

On the Isotope Corrections in Molecular Spectra

J. H. Van Vleck

Citation: [The Journal of Chemical Physics](#) **4**, 327 (1936); doi: 10.1063/1.1749853

View online: <http://dx.doi.org/10.1063/1.1749853>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/4/6?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Spectra of isotopic ice mixtures](#)

J. Chem. Phys. **99**, 2332 (1993); 10.1063/1.465248

[A molecular model for dielectric shifts in infrared spectra of pure liquid phases and vapor pressure isotope effects](#)

J. Chem. Phys. **80**, 3087 (1984); 10.1063/1.447122

[Isotope shifts in EPR spectra](#)

J. Chem. Phys. **75**, 1126 (1981); 10.1063/1.442159

[Vibrational, torsional, and librational excitons in molecular crystals: Raman spectra of neat and isotopic mixed durene](#)

J. Chem. Phys. **58**, 126 (1973); 10.1063/1.1678896

[The Microwave Spectra of Isotopic Methyl Chloride](#)

J. Chem. Phys. **18**, 332 (1950); 10.1063/1.1747627



THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 4

JUNE, 1936

NUMBER 6

On the Isotope Corrections in Molecular Spectra

J. H. VAN VLECK, *Harvard University*¹

(Received April 3, 1936)

According to the simple theory of the rigid rotator and harmonic oscillator, the coefficients of $J(J+1)$ and $(v+\frac{1}{2})$ in the energy should be inversely proportional to respectively the reduced mass and the square root thereof. Actually various small corrections, important only in compounds containing hydrogen or deuterium, make the mass dependence slightly different, and hence, at least in principle, explain why spectroscopic observations may yield slightly incorrect mass ratios for isotopes. The corrections are due to four causes (a) anharmonicity, (b) interaction between vibration and electronic motion even when perturbations between different electronic states are neglected, (c) L uncoupling or in other words perturbations between states differing by one unit in Λ , (d) interaction between states of equal Λ . The formulas for the various corrections are collected—some old, some new or more

exact than previously. The relative magnitudes of the different effects are estimated. Incidentally, perturbations between states of equal Λ are studied in general. They should increase in intensity with the vibrational quantum number v , all other things being equal, in contrast to the perturbations due to L uncoupling, which increase with J . The electronic isotope shift, or displacement in the absolute value of the energy is also treated. Here the correction for the motion of the center of gravity of the molecule, usually neglected, is shown to be fully coordinate in importance with other terms. Shifts for ultraviolet lines of hydrogen are calculated with the Wang wave functions, and agree qualitatively with experiment. A concluding section is included on the mean square angular momentum of H_2 , which enters in connection with diamagnetism and the Stern-Gerlach effect.

THE observed energies of singlet states of diatomic molecules are ordinarily represented by a formula

$$W = W_0^* + h\omega^*(v + \frac{1}{2}) + B^*J(J+1) + \dots, \quad (1)$$

where v and J , are respectively, the vibrational and rotational quantum numbers. The coefficients ω^* , B^* , however, do not have exactly the ideal values

$$\omega_0 = (1/2\pi)(a/M)^{\frac{1}{2}}, \quad B_0 = h^2/8\pi^2 Mr_0^2 \quad (2)$$

characteristic of the harmonic oscillator and rigid rotator respectively. The notation M is used for the reduced mass $M_1M_2/(M_1+M_2)$; r_0 is the equilibrium internuclear distance for an

irrotational molecule devoid of centrifugal distortion, and a is identified with the coefficient of the first term of the usual expansion

$$E_n(r) = W_0 + \frac{1}{2}ar_0^2(\xi^2 + a_1\xi^3 + a_2\xi^4 + \dots) \quad (3)$$

of the radial potential energy. Here $\xi = (r - r_0)/r_0$.

Let primes and double primes refer to two different isotopes. Both theoretically and empirically, the ratios $\omega^*/\omega^{*''}$ and $(B^*/B^{*'})^{\frac{1}{2}}$ deviate slightly from the simple value

$$\omega_0'/\omega_0'' = (B_0'/B_0'')^{\frac{1}{2}} = (M''/M')^{\frac{1}{2}} \quad (4)$$

obtained from (2). There are many small corrections which cause B^* , ω^* to differ from B_0 , ω , and which hence make the apparent isotope ratios, as revealed by band spectra, somewhat different from (4). The literature is in a rather confused state regarding their number and

¹ A preliminary account of the present paper was given at the St. Louis meeting of the Am. Phys. Soc., Phys. Rev. 49, 417 (1936).

nature. The purpose of the present paper is to summarize the various correction terms which have been given to date, and especially to present certain additional terms which appear to have previously been overlooked although they may be as large as the others. We must, however, not fail to mention that notable theoretical work on isotope corrections has recently been published by Dieke, and the approximations which he makes are adequate in the examples which he studies. To avoid undue complication, we throughout confine our attention to singlet states.

The corrections are all sufficiently small that they may be considered additive. In other words, if (a) is some effect which, taken by itself, makes B^* acquire a value $B_0(1+\gamma_a)$ different from (2), and if there are other disturbing influences (b), (c), (d), the final formula is

$$B^* = B_0(1 + \gamma_a + \gamma_b + \gamma_c + \gamma_d) = B_0(1 + \gamma). \quad (5)$$

Similarly we can take

$$\omega^* = \omega_0[1 + \delta_a + \delta_b + \delta_c + \delta_d] = \omega_0[1 + \delta]. \quad (6)$$

The apparent isotope ratio $(B^*/B'')^{1/2}$ in the rotational case should differ from (4) by a factor $1 + \frac{1}{2}\gamma' - \frac{1}{2}\gamma''$. In the vibrational isotope effect, the analogous relation is

$$\omega^*/\omega'' = (M''/M')^{1/2}(1 + \delta' - \delta'').$$

The value of δ is not in general the same as that of $\frac{1}{2}\gamma$. Hence the correction factor to (4) is unlike for rotation and vibration. The reason that γ' differs from γ'' , or δ' from δ'' , is that γ , δ are functions of the nuclear masses. Since γ , δ are themselves very small quantities, the expressions $\gamma' - \gamma''$ and $\delta' - \delta''$ will be quite negligible unless the ratio of the reduced masses for the two isotopes differs markedly from unity. Hence all the corrections which we discuss are important only when the pair of isotopes is a hydride and a deuteride. In fact, it is only the discovery of deuterium that makes most of the present paper of other than academic interest.

We may distinguish between four effects (a), (b), (c), (d), all of which make the empirical isotope ratios differ from the ideal values (4).

(a) ANHARMONICITY

Even for a vibrator-rotator, involving only nuclear in distinction from electronic coordinates, there will be departures from (4) if the restoring forces are not simple harmonic. The resulting modifications have been studied particularly by Dunham² and Crawford.³ Dunham's formulas show that

$$\gamma_a = (B_0^2/2\omega_0^2)[15 + 41a_1 - 9a_2 + 15a_3 - 23a_1a_2 + 21(\frac{1}{2}a_1^2 + \frac{1}{2}a_1^3)], \quad (7)$$

$$\delta_a = (B_0^2/32\omega_0^2)(200a_4 - 380a_1a_3 - 134a_2^2 + 459a_1^2a_2), \quad (8)$$

with $a_1 \cdots a_4$ as in (3).

(b) DIAGONAL ELEMENTS

All perturbation calculations on diatomic molecules start with a set of initial wave functions Ψ in which the nuclear and electronic variables are separated, so that⁴

$$\Psi = \Phi_n(x_1, \cdots, z_f, r) R_{nv}(r) u_{J\Lambda}(\theta, \varphi) f(X, Y, Z). \quad (9)$$

Here Φ_n is a function of the coordinates $x_1 \cdots z_f$ of the electrons relative to the center of gravity as origin; R_{nv} depends only on the internuclear distance r , and $u_{J\Lambda}$ is a symmetrical top function which involves merely the angular variables θ , φ specifying the spatial orientation of the molecular axis. The function f depends only on the coordinates X , Y , Z of the center of gravity, and has the usual plane wave exponential form. The factor Φ_n contains r as a parameter, and satisfies the wave equation

$$[\mathbf{H} - E_n(r)]\Phi_n = 0 \quad (10)$$

for "clamped nuclei." The eigenvalue of (10) for a given state n involves r parametrically, and is the same as the radial potential function (3). It is usually assumed that the differential equation

² J. L. Dunham, Phys. Rev. **41**, 721 (1932).

³ F. H. Crawford and T. Jorgensen, Jr., Phys. Rev. **47**, 931 (1935).

⁴ R. de L. Kronig, *Band Spectra and Molecular Structure*, p. 42; or J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

satisfied by R_{nv} is that of a system of one degree of freedom with the potential (3) supplemented by the ordinary centrifugal term $[J(J+1)-\Lambda^2]\hbar^2/8\pi^2Mr^2$. This supposition, however, is not quite right. Instead the wave equation appropriate to R_{nv} is

$$(-\hbar^2/8\pi^2Mg)(d^2R_{nv}/dr^2) + [E_n(r) + P_{nn} + Q_{nn} + S_{nn} + (J^2 + J - \Lambda^2)\hbar^2/8\pi^2Mr^2]R_{nv} - WR_{nv} = 0, \quad (11)$$

where $P_{n'n}(r) = (\hbar^2/8\pi^2Mr^2)\Xi_{n'n}$ with $\Xi_{n'n} = \int \cdots \int \Phi_{n'}^\dagger (\mathbf{P}_x^2 + \mathbf{P}_y^2) \Phi_n d\tau$, (12)

$$Q_{n'n}(r) = (\hbar^2/8\pi^2M) \int \cdots \int -\Phi_{n'}^\dagger \partial^2 \Phi_n / \partial r^2 d\tau. \quad (13)$$

The formula for S_{nn} is furnished later in Eq. (14). $d\tau$ is an abbreviation for the 3f-dimensional volume element $dv_1 \cdots dv_f$. In (12), \mathbf{P}_x is the operator $i^{-1}\Sigma_k(y_k\partial \cdots / \partial z_k - z_k\partial \cdots / \partial y_k)$ which gives the electronic angular momentum about the x axis, measured in multiples of $\hbar/2\pi$, while \mathbf{P}_y is the corresponding operator for the y axis. It is assumed throughout that the z axis connects the nuclei. The dagger is used to denote the conjugate imaginary, and for present purposes we take $n'=n$. In writing (11), we have used a radial wave function normalized with respect to dr (rather than to r^2dr as in reference 4), for this procedure makes the formulas more compact.

The extra terms P_{nn} , Q_{nn} in (11) may be qualitatively described as representing coupling between vibration and electronic motion. They have already been given by Kronig and others.⁴ The remaining additional term S_{nn} owes its origin to the fact that the center of gravity of the molecule does not quite coincide with the center of gravity of the nuclei, so that the latter wobbles about the former. This term does not appear to have been explicitly written down previously in connection with the radial equation, because it has commonly been assumed that the distinction between the two centers of gravity is of no account in view of the light mass of the electrons. However, we shall see later in the article that the S_{nn} term is often as important as the P_{nn} , Q_{nn} ones, and that all three should be considered as an organic whole in treating the coupling of electronic and nuclear motions. The formula for $S_{n'n}$ is

$$S_{n'n}(r) = -(\hbar^2/8\pi^2M_{1+2}) \int \cdots \int \Phi_{n'}^\dagger (\Sigma_i \nabla_i^2 + 2\Sigma_{i>j} \nabla_i \cdot \nabla_j) \Phi_n d\tau, \quad (14)$$

where M_{1+2} is the total mass $M_1 + M_2$ of the two nuclei. The symbols ∇_i and ∇_i^2 are respectively the gradient and Laplacian operators in the x_i, y_i, z_i space and we shall let ∇_{XYZ} , ∇_{XYZ}^2 have similar significance in the X, Y, Z coordinate system.

To derive (14), we note that motion of the center of gravity introduces the term $-(\hbar^2/8\pi^2M_{1+2})\nabla_{XYZ}^2$ in the Hamiltonian function. Despite the fact that Φ does not apparently contain X, Y, Z explicitly, $\nabla_{XYZ}\Phi$ does not vanish, as in differentiation with respect to X, Y, Z it must be supposed that the electronic coordinates are kept fixed in space rather than fixed relative to the nucleus. Hence when X is given a variation δX , one has $\delta X_1 = \cdots = \delta X_n = -\delta X$ and so

$$-(\hbar^2/8\pi^2M_{1+2})\nabla_{XYZ}^2\Psi = -(\hbar^2/8\pi^2M_{1+2})Ru[\Phi_n\nabla_{XYZ}^2f - 2\nabla_{XYZ}f\Sigma_i\nabla_i\Phi_n + f(\Sigma_i\nabla_i^2\Phi_n + 2\Sigma_{i>j}\nabla_i\nabla_j\Phi_n). \quad (15)$$

To obtain (14), one integrates over the electronic coordinates in the usual way. The cross terms in $\nabla f \cdot \nabla \Phi_n$ in (15) vanish on integration in the diagonal case $n'=n$ because the mean momentum of the electrons relative to the center of gravity is zero. The first term of (15) merely governs the uniform motion of the center of gravity, and need not be considered for our purposes.

To proceed further, we develop $P_{nn} + Q_{nn} + S_{nn}$ as a Taylor's series

$$P_{nn} + Q_{nn} + S_{nn} = B_0[k_0 + k_1\xi + k_2\xi^2 + \cdots] \quad (16)$$

about the equilibrium position r_0 associated with (4). A perturbation calculation then shows that the resulting correction factors entering in (5) (6) are

$$\gamma_b = 4k_1B_0^2/\hbar^2\omega^2, \quad \delta_b = (2k_2 - 3k_1a_1)B_0^2/\hbar^2\omega^2. \quad (17)$$

A simple proof of (17) is as follows: After the addition of the P_{nn} , Q_{nn} , S_{nn} and centrifugal terms, the equilibrium distance is no longer quite r_0 , but is very approximately

$$r_0' = r_0 - (k_1 B_0 / a r_0) + 2(B_0 / a r_0) J(J+1) \quad (18)$$

as is seen by taking the minimum of the total effective potential in (11) and retaining only terms of lowest order. When we expand about the new equilibrium position, this potential becomes

$$W_0 + B_0[J(J+1) + k_0] + \frac{1}{2}(B_0^2 / a r_0^2)[-k_1^2 + 4k_1 J(J+1) - 4J^2(J+1)^2] + \frac{1}{2}a(r-r_0')^2 + B_0 r_0^{-2}[k_2 + 3J(J+1) - \frac{1}{2}a_1(3k_1 - 6J^2 - 6J)](r_0 - r_0')^2 + \dots \quad (19)$$

In accordance with perturbation theory, we may replace $(r-r_0')^2$ by its mean value, which to a sufficient approximation⁵ is the same as that of $(r-r_0)^2$ for the unperturbed motion. The latter is immediately obtained from the theorem that the mean kinetic and potential energies for a harmonic oscillator are each half the total energy, i.e.,

$$\frac{1}{2}a\overline{(r-r_0)^2} = \frac{1}{2}\overline{p^2}/M = \frac{1}{2}\hbar\omega_0(v + \frac{1}{2}). \quad (20)$$

$$\text{Thus } W = W_0 + B_0[k_0 - (k_1 B_0 / \hbar\omega_0)^2] + B_0(1 + \gamma_b)J(J+1) + \hbar\omega_0(1 + \delta_b)(v + \frac{1}{2}) + D J^2(J+1)^2 - \alpha(v + \frac{1}{2})J(J+1), \quad (21)$$

where γ_b , δ_b are defined as in (17); and where

$$D = -4B_0^3/\hbar^2\omega_0^2, \quad \alpha = -6(B_0^2/\hbar\omega_0)(1 + a_1). \quad (22)$$

Eqs. (17) are thus established. The formulas for D and α are the usual ones of the band spectroscopists for centrifugal expansion and the interaction of rotation and vibration.⁶ As an incidental to our work, it is thus seen that the α , as well as, of course, the D term can be derived by a quite elementary perturbation calculation rather than, for instance, employing the Kratzer potential.⁷ If we are interested in the effect of the various extra terms on the vibrational wave functions, this is, to a sufficient approximation, merely a shift in origin by an amount $r_0' - r_0$ given by (18).⁸

Eq. (21) does not contain higher powers than the first in $v + \frac{1}{2}$, as we have in (19) neglected terms of the third and higher orders in $(r-r_0')$ (also unimportant terms proportional to $(r_0' - r_0)^2(r-r_0)$ or $(r_0 - r_0')^3$, etc., have been discarded in Eq. (19)). For most purposes, the coefficients of the higher powers of $v + \frac{1}{2}$ can be considered the same as when the extra terms in (11) are omitted. The coefficient of $v + \frac{1}{2}$ is slightly modified by the anharmonicity, essentially because v^m in the old quantum theory is replaced in the new mechanics by a polynomial in $v + \frac{1}{2}$ rather than simply $(v + \frac{1}{2})^m$. This is the Dunham-Crawford effect already included in (a).

In writing (19) and (21), we have not carried the development far enough to find the small correction factors to the coefficient of $(v + \frac{1}{2})J(J+1)$ which are comparable with those in (5)-(6) and which depend on the isotope. Further calculations, in which the equilibrium distance must be obtained more accurately than in (18), show that a more accurate value of this coefficient than α as given in (20) is⁹

$$\alpha^* = \alpha + (\alpha B_0^2/\hbar^2\omega_0^2)[9a_1k_1 + (1 + a_1)^{-1}(8k_1 - 2k_2 - 6a_1k_2 + 4k_3 - 8a_2k_1)].$$

The corresponding correction formula to the coefficient $-x\hbar\omega_0$ of $(v + \frac{1}{2})$ is

$$(x\hbar\omega)^* = x\hbar\omega_0 + (4B_0^2x/\hbar\omega_0)(12a_2 - 15a_1^2)^{-1}(-30a_3k_1 + 12k_4 - 12a_2k_2 + 78a_1a_2k_1 - 30a_1k_3 + 30a_1^2k_2 - 45a_1^3k_1).$$

In the present case $n' = n$, the expression Q_{nn} defined in (13) may be transformed into

$$Q_{nn}(r) = (\hbar^2/8\pi^2M)\Theta_{nn} \quad \text{with} \quad \Theta_{nn} = \int \dots \int |\partial\Phi_n/\partial r|^2 d\tau, \quad (23)$$

and is therefore positive. The relation (23) is proved from (13) by differentiating twice with respect to r the normalization integral

$$\int \dots \int \Phi_n^* \Phi_n d\tau = \delta_{nn'}. \quad (24)$$

Eq. (24) is valid for all values of the parameter r since throughout the article we shall suppose the electronic wave functions normalized to unity regardless of the internuclear distance. The result (23) then follows immediately in the real case $\Phi_n^* = \Phi_n$. If Φ_n is complex, the proof can still be carried through when use is made of the fact that without

⁵ This statement does not contradict the fact that it is precisely the difference between r_0 and r_0' which causes the effects in question, as the shift in origin has eliminated first order expressions in $r - r_0'$, and the second-order terms need not be evaluated as accurately. In calculating $\alpha^* - \alpha$ it is necessary, however, to distinguish between the means of $(r-r_0)^2$ and of $(r-r_0')^2$.

⁶ Cf., for instance, R. S. Mulliken, Rev. Mod. Phys. **1**, 67 (1930). In general we use the notation approved by Mulliken. His anharmonicity coefficients, however, relate to expansion about a Kratzer rather than harmonic potential, and so differ from ours. Thus his $-2b^* - 2$ is the same as our a_1 .

⁷ The linear term in ξ in (16) or in the expansion of the centrifugal potential no longer vanishes when the potential is unsymmetrical. This is the physical reason why the cubic term a_1 in (3) contributes to the quadratic part of

(19). Neglect of this contribution explains why Morse originally obtained an incorrect formula for α (Phys. Rev. **34**, 57 (1929)).

⁸ Unless one is interested in extreme accuracy it is thus not necessary to resort to an elaborate perturbation calculation such as that of Pekeris (Phys. Rev. **45**, 98 (1934)).

⁹ There are also modifications in α due to effects (a), (c), (d) and in $x\omega$ due to (a) and (d). Dunham² has treated (a). It can be shown that with the same hypotheses as in (28), (c) alters α by a factor

$$1 + B_0(5 + 6a_1)2(L^2 + L)/3(1 + a_1)\hbar\nu(\Sigma; \Pi).$$

The correction formulas due to (d) involve $B_0/\hbar\nu$, rather than $B_0^2/\hbar^2\omega_0^2$ like (b). We shall not give their explicit form, since they are rather complicated and hard to use quantitatively as they require knowledge of the constants $\Omega_{nn'}^1$, $\Omega_{nn'}^2$ defined before (37).

loss of generality, Φ_n may be assumed to have the structure $F+iG$, where F, G are real and respectively even and odd with respect to reflection in some given plane containing the molecular axis. Consequently, $F, \partial F/\partial r, \partial^2 F/\partial r^2$ are all orthogonal to G , or derivatives thereof, and no cross terms in FG are involved in (24) or (13).

Furthermore, (14) may be transformed by partial integration into

$$S_{nn}(r) = (\hbar^2/8\pi^2 M_{1+2}) \int \cdots \int |\Sigma_i \nabla_i \Phi_n|^2 d\tau \quad (25)$$

and is also positive. There is no trouble in the complex case, as $\nabla_i F$ is orthogonal to $\nabla_i G$, and F to $\nabla_i^2 G$.

To simplify (17) it is customary to assume that Q_{nn}, S_{nn} are small compared with P_{nn} and to make use of the hypothesis of pure precession, in which the square of the total angular momentum is assumed to have a quantized value $L(L+1)$ like in an atom. Since in reality only the axial component Λ of electronic angular momentum is constant, this approximation is a crude one strictly allowable only in the limiting case of the "united atom" formed by coalescence of the nuclei. With the hypothesis of pure precession, the integral Ξ_{nn} in (12) has a value $L(L+1) - \Lambda^2$ independent of r , and then k_1, k_2 in (16) owe their existence (provided we disregard Q_{nn}, S_{nn}) entirely to the factor $1/r^2$ in (12). If we use (22), thus Eqs. (17) reduce to formulas

$$\left. \begin{aligned} \gamma_b &= -8[L(L+1) - \Lambda^2]B_0^2/\hbar^2\omega^2, \\ \delta_b &= -[L(L+1) - \Lambda^2]\alpha/\hbar\omega \end{aligned} \right\} \quad (26)$$

previously given by Kronig¹⁰ and Dieke,¹¹ respectively. Here α is defined as in (22). It is to be cautioned that use of (26), even in a first approximation, is allowable only when the molecule is in a paramagnetic state $L \neq 0$ in the united atom approximation. When $L=0$, it is not allowable to disregard Q_{nn}, S_{nn} in comparison with P_{nn} , or overlook the variation of the integral in (12) with r . Even when $L \neq 0$, this procedure is questionable unless we are dealing with highly excited states in which the molecule behaves nearly like the united atom.

(c) L UNCOUPLING

The remaining isotope corrections (c-d) arise because the separation of variables (9) is not accurate, or in other words because rotation and vibration introduce interactions between different electronic states. These interactions can be divided into two types: (c) Those connecting

states whose Λ 's differ by one unit and (d) those joining states of equal Λ .

We shall not write down the perturbing terms in the Hamiltonian function which introduce matrix elements between states differing by unity in Λ . Such terms are well known, and give rise to the phenomenon commonly called L uncoupling. They make B^* different from B , and so influence the isotope ratios, as Professor Mulliken first pointed out to me.¹² In the case of a Σ state, calculation shows¹³ that

$$\gamma_c = 4B_0 \sum_{\Pi} |P_y(\Pi; \Sigma)|^2 / \hbar\nu(\Sigma; \Pi), \quad (27)$$

where $P_y(\Pi\Sigma) = \int \cdots \int \Phi_{\Pi}^{\dagger} \mathbf{P}_y \Phi_{\Sigma} d\tau$,

with \mathbf{P}_y defined as after (13) and where the summation is over all Π levels. In writing (27), we have assumed that in electron bands, the electronic frequencies are not appreciably modified by vibration. With the hypothesis of pure precession explained above near the end of fine print, only one of the Π states gives a perturbation, and (27) reduces to

$$\gamma_c = 2B_0 L(L+1) / \hbar\nu(\Sigma; \Pi). \quad (28)$$

The reader is referred elsewhere¹⁴ for the formulas in the case of Π levels. Here B^* is different for the two components of a Λ doublet. In fact, it is precisely this difference which causes the doubling.

¹² It is hard to say where it was first seriously suggested that L uncoupling modifies the isotope effect. Even before wave mechanics, Mulliken intimated that interaction between electronic motion and vibration might modify isotope behavior (Phys. Rev. **25**, 126 (1925)). The requisite formulas of quantum mechanics were given in reference 4, while later papers by Mulliken repeatedly stressed the distinction between B^* and B , including the case of Σ states (cf. Mulliken and Christy, Phys. Rev. **38**, 92 (1931), Eq. (8)). Very specific applications to the isotope effect have been made by Dieke.²⁰

¹³ Mulliken and Christy's Eq. (8) has a factor 8 rather than 4 as in our (27) because their convention is to include in the Π summation only one Λ -doublet component in a $\Lambda=1, -1$ system of representation. In such a system both components contribute equally, whereas only one component is effective if passage is made to wave functions of the proper final $+$ -symmetry.

¹⁴ J. H. Van Vleck, Phys. Rev. **33**, 487 (1929).

¹⁰ R. de L. Kronig, Physica **1**, 617 (1934).

¹¹ G. H. Dieke, Phys. Rev. **47**, 661 (1935).

L uncoupling is primarily a rotational effect, and so one would expect it not to affect the vibrational isotope ratio. More detailed investigation shows this to indeed be the case, so that one can take

$$\delta_c = 0. \quad (29)$$

(d) INTERACTION BETWEEN STATES OF EQUAL Λ

We have postponed discussion of this interaction until now, as its influence on ω^* has not previously been treated, and requires some study. Let n and n' be two different electronic states of equal Λ whose vibrational quantum numbers are v and v' . The perturbing Hamiltonian matrix element connecting them is¹⁵

$$H_{nn'}(v; v') = \int R_{nv}^\dagger [P_{nn'} + Q_{nn'} + S_{nn'} + (-ih/2\pi M)\Omega_{nn'} \mathbf{p}_r] R_{n'v'} dr, \quad (30)$$

where \mathbf{p}_r is the operator $\hbar \partial \cdots / 2\pi i \partial r$, where $P_{nn'}$, $Q_{nn'}$, $S_{nn'}$ are defined as in (12), (13), (14) and where

$$\Omega_{nn'} = \int \Phi_n^\dagger (\partial \Phi_{n'} / \partial r) dr. \quad (31)$$

The centrifugal term $[J(J+1) - \Lambda^2] \hbar^2 / 8\pi^2 M r^2$ does not appear in (30), as it makes no contribution because of the orthogonality of Φ_n , $\Phi_{n'}$. Hence the present effect (d) does not influence the rotational isotope behavior, and we can take

$$\gamma_d = 0. \quad (32)$$

On the other hand, it gives a modification in the vibrational case, as we shall show that

$$\delta_d = 2 \sum_{n'} \frac{r_0^2 |\Omega_{nn'}^0|^2 B_0}{h\nu(n; n')}. \quad (33)$$

Here the summation is over all states of the same Λ as the given state n . When dealing with Σ states, however, only states of the same $+$ -symmetry need be considered, as (30) vanishes if n relates to a Σ^+ , and n' to a Σ^- state, or *vice versa*.¹⁶ The zero superscript in (33) means that (31) is to be evaluated at $r = r_0$.

¹⁵ See reference 4 for the mathematical basis underlying the construction of the matrix elements (30). Besides the terms in (30), there are nondiagonal matrix elements due to the cross products between ∇f and $\nabla \Phi_n$ in (15), which no longer necessarily give a vanishing effect when $n \neq n'$. The resulting contribution, however, does not depend appreciably on the vibrational quantum number, but rather primarily on the translational energy of the molecule, and so can be omitted for our purposes.

¹⁶ For what is meant by Σ^+ and Σ^- states, see R. S. Mulliken, Rev. Mod. Phys. 3, 92 (1931).

It will be noted that (33) involves Ω but not P , Q , S despite the fact that P , Q , S and Ω appear additively in (30). The reason is that the matrix elements due to P , Q , S are smaller than nonvanishing elements due to $(\hbar/2\pi M)\Omega$ by a factor of the order of magnitude $(B_0/\hbar\omega_0)^{1/2}$ as is seen by a simple dimensional examination. Hence we have not bothered to include any of the former in (33), nor shall we in future Eqs. (36), etc. The physical basis of this diversity in size is that $R_{n'v'}$ varies much more rapidly with r than $\Phi_{n'}$ does; i.e., the operator $\hbar \partial \cdots / 2\pi i \partial r$ applied to $\Phi_{n'}$ as in (13) is equivalent in order of magnitude to multiplication by $\hbar/2\pi r_0$, whereas when applied to $R_{n'v'}$, it is the vibrational momentum operator \mathbf{p}_r , which is of the order $(M\hbar\omega_0)^{1/2}$ by (20). The larger size of the Ω than the other perturbing terms appears to have previously been overlooked, and explains why the Ω terms are able appreciably to modify ω^* despite the fact that they appear only connecting different electronic states, and so enter finally only in formulas involving the electronic frequencies in the denominator. The usual L uncoupling terms, to be sure, are able to modify B^* , but then B^* represents a smaller energy term than ω^* . Fortunately, the Ω terms vanish in the diagonal case $n = n'$, as one can prove that Ω_{nn} equals zero by differentiating (24) with respect to r . The proof applies even when Φ_n is complex, provided one utilizes the structure of Φ_n explained after Eq. (24). Since $\Omega_{nn} = 0$, we omitted any mention of the Ω terms in discussing the diagonal effect (b).

Proof of (33). By a common formula of perturbation theory, the shift in energy due to the totality of matrix elements (30) is

$$\Delta W = \Sigma_{n',v'} H_{nn'}(v; v') H_{n'n}(v'; v) / h\nu(nv; n'v'). \quad (34)$$

Usually the denominators of (34) depend but to a small extent on the vibrational quantum number, and may be replaced to a sufficient approximation by expressions $h\nu(n; n')$ which can be taken outside the v' summation. Then (34) becomes

$$\Delta W = \Sigma_{n'} \{ [\Sigma_v H_{nn'}(v; v') H_{n'n}(v'; v)] / h\nu(n; n') \}. \quad (35)$$

Furthermore

$$\begin{aligned} \Sigma_v H_{nn'}(v; v') H_{n'n}(v'; v) \\ = (-\hbar i / 2\pi M)^2 \int R_{nv}^\dagger \Omega_{nn'} \mathbf{p}_r \Omega_{n'n} \mathbf{p}_r R_{n'v'} dr. \end{aligned} \quad (36)$$

It is clearly to be understood that the summation in (36) does not lead to true matrix multiplication, as the initial and final wave functions in (33) belong to different sets of orthogonal functions because the states n and n' have

different radial constants. Summation over n' in addition to v' would be necessary to give the ordinary case. However, the writer has shown elsewhere that even without summing over n' it is allowable to use formulas such as (36).¹⁷

The important point is that in (36) we have an expression which does not require knowledge of the vibrational wave functions for the perturbing electronic state n' . To evaluate (36) we expand $\Omega_{nn'}$ (and $\Omega_{n'n}$) as a Taylor's series

$$\Omega_{nn'} = \Omega_{nn'}^0 + \Omega_{nn'}^{(1)}(r - r_0) + \dots$$

about the equilibrium position for the state n . For our purposes, only the constant term $\Omega_{nn'}^0$ is needed, as the remainder would introduce higher powers of $(v + \frac{1}{2})$ or of $B/h\nu_0$. With this approximation, (35) becomes

$$\Delta W = (\hbar^2/4\pi^2 M^2) p_{nn'}^2(v; v) \Sigma_{n'} |\Omega_{nn'}^0|^2 / h\nu(n; n'). \quad (37)$$

Here use has been made of the relation $\Omega_{n'n} = -\Omega_{nn'}^\dagger$ obtained by differentiating (24) with respect to r . The diagonal element $p_{nn'}^2(v; v)$ is the same as the mean value of p_r^2 and so can immediately be obtained from (20). The latter shows that (37) is proportional to $v + \frac{1}{2}$ and so contributes to the ω^* part of (1). Formula (33) for δ_d then follows when one uses the definatory relation (6).

SIGNS AND RELATIVE MAGNITUDES OF THE VARIOUS CORRECTIONS

First we shall consider the subject of sign. Usually the empirical isotope ratios are nearer unity than are the ideal values (4). This behavior is predicted by theory if γ and δ are negative since in all four cases the corrections to (4) become more important the smaller the reduced mass.¹⁸ Now any of the four effects (a-b-c-d) are more apt to give negative than positive contributions to γ or δ and so the observed behavior is quite understandable. The detailed situation on sign for each effect is as follows. In (a), the sign of γ_a or δ_a depends by (7-8) on the a_i in (3) or in other words on the type of anharmonicity or exact shape of the potential curve. In only two cases, *viz.*,¹⁹ the $(2s\sigma)^2 \ ^1\Sigma$ and $2s\sigma 2p\sigma \ ^1\Sigma$ states of LiH, is this information known with sufficient accuracy to permit the calculation of γ_a , δ_a . In both cases γ_a is negative, also δ_a for $2s\sigma 2p\sigma \ ^1\Sigma$, but δ_a is positive for $(2s\sigma)^2 \ ^1\Sigma$. The values of γ_b and δ_b are negative if one uses the approximation

(26) based on pure precession, since the spectroscopic constant α is usually positive. The same sign behavior will also be found true (cf. Eqs. (43)) when we develop approximations for other limiting conditions. So γ_b and δ_b are probably usually negative. Both δ_c and γ_d vanish, while Eqs. (27) and (33) show that γ_c and δ_d are negative if the dominant frequency denominators are negative (i.e., relate to absorption), which is surely the case if the given state is the ground level of the molecule.

As to the relative importance of the various corrections, it is hard to make a definite prediction. The effect (c) should have a preponderant influence if there is close by a state differing by one unit in Λ . Since $\delta_c = 0$, the departures from (4) should then be very much greater in the rotational than in the vibrational isotope effect. Dieke²⁰ has shown that an interesting example of precisely this situation is provided by the $3p \ ^3\Sigma$ state of the hydrogen molecule, and that the observed deviation from (4) agrees remarkably well with that calculated from (28), which is here more important than any other correction by a factor ten or so.

Similarly, (d) should be the most important effect if there is a nearby state of the same Λ and same $+-$ symmetry as the level under consideration. Since $\gamma_d = 0$, there would then be a much larger correction to the vibrational than to the rotational isotope effect. It would be very gratifying if this point could be tested experimentally.

When there are no nearby states, so that one does not have the resonance cases just cited and instead the frequency denominators are comparable with ionization potentials, it is impossible to say which of the various corrections is the largest without detailed and laborious investigation. The different effects (a-b-c-d) are then of the same rough order of magnitude, as we will later show more fully by some illustrative calculations (except for effect a) on the ground state of the hydrogen molecule. Too much weight should not be attached to the fact that (7), (8), and (17) are proportional to $B_0^2/h^2\omega_0^2$, and (27) and (33) to $B_0/h\nu$, where ω_0 and ν are respectively vibrational and electronic frequencies. To be sure, $B_0^2/h^2\omega_0^2$, being quadratic in B_0 , is some-

¹⁷ J. H. Van Vleck, Proc. Nat. Acad. Sci. **15**, 754 (1929).

¹⁸ In all cases (a)-(d), γ and δ involve factors $B_0^2/h^2\omega_0^2$ or $B_0/h\nu$ and so are apparently inversely proportional to the reduced mass M . However, the terms $k_1 k_2$ in (17), or Ξ , Θ in (38) may involve M_1/M_2 . This is shown by (43) or (46-7-8). Even though the mass dependence can thus be more complicated, the dominant factor is usually $1/M$.

¹⁹ F. H. Crawford and T. Jorgensen, Jr., Phys. Rev. **49**, 745 (1936).

²⁰ G. H. Dieke, Phys. Rev. **48**, 606, 610 (1935).

what smaller than $B_0/h\nu$ even when one is well away from resonance. For example, the former is 0.0002 and the latter 0.0006 in the case of the ground state of the hydrogen molecule, a rather extreme example of nonresonance as $\nu = 0.9 \times 10^6 \text{ cm}^{-1}$. However, the difference in magnitude is not large, and we shall later see (cf. Eqs. (43)) that under certain limiting conditions (17) can be transformed into formulas not involving ω_0 at all. Any disparity resulting from the diversity in size of $B_0^2/h^2\omega_0^2$ and $B_0/h\nu$ can easily be offset by abnormally small or large numerical coefficients in the formulas. In particular the large numbers occurring in (7) and (8) are to be noted as they may make the anharmonic effect (a) fully as important as any of the other corrections except near resonance. However, Crawford and Jorgensen¹⁹ find that in LiH, (a) is able to account for only a fraction of the empirical isotope correction; namely, the empirical values of γ , δ for the $(2s\sigma)^2 \text{ } ^1\Sigma$ state are -0.0005 , -0.00019 , while the calculated values of γ_a , δ_a are -0.0001 , $+0.00008$; for the $2s\sigma 2p\sigma \text{ } ^1\Sigma$ level, γ , δ are -0.010 , -0.027 , and γ_a , δ_a give -0.003 , -0.004 . It is interesting that γ_a/γ has about the same value for both levels despite the fact that one has a γ twenty times as large as the other. The large value -0.027 of δ in the upper state is perhaps indicative of a large effect of type (d). At any rate, the inadequacy of (a) alone seems to corroborate our statement that (a-b-c-d) likely simultaneously can play an appreciable role. When the united atom has an angular momentum, (b) is more important than otherwise (cf. remarks following Eq. (40)).

DIGRESSION ON PERTURBATIONS IN BAND SPECTRA

At this point we shall insert a few words on perturbations in general in diatomic spectra, for the underlying mathematical analysis is the same as for the isotope corrections. Dieke²¹ has called attention to the fact that perturbations connecting states differing by one unit in Λ increase rapidly with the rotational quantum number J , all other things being equal, and cites confirmatory experimental evidence. Eq. (37)

shows that interaction between states of equal Λ increases with the vibrational quantum number v . This fact has not apparently been stressed previously, and it would be very interesting if appropriate experimental evidence could be obtained.^{21a} The confirmation would be more difficult than in the preceding case $\Delta\Lambda = \pm 1$, for the dependence on the quantum number is masked if there is much alteration in the frequency denominator, and of course the frequency depends much more on the vibrational than on the rotational quantum number. In other words, in studying perturbations in band spectra, one is apt to be near resonance, and this is just the place where one cannot pass from (34) to (35). Effect (c), L uncoupling, is primarily a rotational phenomenon, whereas (d) is due mainly to vibration, and this distinction explains why one type of perturbation should vary markedly with J and the other with v .

SIMPLIFICATION OF THE FORMULAS UNDER LIMITING CONDITIONS

For estimating orders of magnitude, it is convenient to simplify some of the formulas further.

Centroid approximation. If we assume that all the frequency denominators can be regarded as having sensibly the same value $h\nu$, an assumption warranted if at all only when one is well away from resonance, then (27) and (33) become

$$\gamma_c = 2B_0\Xi_0/h\nu, \quad \delta_d = 2B_0r_0^2\Theta_0/h\nu, \quad (38)$$

where Ξ_0 and Θ_0 denote the integrals defined in (12) and (23), respectively, evaluated for $r=r_0$, $n'=n$. The first formula of (38) follows from (27) by simple matrix multiplication, if ν is constant, inasmuch as \mathbf{P}_x^2 and \mathbf{P}_y^2 contribute equally to Ξ . The second relation is established from (33) in an analogous fashion by noting that the $\Omega_{nn'}$ are the coefficients in the expansion of $\partial\Phi_{n'}/\partial r$ in terms of the orthogonal functions Φ_n (cf. Eq. (31)).

Behavior of P_{nn} , Q_{nn} , S_{nn} for separated and united atoms. Especially in connection with the specific isotope shift to be considered later, it is illuminating to study the limiting values of P ,

^{21a} Note added in proof. Dieke finds that an example is furnished by the $1s\sigma 2s\sigma \text{ } ^1\Sigma$ state of H_2 (paper presented at Washington meeting of Am. Phys. Soc., 1936).

²¹ G. H. Dieke, Phys. Rev. **47**, 870 (1935).

Q , S , defined in (12)–(13)–(14) when the nuclei 1, 2 are infinitely far apart or coalesced together. The results are as follows

$$r = \infty \left\{ \begin{array}{l} P_{nn} \text{ or } 2Q_{nn} \rightarrow \frac{2}{3}(M_1w_2 + M_2w_1)/M_{1+2}, \\ S_{nn} \rightarrow (M_1w_1 + M_2w_2)/M_{1+2}, \end{array} \right\} \quad (39)$$

$$r = 0 \left\{ \begin{array}{l} P_{nn} \text{ or } 2Q_{nn} \rightarrow \frac{2}{3}(M_1Z_2 - M_2Z_1)^2w_{1+2}/M_1M_2Z_{1+2}^2, \\ S_{nn} \rightarrow w_{1+2}. \end{array} \right\} \quad (40)$$

Here w_1 , w_2 denote the energy corrections for the motion of the nucleus for isolated atoms 1, 2, respectively, and w_{1+2} that for the united atom. Z_1 and Z_2 are the nuclear charges of atoms 1 and 2. Eq. (39) applies only if the dissociation products are atoms in S states, as the proof assumes that the kinetic energy, etc., is prorated equally between the x , y , and z directions. If this condition is not fulfilled, the sum $P_{nn} + Q_{nn}$ is still given correctly by (39). Similarly, if the united atom has an angular momentum, (40) should be used only to obtain the sum $P_{nn} + Q_{nn}$, and furthermore in this case there is the extra term $[L^2 + L - \Lambda^2]/8\pi^2Mr^2$ not included in (40) (cf. Eq. (26)). Its inclusion means that P_{nn} becomes infinite when $r \rightarrow 0$ if $L \neq 0$. This apparently absurd result is obtained because the perturbation calculations all assume that the electronic charge cloud rotates with the nuclei; actually the two will become decoupled when r is made too small. However, for actual values of r , the decoupling has usually only started, and the large values in the limit $r=0$ explain why $P_{nn}(r)$, and hence effects (b)–(c), are abnormally important when the united atom has an angular momentum. It is usually assumed that in (12) the integral Ξ_{nn} does not vary much with r , but (39) shows that for large values of r , the factor Ξ_{nn} is proportional to r^2 inasmuch as $P_{nn} = \Xi_{nn}h^2/8\pi^2Mr^2$ is independent of r when $r \rightarrow \infty$.

A sketch of the arguments used to obtain (39)–(40) is as follows: The values of S_{nn} for $r = \infty$ and $r = 0$ are quite obvious, as for $r = 0$ S_{nn} is simply the usual correction term for nuclear motion,²² while for $r = \infty$ it would be except that it has a mass factor $1/M_{1+2}$ rather than $1/M_1$ or $1/M_2$. The behavior of $P_{nn} + Q_{nn}$ at $r = \infty$ is obtained by noting that when r is varied with the center of gravity held fast, the origin of atom 1 is displaced by an amount M_2/M_{1+2} and that of atom 2 by M_1/M_{1+2} . Furthermore the P_{nn} and Q_{nn} terms then combine to involve essentially the Laplacian operator ∇^2_{XYZ} , as far as each nucleus is concerned, except for a numerical factor $-(h^2/8\pi^2)(M_2^2/MM^2_{1+2})$ or

$-(h^2/8\pi^2)(M_1^2/MM^2_{1+2})$. Here M is the reduced mass M_1M_2/M_{1+2} . As already stated, the apportionment between P_{nn} and Q_{nn} given in (39) is correct only if the isolated atoms are isotropic. The behavior of $P_{nn} + Q_{nn}$ at $r = 0$ follows on observing that if the nuclei are drawn infinitesimally far apart with their center of gravity preserved at the origin, the change in the potential field may be regarded as equivalent to that of a dipole, and the dipole is $(Z_1M_2 - Z_2M_1)/M_{1+2}Z_{1+2}$ times as intense as for the purely translational or S effect. This accounts for a factor $(Z_1M_2 - Z_2M_1)^2/M_{1+2}^2Z_{1+2}^2$ in the behavior of $P_{nn} + Q_{nn}$ as compared with S_{nn} ; the remaining factor M_{1+2}^2/M_1M_2 is because of the different mass denominators in (12–13) and (14). It may seem strange that P_{nn} does not vanish at $r = 0$ when $L = 0$; the reason for this paradox is that the center of gravity does not coincide with the nuclear midpoint, so that the angular momentum about the former need not vanish even though that about the latter does.

If one neglects the cross terms $j \neq i$ in (14), the expression w_1 equals m/M_1 times the kinetic energy of atom 1. With a similar approximation, w_{1+2} is m/M_{1+2} times the kinetic energy of the united atom, where m is the mass of one electron. Actually, nonvanishing cross terms owe their existence to the fact that the complete wave function is not expressible as the product of wave functions of individual electrons, either because of antisymmetrization, or because the interelectronic distances enter explicitly as arguments. The calculations of Hylleraas²² show that the cross terms resulting from the latter cause, are unimportant, at least in the ground state of helium. The work of Hughes and Eckart²³ indicates that in atoms the antisymmetrization affects the nuclear corrections appreciably only if at least one electron is in a p state. In molecules, it will give an appreciable contribution at medium internuclear distances even when electrons are only in s states, due to the overlap of wave functions of the different atoms. However, at any internuclear distance, we can neglect the cross terms if we are interested only in orders of magnitudes, and so a very simple rough formula for S_{nn} is

$$S_{nn} = (m/M_{1+2})T, \quad (41)$$

where T is the total kinetic energy of the electrons. The virial theorem²⁴ tells us that

$$T = -E_n - r\partial E_n/\partial r, \quad (42)$$

²² D. S. Hughes and C. Eckart, Phys. Rev. **36**, 694 (1930).

²⁴ Cf. J. C. Slater, J. Chem. Phys. **1**, 687 (1933); W. Pauli, Ann. d. Physik **68**, 177 (1922).

²² Cf. E. A. Hylleraas, Zeits. f. Physik **54**, 364 (1929).

and so if (41) is accepted, the variation of S with r , as required for (16), can immediately determine if we know the potential energy curve $E_n(r)$, as in (3). In (42) the origin for the energy E_n must be so chosen that E_n vanishes when the molecule is blown completely to pieces (individual isolated charges). Eqs. (40) show that

in symmetrical molecules the P and Q terms are negligible compared with S at small internuclear distances, provided $L=0$, and so for estimating orders of magnitude, it is natural to neglect P , Q in comparison with S , and use (41–42) and (3). Then (17) becomes

$$\gamma_b = -2m/M_{1+2}, \quad \delta_b = -3m/2M_{1+2}. \quad (43)$$

CALCULATION OF P_{nn} , Q_{nn} , S_{nn} FOR WANG HYDROGEN FUNCTIONS

The values of P_{nn} , Q_{nn} , S_{nn} can be computed for any value of r for the normal state of the hydrogen molecule if one use the well-known Wang²⁵ wave functions

$$\Phi_n = A(e^{-b(r_{1a}+r_{2b})} + e^{-b(r_{1b}+r_{2a})}). \quad (44)$$

Here r_{1a} is the distance of electron a from nucleus 1, etc., and the normalization constant A has the value

$$1/A^2 = (2\pi^2/b^6)[1 + e^{-2br}(\frac{1}{3}b^2r^2 + br + 1)^2]. \quad (45)$$

By simple integrations, most easily made in elliptic coordinates, one finds that

$$P_{nn} = B_0(4\pi^2r_0^2A^2/18b^4)[3 - e^{-2br}(b^2r^2 + 3br + 3)(br + 1)] + [(M_1 - M_2)/2M_{1+2}]^2B_0g, \quad (46)$$

$$Q_{nn} = -B_0(r_0\partial \log A/\partial r)^2 + [2(M_2^2 + M_1^2)/M_{1+2}^2]\alpha B_0 - 4(M_1M_2/M_{1+2}^2)\beta B_0, \quad (47)$$

$$S_{nn} = B_0g(M_1M_2/M_{1+2}^2) + 4(M_1M_2/M_{1+2}^2)(\alpha + \beta)B_0, \quad (48)$$

with

$$g = (8\pi^2r_0^2A^2/3b^4)[1 + e^{-2br}(br + 1)(\frac{1}{3}b^2r^2 + br + 1)], \quad (49)$$

$$\alpha = (\pi^2r_0^2A^2/3b^4)[1 + \frac{1}{3}(br + b^2r^2)^2e^{-2br}], \quad (50)$$

$$\beta = (\pi^2b^2r_0^2A^2/3b^4)(-b^2r^2 + br + 1)(1 + br + \frac{1}{3}b^2r^2)e^{-2br}. \quad (51)$$

These formulas conform to (39–40) in the limiting cases.²⁶

ESTIMATE OF THE VARIOUS TERMS FOR THE GROUND STATE OF THE HYDROGEN MOLECULE

The shape of the potential curve is not known with sufficient precision for the ground level of hydrogen so that γ_a , δ_a can be evaluated. However, the preceding calculations enable us to determine roughly the corrections due to the other causes (b–c–d). We shall let primes refer to H_2 , double primes to HD , and triple primes to D_2 . When Wang's optimum value $1.166/a_0$ is substituted for the screening constant b at the actual internuclear distance $r = 1.406a_0$ ($a_0 = h^2/4\pi^2e^2m$), (46) and (47) give

$$\Xi_0' = \Xi_0''' = 0.394, \quad \Xi_0'' = 0.486, \quad \Theta_0' = \Theta_0''' = 0.335/r_0^2, \quad \Theta_0'' = 0.377/r_0^2. \quad (52)$$

For the centroid frequency ν , following Frank and V. V.,²⁷ we shall use the value $1.23R$, where R is the Rydberg constant. Then (38) yields

$$\begin{aligned} \gamma_c' &= -0.00035, & \gamma_c'' &= -0.00032, & \gamma_c''' &= -0.00017, \\ \delta_d' &= -0.00030, & \delta_d'' &= -0.00025, & \delta_d''' &= -0.00015, \end{aligned} \quad (53)$$

while from (43) we have

$$\begin{aligned} \gamma_b' &= -0.00054, & \gamma_b'' &= -0.00036, & \gamma_b''' &= -0.00027, \\ \delta_b' &= -0.00041, & \delta_b'' &= -0.00027, & \delta_b''' &= -0.00020. \end{aligned} \quad (54)$$

²⁵ S. C. Wang, Phys. Rev. **31**, 579 (1928).
²⁶ The values of w , and w_{1+2} yielded by the Wang functions are, respectively, $h^2b^2/8\pi^2M$, and $2b^2h^2/8\pi^2M_{1+2}$.

²⁷ A. Frank and J. H. Van Vleck, Proc. Nat. Acad. Sci. **15**, 539 (1929). This paper gives details of the calculation of Ξ_0 for H_2 .

Eqs. (54) should be regarded as probably giving only upper limits to the absolute values of γ_b and δ_b , as (43) assumes that $P_{nn} + Q_{nn}$ can be neglected in comparison with S_{nn} . Since the w 's are positive, Eqs. (39)–(40) show that $P_{nn} + Q_{nn}$ is larger for $r = \infty$ than for $r = 0$ whereas the reverse is true of S_{nn} . Hence $\partial(P_{nn} + Q_{nn})/\partial r$ is doubtless opposite in sign to $\partial S_{nn}/\partial r$. So $P_{nn} + Q_{nn}$ gives a contribution to k_1 in an opposite direction to that from S_{nn} (cf. Eq. (16)) and so by (17) tends to offset the S_{nn} effect in γ_b and in at least part of δ_b . Of course one can reckon γ_b , δ_b without disregarding $P_{nn} + Q_{nn}$ in comparison with S_{nn} , by expanding (46)–(47)–(48) about the equilibrium position. If one neglects the variation of b with r , then one obtains a value 0.0004 for γ_b which is of the opposite sign from that given in (54). In all likelihood γ_b is actually negative since (39)–(40) show that $P_{nn} + Q_{nn} + S_{nn}$ is greater for $r = 0$ than for $r = \infty$,²⁸ making $\partial(P_{nn} + Q_{nn} + S_{nn})/\partial r$ presumably negative. On the other hand (46)–(47)–(48) yield a smaller value of $P_{nn} + Q_{nn} + S_{nn}$ for $r = 0$ than for $r = \infty$ if the same value of b is used in both limits. This fact makes it clear why expansion of (46)–(47)–(48) gives a γ_b of the wrong sign if b is treated as constant. A more refined calculation, in which b varies with r , does not seem repaying at the present time. Even the leading term $k_0 B_0$ in (16) as obtained from (46)–(47)–(48) involves some error because b was regarded as independent of r in computing the integral Θ_{nn} in (23). However, the error is probably not as serious as in the higher r derivatives involved in connection with k_1 , k_2 in (16), and Wang's success in computing ω_3 without letting b depend on r is indicative that the variation of b with r is not too important in lower derivatives.

Unfortunately, no adequate experimental data on the ground state of the hydrogen molecule are available to test (53)–(54). For excited states, Dieke¹¹ calculates from (26) isotope corrections not a great deal larger than (53)–(54), being still of the order of magnitude $\gamma' - \gamma'' \sim 10^{-4}$. The effect (26) considered by him is present only when the united atom has a nonvanishing angular momentum L . The ground state of the hydrogen molecule has $L = 0$, and our main purpose in presenting (53)–(54) is to show that even without the anharmonic effect (a), not all of the isotope correction is connected with the existence of an $L \neq 0$.

THE ELECTRONIC ISOTOPE SHIFT

The difference in the constant terms in the energy for two isotopes is usually called the electronic isotope shift. It consists mainly in the difference in the constant part $k_0 B_0$ of (16), or in other words in $P_{nn} + Q_{nn} + S_{nn}$ evaluated at $r = r_0$, for the two isotopes. Dieke has had some success in explaining approximately the observed isotope shifts by neglecting Q_{nn} , S_{nn} in comparison with P_{nn} , and assuming for the latter the value

$$P_{nn} = B_0 [L(L+1) - \Lambda^2] \quad (55)$$

furnished by the hypothesis of pure precession. A somewhat better approximation is probably to add to (55) the value of S_{nn} furnished by (41)–(42). As noted by Dunham² and Dieke,¹¹ the anharmonic correction (a) also makes a contribution

$$Y_{00} = (B_0/8)(3a_2 - 7a_1^2/4) \quad (56)$$

to the constant part of the energy. In the cases studied by Dieke,¹¹ the effect of (56) is unimportant. The inclusion of S_{nn} , however, alters the calculated values somewhat, as shown in the following table. Our various formulas, though ostensibly for singlets, can be applied to triplets in hydrogen since here the multiplet width is negligible.

	H ₂ –HD CALCULATED		OBS.	HD–D ₂ CALCULATED		OBS.
	(55)–(56)	(41)–(55)–(56)		(55)–(56)	(41)–(55)–(56)	
$3p \ ^3\Pi - 2s \ ^3\Sigma$	7.60	6.07 cm ⁻¹	5.01	7.66	6.89 cm ⁻¹	4.94
$3p \ ^3\Sigma - 2s \ ^3\Sigma$	13.00	11.92	13.23	12.17	11.64	12.28

Clearly it is not allowable to neglect $Q_{nn} + S_{nn}$ in comparison with P_{nn} unless at least either the initial or final state has $L = 0$. Even when this condition is met, it is no longer allowable to overlook $Q_{nn} + S_{nn}$ if the line is in the ultraviolet. By (41), the S_{nn} effect is more important the shorter the wave-length, as then there is more difference, and hence less cancelation, between the values of (41) for the initial and final states. Examples are the lines, all in the ultraviolet, terminating on the ground state of the hydrogen molecule. To make an approximate calculation, we can use (46)–(47)–(48)

²⁸ If one neglects the cross terms in (14), then use of observed energies and the virial theorem shows that the actual values of w_1 and w_{1+2} for H and ²He₂ are, respectively, $R/1840$ and $5.8R/3680$, where R is the Rydberg constant.

for the ground state, and assume that in the upper state, the effect of the inner electron can be computed by using the Finkelstein-Horowitz²⁹ wave function $C(e^{-dr_{1a}} + e^{-dr_{2a}})$ for H_2^+ . The latter yields

$$P_{nn} + Q_{nn} + S_{nn} = B_0[(C^2 \pi r_0^2/d) - (r_0 \partial \log C / \partial r)^2] \quad (57)$$

with $d^3/2\pi C^2 = 1 + e^{-dr}(\frac{1}{3}d^2r^2 + dr + 1)$. The optimum value of dr is 2.46. From (46)–(47)–(48) one finds

Ground state	H ₂	HD	D ₂
$P_{nn} + Q_{nn} + S_{nn}$	114	85	57 cm ⁻¹

The corresponding values for H_2^+ , HD^+ , D_2^+ furnished by (57) are, respectively, 59, 44, 29 cm⁻¹. In the case of H_2 , the apportionment of 114 between P_{nn} , Q_{nn} , and S_{nn} is, respectively, 23, 20, and 71 cm⁻¹; Eq. (41) would give 69 cm⁻¹ for S_{nn} . (In HD, the apportionment between P_{nn} , Q_{nn} , S_{nn} is different, but the total effect is inversely proportional to the reduced mass M , as one sees by adding (46), (47), (48).) To obtain the total shift, one must add the anharmonic correction obtained from (56), and, in the upper state, the effect of the outer electron as given by (55). The corresponding isotope shifts for H_2 –HD are shown in the following table. It is seen that the largest contribution comes from (46)–(47)–(48)–(57), i.e., from the S_{nn} terms, while (55) alone does not even give the right sign

H ₂ –HD Calculated	Eq. (55)	(56)	(46)–(47)–(48)–(57)	Total	H ₂ –HD Obs.	$\frac{1}{2}(H_2 - D_2)$ Obs.
$2p\ ^1\Pi - 1s\ ^1\Sigma$	+7.4	-2.7	-13.8	-9.1	-8 cm ⁻¹	-12 cm ⁻¹
$2p\ ^1\Sigma - 1s\ ^1\Sigma$	+9.7	-0.8	-13.8	-4.9	-12	-2

The discrepancies here may be due to the very considerable experimental error, estimated by Dieke as 5 to 10 cm⁻¹, and to the inaccuracies of the Wang and Finkelstein-Horowitz wave functions.³⁰ The $2p\ ^1\Sigma$ state has an equilibrium distance 1.31×10^{-8} cm whereas $2p\ ^1\Pi$ has almost exactly that 1.06×10^{-8} of H_2^+ . Our H_2^+ treatment of the inner electron should thus apply better to $2p\ ^1\Pi$, and possibly this circumstance explains the greater disagreement for the transition involving $2^1p\ ^1\Sigma$. At any rate, the observed shifts are qualitatively understandable. In the table we have also included half the observed displacement between H_2 and D_2 . This should equal the H_2 –HD shift according to our formulas, and doubtless more generally. The discrepancy between the measured value for H_2 –HD and half that for H_2 – D_2 is hence indicative of a considerable experimental error.

THE MEAN SQUARE ANGULAR MOMENTUM OF THE NORMAL H_2 MOLECULE

In connection with the diamagnetism of H_2 , as well as with the determination of nuclear spin by means of Stern-Gerlach experiments on the hydrogen molecule, it is necessary to evaluate the integral Ξ_{nn} defined in (12). Miss Frank and the writer obtained 0.394 with the Wang wave functions (cf. Eq. (52)). Wick³¹ obtained $\Xi_{nn} = 0.02$ with other wave functions $De^{-(r_{1a} + r_{2a} + r_{1b} + r_{2b})}$, and suggested that our value was only an upper limit. Eq. (39) makes it clear why Wick obtained such a low result. The type of wave function

²⁹ B. N. Finkelstein and G. E. Horowitz, *Zeits. f. Physik* **48**, 118 (1928).

³⁰ In applying (56), we use the values of a_1 , a_2 corresponding to the values of α , x given in Miss Spomer's tables. Uncertainty in these constants may be a subsidiary source of error. The experimental value for the H_2 –HD shift used in the table is by Jeppesen, as revised by Dieke;³¹ that for H_2 – D_2 is furnished by very recent work of Jeppesen (paper at Washington meeting, 1936).

³¹ G. C. Wick, *Zeits. f. Physik* **85**, 25 (1933).

which he used makes P_{nn} vanish at $r = \infty$, whereas the Wang wave function gives the correct limit. Hence we do not believe that our value is necessarily much, if any too high. It is well below the asymptotic value $\frac{1}{3}b^2r_0^2$ characteristic of large r , which yields $\Xi_{nn} = 0.9$ at the actual internuclear distance.

In adapting calculations on the Stern-Gerlach effect to HD rather than H_2 , allowance must be made not merely for the altered reduced mass, but also for the somewhat different value of Ξ_{nn} (cf. Eq. (52)), which arises because the center of gravity no longer coincides with the nuclear midpoint. In calculations on diamagnetism, however, it is not necessary to consider this distinction, as the formula for the susceptibility is invariant of the origin.

The writer is indebted to Professors F. H. Crawford and R. S. Mulliken for valuable discussions.