. The contribution of the first term in (3) to the energy is therefore, if we take for r its equilibrium value, $B_e[L(L+1) - \Lambda^2]$. To obtain a better approximation, we remember that (4) means averaging over the electronic motion and the nuclear vibrations. The averaging over the electronic motion is taken care of by (5), whereas the averaging over the nuclear vibrations concerns only the quantity $B = h/8\pi^2\mu r^2$. This same average occurs when the rotational energy of a rotating oscillator is calculated and its value is

[2] W. Holst and E. Hulthén, Nature 133, 496 (1934); Zeits. f. Physik 90, 712 (1934).

[3] J. H. Van Vleck, Phys. Rev. 33, 467 (1929). See also R. de L. Kronig, *Band Spectra and Molecular Structure*, Cambridge, 1930.

[4] We restrict ourselves then to singlet levels, as in general $\mathbf{M}$ is the *total* angular momentum. We can nevertheless apply the results obtained in this way to the triplet bands of hydrogen, as in this case the spin is so loosely coupled to the rest of the molecule that for all practical purposes the properties of the triplet levels are the same as those of singlet levels.

$B_e - \alpha(V + \frac{1}{2}) + \cdots$. It is essential for this that the deviations from harmonic oscillations are taken into account, for otherwise α would have the same order of magnitude but opposite sign. The contribution of the first term in (3) to the energy is thus

$$W_1' = [B_e - \alpha(V + \tfrac{1}{2})][L(L+1) - \Lambda^2]. \quad (6)$$

The part independent of the vibrational quantum number V would in the usual empirical analysis of the energy levels of a diatomic molecule be classed with the electronic energy. It differs however from it because it depends on the mass of the nuclei and does not occur in the energy of the molecule with fixed nuclei. Its physical significance is that it represents the reaction of the nuclei to the precession of the electronic angular momentum about the internuclear axis. (3) shows that it is proportional to the square of the component of the angular momentum perpendicular to the internuclear axis, and it is evident that this must be present also for the nonvibrating and nonrotating molecule. The magnitude of this term can be easily calculated as all the constants are known from the rotational and vibrational analysis of the corresponding bands. The term is zero only for $S\Sigma$ levels. As this and all other similar terms are proportional to B it is evident that they are most significant for the hydrogen molecule because on account of the light masses of the hydrogen nuclei B is so much larger than for any other molecule.

§2.

COMPARISON WITH EXPERIMENTAL VALUES

It is obvious that the constant part of (6) cannot be separated from the true electronic energy if only the H_2 levels were known, but if also the corresponding HD or D_2 levels are known the two parts can be determined separately. There are in the spectrum of the hydrogen molecule two levels which are analyzed with sufficient detail and accuracy to allow an experimental test of the above formula. These are the $3p^3\Pi$ level[5] for which $L = 1$ and $\Lambda = 1$ and the $3p^3\Sigma$ level[6] for which $L = 1$ and $\Lambda = 0$. The observed origins of

[5] G. H. Dieke and R. W. Blue, Phys. Rev. **47**, 261 (1935).

[6] G. H. Dieke, to appear shortly in Phys. Rev.

the band systems corresponding to transitions from these two levels to $2s^3\Sigma$ are:

	H_2	HD	D_2
$3p^3\Pi \to 2s^3\Sigma$	16,793.87	16,788.86	16,783.92
$3p^3\Sigma \to 2s^3\Sigma$	11,838.91	11,825.68	11,813.40

The observed shifts and those calculated from (6) are:

	$H_2 - HD$		$HD - D_2$	
	obs.	calc.	obs.	calc.
$3p^3\Pi \to 2s^3\Sigma$	5.01	7.55	4.94	7.61
$3p^3\Pi \to 2s^3\Sigma$	13.23	13.44	12.28	12.62

It is difficult to judge the accuracy of the observed origins. They must be obtained by extrapolation from many observed lines and there is always the danger of systematic errors of uncertain magnitude if the formula used is not a sufficiently good approximation. The uncertainty due to errors in the measurements is only a few hundredths of a wave number and it is estimated that the total uncertainty is not more than one wave number, probably much less. The only exception is perhaps the value for the origin of $3p^3\Sigma \to 2s^3\Sigma$ of H_2 for which Richardson's value was taken which was computed from less complete data, and may have therefore possibly a larger error.

It is seen that the general agreement between the empirical and theoretical values is very satisfactory, which shows that very probably the largest part of the observed shifts is given by (6). In particular the isotopic shifts have the right sign and the shift for the $p^3\Sigma$ levels is about twice that of the $p^3\Pi$ level as it should be.

As a rule there is no difficulty in finding the Λ value for a given electronic level from the structure of the bands in question. To find the L values is much more difficult and requires a much more complete knowledge of the whole spectrum. With the isotope effect discussed here·it may be often possible to fix the L-values in cases of doubt.

The remaining discrepancies between the observed and calculated values may be partly due to the neglected second term in (3). This term must also be positive, but there is no reason why it should be zero for $s\Sigma$ states. It must be expected that its contribution will be larger for the lower states, so that the difference between the contribution of the initial and final state which

enters into the band origins will be negative. The corrections due to the second term in (3) have therefore the right sign to reduce the discrepancies between the above theoretical and observed values.

There are two other band systems of hydrogen for which at present there are sufficient data for a calculation of the electronic shifts. They are the ultraviolet band systems $2p^1\Pi\rightarrow1s^1\Sigma^7$ and $2p^1\Sigma$ $\rightarrow1s^1\Sigma$.[8] The difference between the H_2 and HD origins of both systems has the opposite sign from that of the two visible systems. The values of the shifts are 8 cm^{-1} for $2p^1\Pi\rightarrow1s^1\Sigma$ and 12 cm^{-1} for $2p^1\Pi\rightarrow1s^1\Sigma$ with a probable error of about 5 to 10 cm^{-1}. If these values are correct it shows that the second term in (3) must be much larger for the normal state $1s^1\Sigma$ than for any excited state, so that it can compensate for the positive shifts due to the first term in (3) which are of the same order of magnitude as those found for the visible bands. Such an assumption does not seem altogether improbable.

For the lines of the hydrogen and deuterium atoms we find a shift due to the common motion of nucleus and electron about the center of gravity. It is 8.25 cm^{-1} for $H\alpha$ and 44.5 cm^{-1} for $L\alpha$, the line of the heavier atom having the higher frequency. Such an effect, because of the fact that the center of gravity of the nuclei and electrons do not coincide, is not taken into account in Van Vleck's treatment of diatomic molecules on which the foregoing considerations are based. It must be expected, however, to be much smaller for systems with more than one electron. The motion which the center of gravity of the nuclei executes because of the motion of one electron is at least partly counterbalanced by the motion of the second electron. Therefore the total effect will be much smaller. This is analogous to the fact that the energy level series of the helium atom are best represented with the Rydberg constant for an infinite mass and not with that for a mass four.

§3.

THE EFFECT ON THE VIBRATIONAL FREQUENCY

The term linear in $V+\frac{1}{2}$ of (6) has the effect that the frequency ω_e calculated according to

(2) with $V_e(r)$ as potential must be diminished by $\alpha[L(L+1)-\Lambda^2]$ in order to obtain the total coefficient ω_e' of $V+\frac{1}{2}$ in the energy formula. ω_e' is the quantity which is determined empirically and usually designated as the vibrational frequency.

In going from one isotope to another ω_e varies with the first power of the transformation coefficient ρ, whereas α varies with the third power.[9] ω_e' which is the quantity empirically determined from the experimental data varies, therefore, not exactly with ρ but should show slight variations. A rigorous experimental proof of this is at present not yet quite possible as the empirical values of the constants are not quite reliable enough. Table I shows the effect of this correction. This

TABLE I.

		HD : H$_2$	D$_2$: H$_2$	D$_2$: HD
$3p^3\Pi$	without corr.	0.86634	0.70764	0.81682
	with α corr.	0.86620	0.70741	0.81668
$3p^3\Sigma$	without corr.	0.86751	0.70881	0.81706
	with α corr.	0.86722	0.70832	0.81676
	calc.	0.86616	0.70744	0.81675

table is given with the intention to show how much these corrections affect the ω_e' ratios rather than to show the agreement with the calculated values of ρ of the last row. The corrections of the next paragraph may be of the same order of magnitude, and it would be necessary to take them into account also if the comparison is intended to be of such a high degree of accuracy. It may be remarked, however, that the agreement between the observed and calculated values for $3p^3\Pi$ is of nearly the same order with and without the corrections. The $3p^3\Sigma$ state offers a better case as the corrections are about twice as big as those for the $3p^3\Pi$ state. The agreement in the first two columns is poor in any case. This is very probably because of a too low ω_e' value for H_2, which was calculated by Richardson and Das[10] from much scantier and less accurate empirical material. The last column shows, however, a much better agreement with the correction than without it.

[7] C. R. Jeppesen, Phys. Rev. 45, 480 (1934).
[8] K. Mie, Zeits. f. Physik 91, 475 (1934).

[9] This statement is subject to the corrections of § 4.
[10] O. W. Richardson and K. Das, Proc. Roy. Soc. A125, 309 (1929).

§4.

CORRECTIONS FOR THE ENERGY VALUES OF THE ANHARMONIC OSCILLATOR

The constants in the familiar expression,

$$\omega_e(V+\tfrac{1}{2}) - x(V+\tfrac{1}{2})^2 + y(V+\tfrac{1}{2})^3 - z(V+\tfrac{1}{2})^3 + \cdots$$

for the vibrational energy of an anharmonic oscillator are according to the elementary theory multiplied by the first, second, third and fourth power of ρ, respectively, in an isotopic substitution. This is true, however, only approximately and if one goes to higher approximations, correction terms have to be added which require a different power of ρ as isotopic transformation factors. These corrections do not show in the formulae which Fues[11] first derived with the wave mechanics because he did not go to high enough approximations, but they are fully given in a treatment by Dunham.[12] If the potential energy is written

$$V(r) = a_0\delta^2[1 + a_1\delta + a_2\delta^2 + \cdots]$$

in which $\delta = (r - r_0)/r_0$; all the constants are supposed to be independent of the nuclear masses. The energy of a rotating oscillator having this potential can be written in the form

$$\sum_{l,\,k} Y_{lk}(V+\tfrac{1}{2})^l[J(J+1)]^k$$

and Dunham gives the first 15 of the coefficients Y_{lk}. A few examples are sufficient to show what kind of corrections appear. If $\beta = B_e/\omega_e$, we have

$$Y_{00} = (B_e/8)(3a_2 - 7a_1^2/4),$$

$$Y_{10} = \omega_e[1 + (\beta^2/4)(25a_4 - 95a_1a_3/2$$

$$- 67a_2^2 + 459a_1^2a_2/8 - 1155a_1^4/64)],$$

$$Y_{01} = B_e[1 + (\beta^2/2)(15 + 14a_1 - 9a_2$$

$$+ 15a_3 - 23a_1a_2 + 21(a_1^2 + a_1^3)/2], \text{ etc.}$$

[11] F. Fues, Ann. d. Physik **80**, 367 (1926).

[12] J. L. Dunham, Phys. Rev. **41**, 721 (1932).

It is not the purpose of the present paper to give an accurate evaluation of these corrections,[13] but a few remarks may show of what order of magnitude they are.

Let us consider first the term Y_{00} which can be considered as a correction to the electronic energy. It can be evaluated with ease if we make use of the approximate expressions

$$Y_{20} = -x = (3B_e/2)(a_2 - 5a_1^2/4),$$

$$Y_{11} = -\alpha = 6B_e\beta(1 + a_1).$$

It is sufficient to give the constants for D_2. They are

	β^{-1}	a_1	a_2	Y_{00}
$2s^3\Sigma$	110.4	-1.59	1.83	2.24
$3p^3\Pi$	110.4	-1.67	2.03	2.34
$3p^3\Sigma$	113.1	-1.70	1.95	1.34

For HD Y_{00} is 1.5 times and for H_2 twice as big as for D_2, which means that the shift between H_2 and D_2 is just equal to the value of Y_{00} for D_2 given in the table. The isotopic shift of the origin of the band systems which is the difference between the shifts of initial and final level is therefore $+0.10$ for $3p^3\Pi \rightarrow 2s^3\Sigma$ and -0.90 for $3p^3\Sigma \rightarrow 2s^3\Sigma$. These shifts, though of sufficient magnitude to be noticeable with accurate observations, are small compared with the effect discussed in §2, and will be in general altogether insignificant for heavier molecules.

The effect of these corrections on ω_e and B_e may be of sufficient magnitude to change appreciably the empirical ratios of these constants for the different hydrogen isotopes and should therefore be taken into account, if an accurate test is made. This will be considered in a later paper.

[13] For a reliable calculation of the constants a_1, a_2, a_3 and a_4 which are all necessary for an evaluation of the correction for ω_e it would be necessary to know accurately some of the constants which occur only as small terms in the empirical expression of the energy. It would be a waste of time to attempt this unless the best available data can be used. As we are still improving constantly the empirical data for the three hydrogen molecules, we are postponing a detailed discussion of all these corrections to a later date.