

Vibrational and Centrifugal Effects on Nuclear Interactions and Rotational Moments in Molecules*

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The effects of zero point vibration and centrifugal stretching of molecules upon the spin-spin magnetic interaction, the spin-rotational magnetic interaction, the molecular rotational magnetic moment, the magnetic shielding of the nucleus, and the molecular diamagnetic susceptibility of the molecule are discussed. Expressions for these quantities with vibrational and centrifugal effects included are given in detail for diatomic molecules and numerical calculations for the cases of H_2 and D_2 . It is shown that from measurements of the rotational magnetic moments of both H_2 and D_2 or of H_2 in two different rotational states, one can calculate the variation with internuclear separation of the high frequency terms of the molecular diamagnetic susceptibility. Measurements on the spin-rotational magnetic interactions in both H_2 and D_2 provide information on the variation of this interaction with internuclear spacing and thereby supply important corrections that are needed in calculating the nuclear magnetic shielding from the spin rotational magnetic interaction and in measuring the ratio of the proton magnetic moment to that of the deuteron. These calculations also supply a correction to the spin-spin magnetic interaction that must be used in determining the deuteron quadrupole moment from experiments with D_2 .

I. INTRODUCTION

THE recent high precision experiments¹ on nuclear interactions in molecules make it necessary to include the effects of molecular zero point vibration and of centrifugal stretching in interpreting the results. Thus, the ratio of the rotational magnetic moment of D_2 to that of H_2 is not simply equal to the ratio of the mass of the proton to that of the deuteron as it would be if the two molecules were identical except for a difference in rotational angular velocity. Instead, allowance must be made for the fact that the suitably averaged mean internuclear spacing in the two molecules is different as a result of the difference in zero point vibration amplitude and centrifugal stretching. Similar considerations apply to the spin-spin magnetic interaction, the spin rotational magnetic interaction, the magnetic shielding of the nucleus, the electric quadrupole interaction, and the molecular diamagnetic susceptibility. Although Nordsieck,² Newell,³ and Ramsey^{1,4} have included these corrections for a few of the interactions, most of the cases have never been discussed previously and for the few that have been only specific numerical values were given with all detailed discussion being omitted. There has been no previous discussion of the inferences that can be drawn from the comparison of the above quantities in molecules that are similar except for differences in vibration amplitude and centrifugal stretching.

II. AVERAGE VALUES OF THE INTERACTIONS

In most past discussions of such quantities as molecular rotational magnetic moments, the effects of

zero point vibration and centrifugal stretching have been neglected with the result that the formulas given are for a single discrete internuclear distance. However, averaging these formulas over the vibration, one can obtain suitably averaged expressions.

In the case of rotational magnetic moments, Wick^{5,6} and Ramsey⁷ have discussed molecular hydrogen. Their results are thereby particularly simplified since all the nuclear charges are unity, and the molecule possesses no electric dipole moment. However, their procedure can be extended to an arbitrary $^1\Sigma$ linear molecule and the results may be simplified for a particular choice of gauge as discussed in Ramsey's articles^{8,9} on nuclear magnetic shielding. The most suitable choice is that which corresponds to the electron angular momenta being taken about an axis passing through the centroid of the electron distribution in the molecule (not in general the center of mass of the molecule). With this choice and with the expression averaged over zero point vibrations, one obtains

$$\begin{aligned} \langle \mu_R / J \mu_{NM} \rangle_J = & M_v \langle (1/I) \sum_i Z_i (R_i - R_Z)^2 \rangle_J \\ & + M \langle \sum_i Z_i \rangle_v \langle (1/I) (D^2 - d^2) \rangle_J \\ & - 8M (mc^2/e^2) \langle (1/I) \sum_n [1/(E_n - E_0)] \\ & \times (0 | \sum_k m_{k\sigma} C^0 | n)^2 \rangle_J. \quad (1) \end{aligned}$$

Most of the notation used here and in subsequent expressions is that used in previous related articles⁷⁻⁹ except that R_Z is the coordinate of the centroid of the nuclear charge; the subscripts σ and C indicate, respectively, that the momenta are about an axis perpendicular to the internuclear line and passing through the centroid of the electron distribution; D is the distance from the

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¹ Kolsky, Phipps, Ramsey, and Silsbee, *Phys. Rev.* **81**, 1061 (1951); **87**, 395 (1952).

² A. Nordsieck, *Phys. Rev.* **58**, 310 (1940).

³ G. F. Newell, *Phys. Rev.* **78**, 711 (1950); **80**, 476 (1950).

⁴ N. F. Ramsey, *Phys. Rev.* **85**, 937 (1952).

⁵ G. C. Wick, *Z. Physik* **85**, 25 (1933).

⁶ G. C. Wick, *Nuovo cimento* **10**, 118 (1933).

⁷ N. F. Ramsey, *Phys. Rev.* **58**, 226 (1940).

⁸ N. F. Ramsey, *Phys. Rev.* **78**, 699 (1950).

⁹ N. F. Ramsey, *Phys. Rev.* **85**, 60 (1952).

center of mass to the centroid of the nuclear charge, \bar{d} is the distance from the center of mass to the centroid of the electron distribution, and $\langle \dots \rangle_J$ indicates the expectation value for the molecule x in vibrational state v and rotational state J . It can be seen from Eq. (1) that if the molecule has no permanent electric dipole moment so that \bar{d} and D are equal, the second term in the brackets vanishes. In this case, in a comparison of molecules of different isotopic masses the rotational magnetic moments are approximately inversely proportional to the moments of inertia, I . Owing to the arbitrariness of the axis about which the electronic moments m^0 are taken, Eq. (1) is only one of many alternative expressions for the rotational magnetic moment, but in most respects it is the simplest, particularly in the absence of a permanent electric dipole moment. Although Eq. (1) is limited to linear molecules for simplicity, the methods of the present paper could be extended to polyatomic molecules by combining them with the procedures of Eshbach and Strandberg.¹⁰

Likewise, from the procedures of Van Vleck,¹¹ the mean molar diamagnetic susceptibility of a Σ linear molecule is given by

$$\chi_J = - (e^2 L / 6 m c^2) \langle 0 | \sum_k r_k c^2 | 0 \rangle_J + (4/3) L v \langle \sum_n [1/(E_n - E_0)] | 0 | \sum_k m_{k\sigma} c | n \rangle |^2 \rangle_J, \quad (2)$$

where the notation is as in previous related papers.⁷⁻⁹ Although the origin about which the angular momenta can be calculated is arbitrary, the specific choice of the origin at C , the centroid of the electron distribution, has been made in order to facilitate subsequent comparisons between Eqs. (1) and (2). As pointed out by Ramsey,⁷ if the effects of molecular vibration were negligible, one could use Eq. (1) to provide an experimental evaluation of the second or high frequency term in Eq. (2); as a result of the high frequency term in Eq. (1) being multiplied by $1/I$ in the averaging, this is not true when the vibration is considered. However, means for making this elimination even in the presence of vibration will be given below.

If c_N is the spin-rotational magnetic interaction constant¹² of nucleus N or if H' is the rotational magnetic field at the nucleus,¹¹ the discussions of Wick¹³ and Ramsey^{8,12} show that after suitable averaging for linear molecules

$$v \langle H' \rangle_J / J = 2 \pi v \langle c_N \rangle_J / \gamma_N = 2 \mu_N M v \langle (1/I) \sum_i Z_i / R_i \rangle_J + \hbar^2 v \langle \sum_{n\lambda'} (1/I) [1/(E_n - E_0)] \times [H_{0\sigma n\lambda'} L_{n\lambda'0\sigma} + L_{0\sigma n\lambda'} H_{n\lambda'0\sigma}] \rangle_J, \quad (3)$$

where R_i is the distance of the i 'th nucleus from the

nucleus N that is being shielded, and the remaining quantities are as previously defined.^{8,12}

For magnetic shielding, the theory of Ramsey^{8,12} leads to

$$v \langle \sigma \rangle_J = (e^2 / 3 m c^2) v \langle 0 | \sum_k r_k^{-1} | 0 \rangle_J + \frac{2}{3} \mu_0 v \langle \sum_{n\lambda'} [1/(E_n - E_0)] [H_{0\sigma n\lambda'} L_{n\lambda'0\sigma} - L_{0\sigma n\lambda'} H_{n\lambda'0\sigma}] \rangle_J. \quad (4)$$

It should be noted that if the effects of vibration are negligible, the last bracketed quantity in Eq. (4) can be eliminated with the aid of Eq. (3) but not when vibration effects are included. However, means for making this elimination even in the presence of vibration will be given subsequently.

Another intramolecular interaction for which zero point vibration corrections need to be made is the spin-spin magnetic interaction constant.^{12,14} In the case of molecular hydrogen, for example, this constant is defined by

$$d_H = (4/5 \hbar) \mu_p^2 v \langle R^{-3} \rangle_J. \quad (5)$$

III. DIATOMIC MOLECULES

In each of the above relations except Eq. (5) at least one of the averages cannot readily be evaluated theoretically due to lack of knowledge as to its dependence on the internuclear spacings. However, for diatomic molecules the assumption introduced by Newell³ can be made: that the high frequency terms vary with internuclear spacing, R as R^n , in which case the average can be carried out in terms of n . It should be noted, however, that this is an assumption for simplicity which is not necessarily valid. It will be shown that with this assumption the values of n in the different cases can then be evaluated experimentally by measurements on molecules in different rotational states or with different isotopic masses. In particular, if R_e is the equilibrium internuclear-spacing for a nonvibrating and nonrotating molecule, we assume that

$$\sum_n [1/(E_n - E_0)] | 0 | \sum_k m_{k\sigma} c^0 | n \rangle |^2 = F_e (R/R_e)^l, \quad (6)$$

$$\sum_{n\lambda'} [1/(E_n - E_0)] [H_{0\sigma n\lambda'} L_{n\lambda'0\sigma} + L_{0\sigma n\lambda'} H_{n\lambda'0\sigma}] = G_e (R/R_e)^m. \quad (7)$$

With these assumptions the previous relations reduce to

$$v \langle \mu_R / J \mu_N M \rangle_J = (M/2\mu') \{ 2 Z_1 Z_2 / (Z_1 + Z_2) + 2 (Z_1 + Z_2) v \langle (D^2 - \bar{d}^2) / R^2 \rangle_J - 16 (m c^2 / e^2) R_e^{-2} F_e v \langle (R/R_e)^{l-2} \rangle_J \}, \quad (8)$$

$$v \langle \chi \rangle_J = - (e^2 L / 6 m c^2) v \langle 0 | \sum_k r_k c^2 | 0 \rangle_J + (4/3) L F_e v \langle R/R_e \rangle_J, \quad (9)$$

¹⁰ J. R. Eshbach and M. W. P. Strandberg, Phys. Rev. **85**, 24 (1952).

¹¹ J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

¹² N. F. Ramsey, Phys. Rev. **85**, 60 (1952).

¹³ G. C. Wick, Phys. Rev. **73**, 51 (1948).

¹⁴ N. F. Ramsey, Phys. Rev. **85**, 938 (1952).

$$\begin{aligned} {}^v\langle H' \rangle_J / J &= 2\pi {}^v\langle c_N \rangle_J / \gamma_N \\ &= 2Z\mu_{NM}(M/\mu')R_e^{-3} {}^v\langle (R/R_e)^{-3} \rangle_J \\ &\quad + (\hbar^2/\mu')R_e^{-2}G_e {}^v\langle (R/R_e)^{m-2} \rangle_J, \quad (10) \end{aligned}$$

$$\begin{aligned} {}^v\langle \sigma \rangle_J &= (e^2/3mc^2) {}^v\langle (0|\sum_k r_k^{-1}|0) \rangle_J \\ &\quad + \frac{2}{3}\mu_0 G_e {}^v\langle (R/R_e)^m \rangle_J, \quad (11) \end{aligned}$$

$$d_H = (4/5h)\mu_p^2 R_e^{-3} {}^v\langle (R/R_e)^{-3} \rangle_J, \quad (12)$$

where μ' is the reduced mass of the diatomic molecule and Z is the charge of the nucleus that is not N . The quantity R_e for use in the above can be obtained empirically either from Eq. (12) in combination with an experimental value of d_H or from the molecular spectra determination of B_0 , as by Herzberg,^{15,16} together with the relation¹⁶

$$R_e = \hbar^3 / (8\pi^2 c \mu' B_{0J})^{1/2} {}^v\langle (R/R_e)^{-2} \rangle_J^{1/2}. \quad (13)$$

All quantities on the right side of the above equations that need to be averaged over the zero point vibration are of the form $(R/R_e)^n$ except for three of them. The analogous assumption to Eqs. (6) and (7) could also be made for these three in which case all the expressions to be averaged would be of the form $(R/R_e)^n$. However, since these quantities can sometimes be evaluated and averaged directly theoretically, as in the calculations of Newell,³ they have been left in the form given above. For molecules with no resultant electrical moment, as H_2 and D_2 , the quantity $(D^2 - d^2)/R^2$ vanishes. In view of this, all the quantities that need to be averaged are either known or can be expressed in the form of ${}^v\langle (R/R_e)^n \rangle_J$. Hence, to make the averages for the quantities of interest, one need merely determine the averages of arbitrary powers of the internuclear spacing. Means for obtaining these averages will be discussed in the next section.

In Eq. (8) if all the quantities except F_e and l are known and if μ_R has been measured in two different rotational states of the same molecule or in two isotopically differing molecules, the values of both F_e and l can be obtained by the simultaneous solution of the two equations of the form (8) which result for the two states in which the measurements are made. An example of such a procedure is given in Sec. V below. These values for F_e and l can then be used in Eq. (8) to yield a predicted value of the rotational moment in any other state or in Eq. (9) to provide a definite determination of the high frequency term of the molecular susceptibility for any rotational or vibrational state. For example, if primes designate the state of the molecule

in which the rotational moment was measured,

$$\begin{aligned} {}^v\langle \chi \rangle_J &= -(e^2 L / 6mc^2) {}^v\langle (0|\sum_k r_k c^2|0) \rangle_J \\ &\quad + (e^2 / 12mc^2) R_e^2 L {}^v\langle (R/R_e)^l \rangle_J \\ &\quad \times {}^v\langle (R/R_e)^{l-2} \rangle_J^{-1} \{ 2Z_1 Z_2 / (Z_1 + Z_2) \\ &\quad + 2(Z_1 + Z_2) {}^v\langle (D^2 - d^2) / R^2 \rangle_J \\ &\quad - (2\mu' / M) {}^v\langle \mu_R / J \mu_{NM} \rangle_J \}. \quad (14) \end{aligned}$$

In a similar fashion, measurements of $\langle c_N \rangle$ in two different rotational states provide a determination of G_e and m as is discussed subsequently in greater detail. The value of G_e and m can then be used to predict the value of $\langle c_N \rangle$ in any other rotational state or to determine the high frequency term of the nuclear shielding $\langle \sigma \rangle$ for any rotational state. The latter determination, for example, gives

$$\begin{aligned} {}^v\langle \sigma \rangle_J &= (e^2 / 3mc^2) {}^v\langle (0|\sum_k r_k^{-1}|0) \rangle_J \\ &\quad - (e^2 / 6mc^2) R_e^2 \mu_{NM}^{-1} {}^v\langle (R/R_e)^m \rangle_J \\ &\quad \times {}^v\langle (R/R_e)^{m-2} \rangle_J^{-1} \{ 2Z \mu_{NM} R_e^{-3} {}^v\langle (R/R_e)^{-3} \rangle_J \\ &\quad - (2\pi \mu' / M \gamma_N) {}^v\langle c_N \rangle_J \}. \quad (15) \end{aligned}$$

IV. AVERAGE VALUES

From the preceding equations it can be seen that the quantities to be evaluated in averaging over the molecular vibration are $\langle (R/R_e)^n \rangle$. This average can in turn be expressed in terms of the expectation values of $\langle (R - R_e)^q / R_e^q \rangle$ by the relation

$$\begin{aligned} {}^v\langle (R/R_e)^n \rangle_J &= \sum_{q=0}^{\infty} [n! / (n-q)! q!] {}^v\langle (R - R_e)^q / R_e^q \rangle_J. \quad (16) \end{aligned}$$

A series expansion for the latter expectation values can be obtained if one assumes the nuclear vibrational potential to be approximately of the Morse potential¹⁷ shape. In this case analytic values of the wave functions are known.¹⁷ These can most conveniently be expressed in terms of the variable

$$z = k \exp[-a(R - R_e)], \quad (17)$$

where^{16,17} $1/k = (B_e/\omega_e)(aR_e)^2$ and a is the quantity which determines the asymmetry of the vibrational potential and is usually determined experimentally. In these variables Morse's wave function¹⁷ is such that in the nonrotating and zeroth vibrational state

$$\begin{aligned} {}^v\langle (R - R_e)^q / R_e^q \rangle_0 &= \int_{-\infty}^{\infty} [(R - R_e)^q / R_e^q] \mathcal{R}^2 dR \\ &= [1/\Gamma(k-1)] \int_0^{\infty} [- (1/aR_e) \\ &\quad \times \ln(z/k)]^q e^{-z} z^{k-2} dz. \quad (18) \end{aligned}$$

¹⁵ G. Herzberg, Can. J. Research A28, 144 (1950).

¹⁶ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand and Company, New York, 1950).

¹⁷ P. M. Morse, Phys. Rev. 34, 57 (1929); J. L. Dunham, *ibid.* 34, 446 (1929).

If in Eq. (18) one uses the series expansion for $\ln(z/k)$ about $z/k=1$ and for any given number of terms in this expansion carries out the multiplications to the indicated q 'th power, all terms except for constant factors are of the following integrable form

$$\int_0^\infty z^p e^{-z} dz = \Gamma(p+1).$$

If the series expansions are carried out to terms as high as z^6 and $(1/k)^3$, the resulting expectation values determined in the above manner are

$${}_0^x \langle (R-R_e)^q / R_e^q \rangle_0 = (1/aR_e)^q (\alpha/k + \beta/k^2 + \gamma/k^3), \quad (19)$$

where α , β , and γ are given in Table I for different integral values of q .

The combination of Eq. (19) with Eq. (16) determines ${}_0^x \langle (R/R_e)^n \rangle_0$ for the zeroth rotational state only. However, it can be extended immediately to the J 'th rotational state by the relation¹⁶

$${}_J^x \langle (R/R_e)^n \rangle_J = {}_0^x \langle (R/R_e)^n \rangle_0 [1 + 4nJ(J+1)B_e/\omega_e^2]. \quad (20)$$

The combination of Eqs. (16), (19), and (20) and the omission of terms of higher order than $(B_e/\omega_e)^2$ yield

$$\begin{aligned} {}_0^x \langle (R/R_e)^n \rangle_J &= 1 + (B_e/\omega_e) [(aR_e)C_1 3/2 + C_2] \\ &+ (B_e/\omega_e)^2 [(aR_e)^3 C_1 13/12 + (aR_e)^2 C_2 15/4 \\ &+ (aR_e)C_3 11/2 + 3C_4 + 4C_1 J(J+1)], \end{aligned} \quad (21)$$

where $C_1=n$, $C_2=C_1(n-1)/2$, $C_3=C_2(n-2)/3$, and $C_4=C_3(n-3)/4$. From Eq. (21) the expectation values needed in Eqs. (8-13) can be calculated if n is known.

The determination of n in certain cases can be made by a measurement of a quantity such as the rotational magnetic moment in two different rotational or isotopic states. In this case, the ratio of the two experimental quantities experimentally determines the ratio of ${}_0^x \langle (R/R_e)^n \rangle_{J'}/{}_0^x \langle (R/R_e)^n \rangle_J$, and n is inferred by comparing the experimental value to the theoretical value. There is consequently need for a theoretical expression giving the ratio of the expectation values in two

TABLE I. Coefficients for

$${}_0^x \langle (R-R_e)^q / R_e^q \rangle_0 = (1/aR_e)^q (\alpha/k + \beta/k^2 + \gamma/k^3).$$

q	α	β	γ
1	3/2	13/12	1
2	1	15/4	65/12
3	0	11/2	131/8
4	0	3	61/2
5	0	0	65/2
6	0	0	15

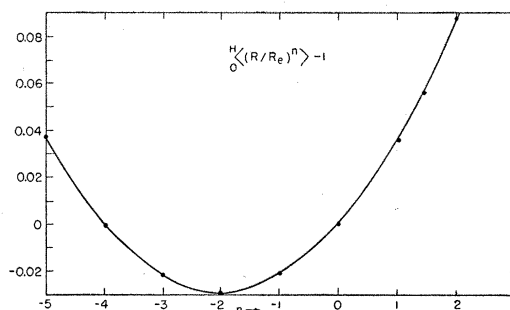


FIG. 1. ${}_0^H \langle (R/R_e)^n \rangle_1 - 1$ as a function of n .

different states. From Eq. (21) the ratio is given by

$$\begin{aligned} {}_0^2 \langle (R/R_e)^n \rangle_{J'}/{}_0^1 \langle (R/R_e)^n \rangle_J &= 1 + [(B_e/\omega_e)_2 - (B_e/\omega_e)_1] [(aR_e)C_1 3/2 + C_2] \\ &+ [(B_e/\omega_e)_2^2 - (B_e/\omega_e)_1^2] [(aR_e)^3 C_1 13/12 \\ &+ (aR_e)^2 C_2 15/4 + (aR_e)C_3 11/2 + 3C_4] + [(B_e/\omega_e)_1^2 \\ &- (B_e/\omega_e)_1 (B_e/\omega_e)_2] [(aR_e)C_1 3/2 + C_2]^2 \\ &+ (B_e/\omega_e)_2^2 4C_1 J'(J'+1) \\ &- (B_e/\omega_e)_1^2 4C_1 J(J+1). \end{aligned} \quad (22)$$

V. SIGNIFICANCE OF MEASUREMENTS ON DIFFERENT STATES OF SIMILAR MOLECULES

It is sometimes possible to determine such quantities as μ_R or C_N in two similar molecules which differ only in rotational state or in isotopic mass. If one assumes that the differences are due only to changes of reduced mass, rotational quantum number, centrifugal stretching, and zero point vibration, and that these differences are in accordance with Eqs. (8) and (10), the values of l and m in such cases can be determined from the experimental measurements. Thus, from Eq. (8) in cases where $D^2 = d^2$,

$$\begin{aligned} {}_0^2 \langle (R/R_e)^{l-2} \rangle_{J'}/{}_0^1 \langle (R/R_e)^{l-2} \rangle_J &= 1 + \frac{{}_0^1 \langle \mu_R / J \mu_{NM} \rangle_J - {}_0^2 \langle \mu_R / J \mu_{NM} \rangle_{J'} (\mu_2'/\mu_1')}{(M/2\mu_1') 2Z_1 Z_2 / (Z_1 + Z_2) - {}_0^1 \langle \mu_R / J \mu_{NM} \rangle_J}. \end{aligned} \quad (23)$$

A comparison of the experimental results obtained from Eq. (23) with the theoretical results given in Eq. (22) determines l . It should be noted that Eq. (23) does not include effects due to small changes of the electrons' reduced mass for different isotopes.

Similarly, if c_N is known in two different states,

$$\begin{aligned} {}_0^2 \langle (R/R_e)^{m-2} \rangle_{J'}/{}_0^1 \langle (R/R_e)^{m-2} \rangle_J &= 1 - \frac{1 - {}_0^2 \langle (R/R_e)^{-3} \rangle_{J'}/{}_0^1 \langle (R/R_e)^{-3} \rangle_J}{1 - 1/[2Z\mu_{NM}R_e^{-3} {}_0^1 \langle (R/R_e)^{-3} \rangle_J \gamma_{N1} M / 2\pi\mu_1' c_{N1}]} \\ &+ \frac{1 - (\mu_2' c_{N2} \gamma_{N1} / \mu_1' c_{N1} \gamma_{N2})}{2Z\mu_{NM}R_e^{-3} {}_0^1 \langle (R/R_e)^{-3} \rangle_J \gamma_{N1} M / 2\pi\mu_1' c_{N1} - 1}. \end{aligned} \quad (24)$$

If experimental values of c_{N2} and c_{N1} are inserted in Eq. (24) and if the resulting value for the expression is compared to Eq. (22), the value of m can be determined.

A quantity of particular importance in nuclear physics measurements is the ratio of the magnetic shielding in two molecules which differ only isotopically. The precision measurements^{18,19} of the ratio of the proton magnetic moment to that of the deuteron depends upon such a quantity.^{3,19,20} From Eq. (11), it can be seen that

$$\begin{aligned} v^2 \langle \sigma \rangle_J / v^1 \langle \sigma \rangle_J = 1 + (e^2/3mc^2) [v^2 \langle (0 | \sum_k r_k^{-1} | 0) \rangle_J - \\ - v^1 \langle (0 | \sum_k r_k^{-1} | 0) \rangle_J] v^1 \langle \sigma \rangle_J^{-1} + [v^1 \langle \sigma \rangle_J - \\ - (e^2/3mc^2) v^2 \langle (0 | \sum_k r_k^{-1} | 0) \rangle_J] v^1 \langle \sigma \rangle_J^{-1} \\ \times [v^2 \langle (R/R_e)^m \rangle_J / v^1 \langle (R/R_e)^m \rangle_J - 1]. \quad (25) \end{aligned}$$

VI. MOLECULAR HYDROGENS

Numerical values of the constants appearing in Eqs. (21) and (22) can be inserted for H_2 and D_2 and the quantities can be plotted as functions of n . Most of the necessary constants are given by Herzberg.¹⁵ However, the parameter aR_e which determines the asymmetry of the Morse potential requires a slight discussion. This parameter is often determined from the molecular dissociation energy. However, the dissociation energy is chiefly affected by the shape of the potential at very large energies, whereas the zero point vibration is chiefly affected by the shape of the potential well at its bottom. Therefore, it is best to proceed as discussed by Newell³ and determine (aR_e) by making the Morse potential agree with the leading terms of the Dunham²¹ power series expansion of the potential. In this case,³ aR_e is 1.608. With these values, Eqs. (21) and (22) yield the results shown in Figs. 1 and 2 for rotational state $J=1$. The superscripts H and D indicate H_2 and D_2 , respectively. These curves are particularly valuable in determining the quantities l and m as discussed in the previous section. A determination of the actual values of l and m that can be inferred for hydrogen molecules will be given in a subsequent paper which describes the experiments.

VII. SPIN-SPIN MAGNETIC INTERACTION

Let the spin-spin magnetic interaction between the two nuclei of a diatomic molecule be called $K(R)$ so that

$${}^x K(R)_J = \mu_1 \mu_2 R_e^{-3} {}^x \langle (R/R_e)^{-3} \rangle_J = 5d_H h/4, \quad (26)$$

where the last step applies only to molecular H_2 . Then from Eq. (13),

$$\begin{aligned} {}^x K(R)_J = \mu_1 \mu_2 (8\pi^2 c \mu_1' B_0 J / h)^{\frac{1}{2}} {}^x \langle (R/R_e)^{-3} \rangle_J \\ \times {}^1 \langle (R/R_e)^{-2} \rangle_J^{-\frac{1}{2}}. \quad (27) \end{aligned}$$

If Eq. (21) is used here and if the calculations are

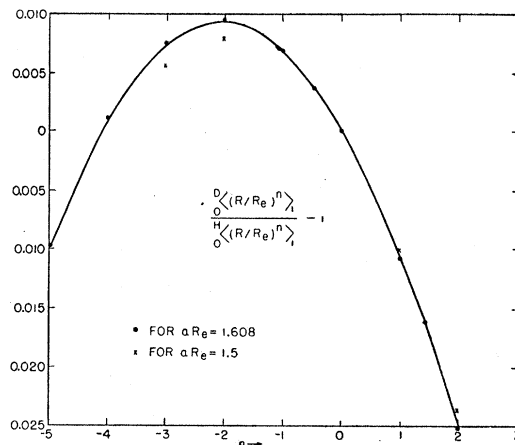


FIG. 2. ${}^D \langle (R/R_e)^n \rangle_1 / {}^H \langle (R/R_e)^n \rangle_1 - 1$ as a function of n .

carried out,

$$\begin{aligned} {}^x K(R)_J = \mu_1 \mu_2 (8\pi^2 c \mu_1' B_0 / h)^{\frac{1}{2}} \{ 1 + (B_e / \omega_e) 3/2 \\ + (B_e / \omega_e)^2 [(aR_e)^{29}/4 - (aR_e)^{17}/2 \\ + 99/8 - 12J(J+1)] \}. \quad (28) \end{aligned}$$

Although this appears quite different from the equation recently published by the author,⁴ it is actually very similar and slightly superior. The empirical quantity γ_e ^{4,15,16} does not appear here since it is more consistent to use the theoretical value for γ_e since the theoretical values must be used elsewhere in the same equation and by using theoretical values throughout there is a tendency for errors introduced thereby partially to cancel. If the numerical constants appropriate to H_2 , as discussed in the previous section, are used,

$${}^H K(R)_1 = (4.7738 \pm 0.0030) \times 10^{-22} \text{ ergs}. \quad (29)$$

This result is in excellent agreement with the experimental results^{1,4} for H_2 :

$$5d_H h/4 = (4.7750 \pm 0.0010) \times 10^{-22} \text{ ergs}. \quad (30)$$

As recently pointed out in a brief note by Ramsey,⁴ this close agreement indicates that any nonmagnetic tensor interaction between two protons at the internuclear distance of H_2 must be very small indeed (less than 10^{-19} Mev).

In the calculation¹ of the deuteron quadrupole moment from the measured interaction in molecular deuterium, it is necessary¹ to subtract off a spin-spin magnetic part of the measured interaction. This is usually done¹ by taking the measured spin-spin magnetic interaction in H_2 and multiplying it by the square of the ratio of the deuteron magnetic moment to that of the deuteron. However, obtaining the correction in this way is not completely accurate since the zero point vibration is different for H_2 and D_2 . The added correction factor to be applied is then from Eq. (22) and the best constants

$${}^D \langle (R/R_e)^{-3} \rangle_1 / {}^H \langle (R/R_e)^{-3} \rangle_1 = 1.0073. \quad (31)$$

¹⁸ G. Lindstrom, Phys. Rev. **78**, 817 (1950).

¹⁹ B. Smaller, Phys. Rev. **83**, 812 (1951).

²⁰ N. F. Ramsey, Phys. Rev. **85**, 688 (1952).

²¹ J. L. Dunham, Phys. Rev. **41**, 713, 721 (1932); **49**, 797 (1936).