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Transport and Relaxation Phenomena in the Hydrogen Isotopes[*]

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Expressions are obtained for the collision cross sections governing the relaxation of angular momentum polarizations in the molecular hydrogen isotopes, making use of the fact that energetically inelastic collisions are very infrequent. A number of interrelationships between the collision cross sections of this type, occurring in NMR and in other transport and relaxation phenomena such as the Senftleben-Beenakker (SB) thermal conductivity effect, and depolarized Rayleigh light scattering, are developed and comparisons between calculated cross sections and those obtained from various experiments are given. For example, in n-H_2 at room temperature, the SB effect for the shear viscosity gives a characteristic cross section of (0.47 ± 0.05) Å^2 to be compared with a calculated cross section of 0.32 Å^2, and a cross section of 0.40 Å^2 which can be extracted from NMR measurements. A calculated value of σ_{DPR}, for the cross section determining the width of the depolarized Rayleigh line, in n-H_2 of 0.48 Å, is obtained, to be compared with the experimental value 0.495 Å^2.

I. INTRODUCTION

The kinetic theory of transport and relaxation phenomena in polyatomic gases, based on the Waldman-Snider (WS) kinetic equation,[1,2] has moved in recent years from a qualitative to a semiquantitative stage. For polyatomic molecules, not only is the number of transport-relaxation phenomena greatly increased but also the description of such phenomena is complicated by an angular momentum dependence of the distribution function density matrix for the gas and by the existence of reorientation and energetically inelastic collisions. A number of new phenomena, such as the Senftleben[3] and Senftleben-Beenakker effects[4] are due solely to this angular momentum dependence. Most of the qualitative and some of the quantitative features of these effects have already been explained,[5] but much yet needs to be done.

One of the steps which has proven to be useful has been the derivation of a number of interrelations, both exact and approximate, between the variety of collision cross sections which appear in these polyatomic gas phenomena. Recent work[6,7] has concentrated on obtaining such relations for (nearly) homonuclear relatively heavy diatomic molecules where the nonspherical part of the interaction potential may be assumed to be given by a single P_2-type term. While the same is true for the different modifications of the homonuclear hydrogen isotopes, the energy-level splitting is so large that the approximate treatment of energetically inelastic collisional events used in Refs. 6 and 7 might be expected to break down. A recent application of the relations given in Ref. 6 to a study of rotational relaxation[8] has shown, however, that even for the hydrogen isotopes, the approximate relations are relatively well obeyed (within 15%). This has been conclusively shown[9] not to be the case for HD; this is not surprising since for this molecule the assumption of a pure P_2-type potential is certainly invalid.

One of the results obtained in Ref. 8 is the fact that collision cross sections depending solely on energetically inelastic collisions are extremely small for the homonuclear hydrogen istopes. Because of this, the contributions from energetically inelastic collision events to collision integrals which also contain a purely elastic or a reorientation (i.e., $\Delta J = 0$, $\Delta M_J \neq 0$) collision contribution may be safely neglected. With this assumption, it is possible, for example, to derive explicit expressions for the reorientation collision cross sections[10] $\sigma\binom{0100}{0100}$ and $\sigma\binom{0200}{0200}$ within the distorted-wave Born approximation (which should be very good for hydrogen). Such a derivation is given in Sec. II. The results of this section allow the temperature dependence of the ratio of the cross sections $\sigma\binom{0200}{0200}$ for any two of the modifications of the homonuclear hydrogen isotopes to be predicted. A typical application of these curves would be the prediction of the position of the low-temperature Senftleben-Beenakker shear viscosity effect on an H/p (magnetic field to pressure) axis for any of the hydrogen isotope modifications from the room-temperature data.

Section III examines some of the predicted ratios and compares the theoretical values (at 300 K) with those obtainable from experiment. Further, two procedures for obtaining the value of $\sigma\binom{0200}{0200}$ from the experimental data are compared and contrasted. One of the methods uses only transport data (and, in principle, allows an independent determination of the rotational g factor). This is a simplification (due to the fact that energetically inelastic collisions can be neglected) of a method used earlier[11] to obtain g_{rot} values for N_2 and CO. The second method makes use of the g_{rot} values as obtained from molecular beam magnetic resonance experiments.

Section IV discusses nuclear magnetic relaxation in n-H_2 from the point of view of kinetic theory[12,13] and the results obtained in Sec. II. At 77 K, the calculated forms of the "transverse" relaxation times T_1 and T_2 as a function of density are consistent with the treatment of a one-level spin system and in agreement with the experimental results obtained by Hardy.[14] A short discussion of the room-temperature result for T_1 found by Lalita, Bloom, and Noble[15] is also given and values of $\sigma\binom{0200}{0200}_{o\text{-}H_2}$ are extracted from the NMR data both at 77 and at 300 K.

Section V shows how the interrelations between the various collision cross sections may be exploited and employed in the calculation of other transport and relaxation phenomena in hydrogen. As examples, the collision cross section determining the width of the depolarized Rayleigh line[16] in light scattering and the self-diffusion coefficient for n-H_2 are calculated and compared with experiment.

II. DERIVATION OF REORIENTATION COLLISION CROSS SECTIONS

The collision integrals which can be associated with the relaxation of the various angular momentum tensor polarizations which exist in a gas can be denoted by $\left[\begin{smallmatrix}0k00\\0k00\end{smallmatrix}\right]$, having the generic form[10]

$$\left[\begin{smallmatrix}0k00\\0k00\end{smallmatrix}\right] \equiv (2k+1)^{-1}\left([\vec{\mathrm{J}}]^{(k)} \odot {}^{k}, \mathcal{R}_0 [\vec{\mathrm{J}}]^{(k)}\right) \quad . \tag{2.1}$$

These collision integrals are density independent, the trivial density factors in the Waldmann-Snider (WS) collision term having been removed. Further, the quantity $[\vec{\mathrm{J}}]^{(k)}$ is the kth-rank irreducible Cartesian tensor[17] of weight k which can be constructed from the vector operator $\vec{\mathrm{J}}$ of the rotational angular momentum of the diatomic molecule and $\mathcal{R}_0$ is the (positive-definite) linearized WS collision superoperator. The inner product appearing in this equation is defined by

$$(A, B) = n^{-1}\mathrm{Tr}\int d\vec{\mathrm{p}}\, f^{(0)} A^{\dagger} B \quad , \tag{2.2}$$

where A and B are single-particle operators, $f^{(0)}$ is the equilibrium distribution function density matrix for the gas, and the trace is to be taken over all internal states of the molecule. It has been shown in Ref. 7 that for the case of a nonspherical intermolecular potential which can be represented as a single P_2-type of interaction, the collision bracket (2.1) has the explicit form

$$\left[\begin{smallmatrix}0k00\\0k00\end{smallmatrix}\right] = \frac{1}{Q}\Big\{\sum_j g_j L^{(k)}(j,j) e^{-Bj(j+1)}\Big\} H^{(0)} + \frac{1}{Q}\sum_{\substack{j,j'\\ j'<j}} \Big\{\big[L^{(k)}(j,j') + L^{(k)}(j',j)\big] e^{-Bj(j+1)} H_{+}^{(0)}(j,j)\Big\} , \tag{2.3}$$

where

$$L^{(k)}(j,j') = \Omega(j,2,j')\, \alpha_j{}^{(k)} \mu^2(j,2,j')\Omega^{1/2}(j,k,j)(-1)^k \times \frac{1}{2k+1}\left[\frac{\alpha_j{}^{(k)} \alpha_{j'}{}^{(0)}}{\alpha_j{}^{(0)}} \frac{\Omega^{1/2}(j,k,j)}{2j+1} - (-1)^k \alpha_{j'}{}^{(k)} \Omega^{1/2}(j',k,j') \begin{Bmatrix} j' & j' & k \\ j & j & 2 \end{Bmatrix}\right] . \tag{2.4}$$

In these expressions j is the magnitude of the angular momentum of a molecule prior to a collision while j' is its magnitude following a collision, B is the reduced rotational constant of the molecule, $B = \hbar^2/2IkT$ (I is the moment of inertia), g_j is the nuclear spin degeneracy of the state characterized by j, and Q is the rotational partition function $Q = \sum_j g_j(2j+1)\exp[-Bj(j+1)]$. The quantities $H^{(0)}$ and $H_{+}^{(0)}(j,j')$ are complicated functionals of the spherical part of the potential and of the (scalar) coefficient potential of the P_2 term: The first of these two functionals is independent of j and j'. Of the remaining quantities, $\left\{\begin{smallmatrix} j' & j' & k \\ j & j & 2 \end{smallmatrix}\right\}$ is a $(6-j)$ symbol while the definitions of and explicit expressions for the quantities $\Omega(j,k,l)$, $\alpha_j{}^{(k)}$, and

TABLE I. Diagonal deorientation collision integrals for a one-level spin system.

j	$\left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right]^{(j)}/H^{(0)}$	$\left[\begin{smallmatrix}0200\\0200\end{smallmatrix}\right]^{(j)}/H^{(0)}$
0	0	0
1	4/15	2/25
2	4/21	34/35
3	8/45	164/75
4	40/231	292/77
5	20/117	226/39

$\mu(j, k, l)$ are to be found in the Appendix.

The first term in Eq. (2.3) represents the energetically elastic contributions to the collision bracket while the second term represents the energetically inelastic contributions. Owing to the scarcity of inelastic collisions in the homonuclear hydrogen isotopes, this latter contribution will be very small in comparison with the former one and to all intents and purposes can be neglected. An important property of the simple P_2-type potential treated in Ref. 7 is the complete absence of the collision partner in Eq. (2.3). Because of this property, the distinction between pure species and mixtures of different (nuclear spin symmetry) species is lost insofar as collisional calculations are concerned: This means that Eq. (2.3) can be applied not only to the pure nuclear spin symmetry species (p-H_2, o-H_2, p-D_2, o-D_2) but also to the more commonly occurring equilibrium mixtures (n-H_2, n-D_2).

The neglect of energetically inelastic collisions and the disappearance of the collision partner in the collision brackets results in their being expressible as a sum of contributions from single-level spin systems weighted according to the population of the system as

$$\left[\begin{smallmatrix}0k00\\0k00\end{smallmatrix}\right] = \sum_j p_j \left[\begin{smallmatrix}0k00\\0k00\end{smallmatrix}\right]^{(j)} \quad , \tag{2.5}$$

where $\left[\begin{smallmatrix}0k00\\0k00\end{smallmatrix}\right]^{(j)}$ means that the square bracket integral $\left[\begin{smallmatrix}0k00\\0k00\end{smallmatrix}\right]$ has been evaluated for a single-level spin system having angular momentum of magnitude j, and p_j is the fractional population of the spin system. The p_j are, for the various modifications of H_2 and D_2, given by

$$\begin{aligned}
p_j(p-H_2) &= \{1+(-1)^j\}S_j/\textstyle\sum_j\{1+(-1)^j\}S_j \quad ,\\
p_j(o-H_2) &= \{1+(-1)^{j+1}\}S_j/\textstyle\sum_j\{1+(-1)^{j+1}\}S_j \quad ,\\
p_j(n-H_2) &= \{2+(-1)^{j+1}\}S_j/\textstyle\sum_j\{2+(-1)^{j+1}\}S_j \quad ,\\
p_j(o-D_2) &= \{1+(-1)^j\}S_j'/\textstyle\sum_j\{1+(-1)^j\}S_j' \quad ,\\
p_j(p-D_2) &= \{1+(-1)^{j+1}\}S_j'/\textstyle\sum_j\{1+(-1)^{j+1}\}S_j' \quad ,\\
p_j(n-D_2) &= \{\tfrac{3}{2}+\tfrac{1}{2}(-1)^j\}S_j'/\textstyle\sum_j\{\tfrac{3}{2}+\tfrac{1}{2}(-1)^j\}S_j' \quad ,
\end{aligned} \tag{2.6}$$

where

$$S_j^{(\prime)} = (2j+1)\exp\{-B^{(\prime)}j(j+1)\} \tag{2.7}$$

with B and B' equal to $84.8/T$ and $42.6/T$, respectively.[18]

For a single-level spin system with magnitude of angular momentum j, Eq. (2.3) reduces to

$$\left[\begin{smallmatrix}0k00\\0k00\end{smallmatrix}\right]^{(j)} = (2j+1)\,L^{(k)}(j,j)H^{(0)} \quad , \tag{2.8}$$

since $Q=g_j(2j+1)\exp[-Bj(j+1)]$. Making use of the explicit expressions for the quantities $\Omega(j,k,l)$, $\alpha_j^{(k)}$, and $\mu(j,k,l)$ given in the Appendix and for the (6-j) symbol,[19] the following expressions may be obtained for the collision brackets having $k=1, 2$:

$$\left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right]^{(j)} = \frac{2}{3}\,\frac{j(j+1)}{(2j-1)(2j+3)}\,H^{(0)} \quad , \tag{2.9}$$

$$\left[\begin{smallmatrix}0200\\0200\end{smallmatrix}\right]^{(j)} = \frac{1}{5}\,\frac{j(j+1)(4j^2+4j-7)}{(2j-1)(2j+3)}\,H^{(0)} \quad . \tag{2.10}$$

These two collision brackets have been singled out because they appear in the Senftleben-Beenakker (SB) effects and in the nuclear magnetic relaxation in the hydrogen isotopes. Values of $\left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right]^{(j)}/H^{(0)}$ and $\left[\begin{smallmatrix}0200\\0200\end{smallmatrix}\right]^{(j)}/H^{(0)}$ have been assembled in Table I for $j=0, 1, \ldots, 5$ while Fig. 1 shows $\left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right]^{(j)}/H^{(0)}$ and $\left[\begin{smallmatrix}0200\\0200\end{smallmatrix}\right]^{(j)}/\{j(j+1)H^{(0)}\}$ as functions of j.

Rather than discussing the collision integrals themselves, it is convenient to discuss the generalized collision cross sections[10] which can be derived from them. The two of specific interest

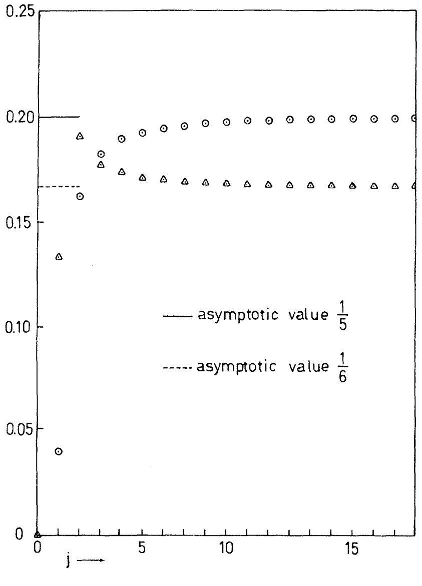

FIG. 1. The qunatities $\left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right]^{(j)}/H^{(0)}$ and $\left[\begin{smallmatrix}0200\\0200\end{smallmatrix}\right]^{(j)}/\{j(j+1)H^{(0)}\}$ as functions of j. △, $\left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right]^{(j)}/H^{(0)}$; ○, $\left[\begin{smallmatrix}0200\\0200\end{smallmatrix}\right]^{(j)}/\{j(j+1)H^{(0)}\}$.

here are

$$\sigma\binom{0100}{0100} \equiv 3\left(\langle J^2\rangle_0 \langle v_{\mathrm{rel}}\rangle_0\right)^{-1}\left[{0100 \atop 0100}\right] \tag{2.11}$$

and

$$\sigma\binom{0200}{0200} \equiv 15\left(2\langle J^2(J^2 - \tfrac{3}{4})\rangle_0 \langle v_{\mathrm{rel}}\rangle_0\right)^{-1}\left[{0200 \atop 0200}\right] \ . \tag{2.12}$$

In the case of purely j-dependent arguments, the average $\langle \cdots \rangle_0$ reduces to a calculation of

$$\langle A(j)\rangle_0 = \textstyle\sum_j p_j A(j) \ . \tag{2.13}$$

The average relative velocity $\langle v_{\mathrm{rel}}\rangle_0$ appearing in the definitions of these cross sections is

$$\langle v_{\mathrm{rel}}\rangle_0 = (16kT/\pi m)^{1/2} \ . \tag{2.14}$$

Using the definitions (2.11) and (2.12) together with the results (2.5), (2.9), and (2.10) the cross sections $\sigma\binom{0100}{0100}$ and $\sigma\binom{0200}{0200}$ are obtained as

$$\sigma\binom{0100}{0100} = \tfrac{4}{3}\langle j(j+1)(2j-1)^{-1}(2j+3)^{-1}\rangle_0 \langle j(j+1)\rangle_0^{-1}\sigma^{(0)} \tag{2.15}$$

and

$$\sigma\binom{0200}{0200} = \langle j(j+1)(4j^2+4j-7)(2j-1)^{-1}(2j+3)^{-1}\rangle_0 \times \langle j(j+1)(j^2+j-\tfrac{3}{4})\rangle_0^{-1}\sigma^{(0)} \ , \tag{2.16}$$

where $\sigma^{(0)}$ is given by

$$\sigma^{(0)} = \tfrac{3}{2}H^{(0)}/\langle v_{\mathrm{rel}}\rangle_0 \ . \tag{2.17}$$

It is to be understood in Eqs. (2.15) and (2.16) that the averages are to be taken with the relevant weight factors for the hydrogen isotope modification being considered [see Eqs. (2.6)] and that $\sigma^{(0)}$ is to be taken as $\sigma^{(0)}_{\mathrm{H}_2}$ for the hydrogen modifications and as $\sigma^{(0)}_{\mathrm{D}_2}$ for the deuterium modifications. It should not be assumed that these latter two quantities are equal. Since $\sigma\binom{0100}{0100}$ shows up only in the nuclear magnetic relaxation measurements while $\sigma\binom{0200}{0200}$ shows up not only in the NMR measurements but also in the SB-effect shear-viscosity measurements and in the closely related thermomagnetic torque[20] measurements, it will be expedient to concentrate more on the latter cross section.

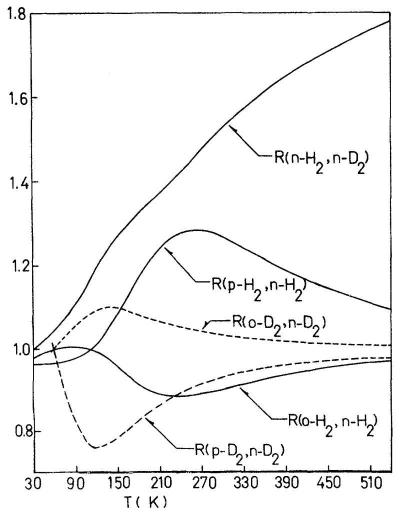

FIG. 2. The ratios $R(p\text{-H}_2, n\text{-H}_2)$, $R(o\text{-H}_2, n\text{-H}_2)$, $R(n\text{-H}_2, n\text{-D}_2)$, $R(o\text{-D}_2, n\text{-D}_2)$, $R(p\text{-D}_2, n\text{-D}_2)$ as functions of the absolute temperature; the ratios $R(A, B)$ are defined in the text.

Once the ratios between the cross sections $\sigma\binom{0200}{0200}$ for the various modifications are known, the measurement of any one will allow the prediction of the relevant effects for any other isotope.[21] Figure 2 gives plots of five ratios of "reduced" $\sigma\binom{0200}{0200}$ cross sections as functions of the temperature T. Specifically, the ratios appearing in these figures are defined by

$$R(A, B) = \{\sigma\tbinom{0200}{0200}_A \sigma_B{}^{(0)}\}/\{\sigma\tbinom{0200}{0200}_B \sigma_A{}^{(0)} \ , \tag{2.18}$$

where A and B are any two of the homonuclear hydrogen isotope modifications.

III COMPARISON WITH SENFTLEBEN-BEENAKKER-EFFECT MEASUREMENTS

There are two methods for obtaining the collision cross section $\sigma\binom{0200}{0200}$ from experimental data on the SB effects and the thermomagnetic torque. The first of these[11] uses only transport data, namely, the field-free thermal conductivity coefficient λ_0, the field-free shear-viscosity coefficient η_0, and the values of the magnetic field to gas pressure ratio (H/p), where the SB effects $\Delta\eta_3/\eta_0$ and $\Delta\lambda_{\parallel}/\lambda_0$ reach half their saturation values. The second of these[22] uses only the $(H/p)_{1/2,\eta_3}$ value together with the value of the rotational g-factor as obtained from molecular beam magnetic resonance experiments. Inherent in the first method is a number of exact and approximate relations[7] between collision cross sections. Two essential types of approximation were utilized in Ref. 7 in deriving the approximate relations: The first approximation was that of nearly classical collisions and the second involved making a Taylor series expansion in the parameter $\Delta E/kT$ (the ratio of the change in the total internal energy of the colliding pair of molecules to kT). For most homonuclear diatomic molecules, such as N_2 and O_2, the effects of these two types of approximation cannot be unraveled and it is therefore not possible to test the approximations separately. However, in the case of the homonuclear hydrogen isotopes, since energetically inelastic collisions (those for which $\Delta E \neq 0$) may essentially be neglected,[23] it is useful to compare the two methods of calculating $\sigma\binom{0200}{0200}$ as a means of checking the approximation of nearly classical collisions.

The required transport data, expressed in terms

TABLE II. Relations between collision cross sections.

Cross section	Expression for Ref. 6	Expression if $\sigma\binom{0010}{0010} \simeq 0$
$\sigma\binom{1010}{1010}$	$\frac{2}{3}\sigma\binom{2000}{2000} + \frac{5}{6}\binom{0010}{0010}$	$\frac{2}{3}\sigma\binom{2000}{2000}$
$\sigma\binom{1010}{1001}$	$\frac{1}{2}r\sigma\binom{0010}{0010}$	0
$\sigma\binom{1001}{1001}$	$\frac{2}{3}\pi R_0^2\Omega^{(1,1)*} + \frac{7}{4}\frac{k}{c_{\text{int}}}\sigma\binom{0010}{0010}$	$\frac{2}{3}\pi R_0^2\Omega^{(1,1)*}$
$\sigma_0\binom{1200}{1200}$	$\frac{2}{3}\pi R_0^2\Omega^{(1,1)*} + \frac{7}{6}\sigma\binom{0200}{0200}$	$\sigma\binom{1001}{1001} + \frac{7}{6}\sigma\binom{0200}{0200}$

of the generalized collision cross sections defined in Ref. 10, are given by[11]

$$\lambda_0 = \frac{5k^2T}{2m\langle v_{\text{rel}}\rangle_0}\,\frac{\sigma\binom{1001}{1001} + 2r^{-1}\sigma\binom{1010}{1001} + r^{-2}\sigma\binom{1010}{1010}}{\sigma\binom{1010}{1010}\sigma\binom{1001}{1001} - \sigma^2\binom{1010}{1001}}$$

$$\simeq \frac{5k^2T}{2m\langle v_{\text{rel}}\rangle_0}\left[\sigma^{-1}\binom{1010}{1010} + r^{-2}\sigma^{-1}\binom{1001}{1001}\right] , \tag{3.1}$$

$$\eta_0 = kT\left[\langle v_{\text{rel}}\rangle_0\,\sigma\binom{2000}{2000}\right]^{-1} , \tag{3.2}$$

$$\mu = (H/p)_{1/2,\lambda_{\parallel}}/(H/p)_{1/2,\eta_3} = \sigma_0\binom{1200}{1200}/\sigma\binom{0200}{0200} , \tag{3.3}$$

where $r = (5k/2c_{\text{int}})^{1/2}$ with c_{int} being the internal heat capacity per molecule. The second (approximate) equality in Eq. (3.1) is obtained upon neglecting $\sigma\binom{1010}{1001}$, a purely energetically inelastic collision cross section. Those relations between collision cross sections in Eqs. (3.1)–(3.3) which are required from Refs. 6 and 7 are given in Table II together with the simplified expressions obtained when energetically inelastic collisions are neglected.

Using the first entry in Table II, Eqs. (3.1) and (3.2) may be solved to give $\sigma\binom{1001}{1001}$ in terms of $\sigma\binom{2000}{2000}$ as

$$\sigma\binom{1001}{1001} = 4(10e - 15)^{-1}(c_{\text{int}}/k)\,\sigma\binom{2000}{2000} , \tag{3.4}$$

where e is the Eucken factor $e = 2m\lambda_0/(5k\eta_0)$. Using the final entry in Table II, Eq. (3.3) allows the expression of $\sigma\binom{0200}{0200}$ as

$$\sigma\binom{0200}{0200} = (\mu - \tfrac{7}{6})^{-1}\sigma\binom{1001}{1001} . \tag{3.5}$$

The data needed for the calculation of $\sigma\binom{0200}{0200}$ in this manner are collected in Table III for p-H_2, n-H_2, o-D_2, and n-D_2. Measurements of both the SB shear-viscosity effect[24] and the thermomagnetic torque may be used to obtain $(H/p)_{1/2,\eta_3}$. While the data of both Ref. 24 and Refs. 25, 26 are rather uncertain due to the extreme smallness of the effects being measured, the data of Refs. 25 and 26 are more to be trusted[27] since it is easier to determine the position of a maximum than the position at which an effect reaches half its saturation value. For all gases so far considered[28] it has been found that the thermomagnetic torque attains its maximum at an (H/p) value equal to one-half of $(H/p)_{1/2,\eta_3}$ and it will be assumed that this is also the case for the hydrogen isotopes. The resulting values of $\sigma\binom{0200}{0200}$ are given (in the fourth column of) Table IV together with $\sigma\binom{1001}{1001}$ and $\sigma_0\binom{1200}{1200}$.

For the second method of calculation of $\sigma\binom{0200}{0200}$ only the value of $(H/p)_{1/2,\eta_3}$ is needed in addition to the value of the rotational g factor since

$$(H/p)_{1/2,\eta_3} = \frac{\hbar\langle v_{\text{rel}}\rangle_0\sigma\binom{1200}{1200}}{\mu_N kT g_{\text{rot}}} , \tag{3.6}$$

where μ_N is the nuclear magneton. The values of $\sigma\binom{0200}{0200}$ obtained from Eq. (3.6) using Ramsey's values[29] of g_{rot} and the $(H/p)_{1/2,\eta_3}$ values derived from Refs. 25 and 26 are also listed in Table IV. A similar calculation of $\sigma_0\binom{1200}{1200}$ can be performed by using the relation between this cross section and $(H/p)_{1/2,\lambda_{\parallel}}$:

$$\left(\frac{H}{p}\right)_{1/2,\lambda_{\parallel}} = \frac{\hbar\langle v_{\text{rel}}\rangle_0\,\sigma_0\binom{1200}{1200}}{\mu_N kT g_{\text{rot}}} . \tag{3.7}$$

Comparison of columns 4 and 5 and 6 and 7[30] of Table IV shows that the agreement between the values of $\sigma\binom{0200}{0200}$ and $\sigma_0\binom{1200}{1200}$ calculated by means of the two methods is quite good. From this, it is possible to conclude that the approximation of nearly classical collisions is a good one and it allows the use of the interrelationships between the collision cross sections with some confidence.

From the values for the cross sections $\sigma\binom{0200}{0200}$ given in Table IV, three ratios may be constructed and a comparison made with the corresponding theoretical values obtained from Fig. 2 for $T = 300$ K. Both sets of values are tabulated in Table V. The two explicitly known ratios compare

TABLE III. Data on the homonuclear hydrogen isotopes at 300 K.

Gas	η_0 (μP)	$\sigma\binom{2000}{2000}$ (Å^2)	λ_0 (erg/cm sec °K)	e	c_{int}/k	$(H/p)_{1/2,\eta_3}$ (kOe/Torr)	$(H/p)_{1/2,\lambda_{\parallel}}$ (kOe/Torr)	μ
p-H_2	88.2[a]	18.4	19200[a]	2.11	1.09[a]	0.114[b]	2.7[c]	23.6
n-H_2	88.2[a]	18.4	18250[a]	2.00	0.96	0.092[b]	3.3[c]	35.9
o-D_2	123[a]	18.7	13100[a]	2.06	1.00	0.180[d]	4.8[c]	26.6
n-D_2	123[a]	18.7	13100[a]	2.06	1.00	0.180[d]	4.3[c]	23.9

[a] Data from Ref. 46.

[b] Data from Ref. 25.

[c] Data from Ref. 30.

[d] Data from Ref. 26.

TABLE IV. g_{rot} values and some digonal cross sections [all errors have been calculated assuming a 10% error in the $(H/p)_{1/2}$ values only].

Gas	g_{rot} [a]	$\sigma\binom{1001}{1001}$ ($\mathrm{\AA}^2$)	$\sigma\binom{0200}{0200}$ ($\mathrm{\AA}^2$) From transport alone	$\sigma\binom{0200}{0200}$ ($\mathrm{\AA}^2$) Using g_{rot}	$\sigma_0\binom{1200}{1200}$ ($\mathrm{\AA}^2$) From transport alone	$\sigma_0\binom{1200}{1200}$ ($\mathrm{\AA}^2$) Using g_{rot} [b]
p-H_2	0.8787	13.2	0.59 ± 0.12	0.61 ± 0.06	14 ± 2	15 ± 2
n-H_2	0.8787	14.1	0.41 ± 0.08	0.47 ± 0.05	15 ± 2	17 ± 2
o-D_2	0.4406	13.4	0.53 ± 0.11	0.66 ± 0.07	14 ± 2	18 ± 2
n-D_2	0.4406	13.4	0.59 ± 0.12	0.66 ± 0.07	14 ± 2	14 ± 1

[a] Data from Ref. 29.

[b] Data from Ref. 30.

very well with experiment. Moreover, the final entry in this table allows the determination of the ratio $\sigma^{(0)}_{D_2}/\sigma^{(0)}_{H_2}$ as 2.2.

IV. NUCLEAR MAGNETIC RELAXATION IN n-H_2

Nuclear magnetic relaxation in gaseous hydrogen has been and still is of considerable interest. Two reasons for this are that the collision dynamics for molecular hydrogen offer some hope of clearly defined collisional calculations being performed and that molecular hydrogen is also one of the few gases in which two different relaxation mechanisms play an important role in the NMR measurements. The first experimental verification of this was given by Hardy[14] in his measurements of the "spin-lattice" and "transverse" relaxation times T_1 and T_2 as functions of density at 77.5 K. More recent measurements by Dorothy[31] have been concerned with the determination of the T_1 minimum at room temperature while Lalita[32] has made a careful study of the temperature dependence of T_1.

Of the hydrogen modifications, only o-H_2 has a resultant nuclear spin ($I = 1$) and hence, as opposed to the SB-effect measurements, only the influence of collisions on the *ortho* molecules can be detected. Because of this, the cross section $\sigma\binom{0200}{0200}$ entering into the NMR measurements at ordinary temperatures will not be quite the same as that entering into the SB-effect determinations. This deviation of the two cross sections from one another will become increasingly obvious as the temperature is increased and more and more rotational states of molecular hydrogen are populated. For heavier homonuclear molecules, such as N_2, where the various spin symmetry modifications are undetectable to all practical purposes, the cross sections entering into the two effects will be in essence equal. The same is true for hydrogen at 77 K since neither the NMR nor the SB shear-viscosity experiment detect the $j = 0$ state; the $j = 1$ state is the only nonzero j state sufficiently populated to be detectable.

For a multilevel spin system Bloom and Oppenheim[32–35] and Chen and Snider[13] have derived the following expressions for T_1 and T_2:

$$T_1^{-1} = \tfrac{2}{3} c^2 \langle j(j+1)\rangle_0 \tau' \frac{1}{1+\omega^2\tau'^2} + \frac{2}{75}\left\langle \frac{j(j+1)}{(2j-1)(2j+3}\right\rangle_0 (2I-1)(2I+3) d^2 a_I^2 \tau'' \left(\frac{1}{1+\omega^2\tau''^2} + \frac{4}{1+4\omega^2\tau''^2}\right) \tag{4.1}$$

and

$$T_2^{-1} = \tfrac{1}{3} c^2 \langle j(j+1)\rangle_0 \tau' \left(1 + \frac{1}{1+\omega^2\tau'^2}\right) + \frac{1}{75}\left\langle \frac{j(j+1)}{(2j-1)(2j+3)}\right\rangle_0 (2I-1)(2I+3) d^2 a_I^2 \tau'' \left(3 + \frac{5}{1+\omega^2\tau''^2} + \frac{2}{1+4\omega^2\tau''^2}\right). \tag{4.2}$$

In these expressions c and d are the (nuclear) spin-rotation and dipolar coupling constants, respectively. The quantity ω is given by

$$\omega = (\gamma_J - \gamma_I) H_0 \,, \tag{4.3}$$

with γ_J and γ_I the gyromagnetic ratios for the rotational angular momentum and for the nuclear spin angular momentum, while H_0 is the strength of the constant magnetic field.

The coupling constants c and d have, for molecular hydrogen, the values[29,36,13]

TABLE V. Ratios of $\sigma\binom{0200}{0200}$ cross sections at 300 K.

Ratio	Theory	Transport alone	Using g_{rot}
$\dfrac{\sigma\binom{0200}{0200}_{p\text{-}H_2}}{\sigma\binom{0200}{0200}_{n\text{-}H_2}}$	1.27	1.4	1.3
$\dfrac{\sigma\binom{0200}{0200}_{o\text{-}D_2}}{\sigma\binom{0200}{0200}_{n\text{-}D_2}}$	1.03	0.9	1.0
$\dfrac{\sigma\binom{0200}{0200}_{n\text{-}H_2}}{\sigma\binom{0200}{0200}_{n\text{-}D_2}}$	$1.52\,\sigma^{(0)}_{H_2}/\sigma^{(0)}_{D_2}$	0.7	0.7

$$c = (4.4967\times 10^{6})\,\mathrm{rad\,sec^{-1}}\,,\qquad d = (34.151\times 10^{6})\,\mathrm{rad\,sec^{-1}}\,. \tag{4.4}$$

At 77 K, molecular hydrogen can be treated as a one-level spin system with $j=1$; moreover, the o-H_2 molecules which contribute to the nuclear signal have an I value of 1 resulting from two coupled spin-$\frac{1}{2}$ nuclei. For such a system $a_I = \frac{1}{2}$ so that, at 77 K, T_1^{-1} and T_2^{-1} are found to be given by

$$T_1^{-1} = \tfrac{4}{3}\, c^2\tau' \frac{1}{1+\omega^2\tau'^2} + \tfrac{1}{75}\, d^2\tau'' \times\left(\frac{1}{1+\omega^2\tau''^2} + \frac{4}{1+4\omega^2\tau''^2}\right), \tag{4.1$'$}$$

$$T_2^{-1} = \tfrac{2}{3}\, c^2\tau'\left(1+\frac{1}{1+\omega^2\tau'^2}\right) + \tfrac{1}{150}\, d^2\tau'' \times\left(3+\frac{5}{1+\omega^2\tau''^2} + \frac{4}{1+4\omega^2\tau''^2}\right)\,. \tag{4.2$'$}$$

The relaxation times τ' and τ'' are, for the cases considered in this paper, given by

$$\frac{1}{\tau'} = \frac{3}{\langle j(j+1)\rangle_0}\, n\sum_j p_j \left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right]^{(j)}\,, \tag{4.5}$$

$$\frac{1}{\tau''} = \frac{15}{2}\,\frac{1}{\langle j(j+1)(j^2+j-\frac{3}{4})\rangle_0}\, n\sum_j p_j \left[\begin{smallmatrix}0200\\0200\end{smallmatrix}\right]^{(j)}\,. \tag{4.6}$$

For the one-level $j=1$ system for o-H_2 at 77 K, these quantities reduce to

$$1/\tau' = \tfrac{2}{5}\, np_1H^{(0)}\,,\quad 1/\tau'' = \tfrac{6}{25}\, np_1H^{(0)}\,. \tag{4.7}$$

Note that the ratio $\tau'/\tau'' = 0.6$, in agreement with the prediction of the correlation function theory of Bloom and Oppenheim[33,34] and within the experimental range of agreement $0.6 < \tau'/\tau'' < 1$ found by Hardy[14] as best fitting his experimental results

In order to determine $H^{(0)}$, a fit must be made to any point on the T_1 or T_2 plot. This is conveniently accomplished by choosing the extreme narrowing or high-density limit where Eqs. (4.1) and (4.2) reduce to

$$T_1 = T_2 = np_1H^{(0)}\left[\tfrac{10}{3}c^2 + \tfrac{5}{18}d^2\right]^{-1}\,. \tag{4.8}$$

At a density of 8 amagat, the common relaxation time as determined by Hardy[14] and Lipsicas and Hartland[37] is $T_1 = T_2 = 1$ msec. This, together with the values for c and d, gives for $p_1H^{(0)}$ the value

$$p_1H^{(0)} = 1.239\times 10^{9}\ \mathrm{sec^{-1}\,amagat^{-1}}\,. \tag{4.9}$$

Using this value of $p_1H^{(0)}$ and the values of τ' and τ'', T_1 and T_2 for n-H_2 at 77 K have been calculated using Eqs. (4.1) and (4.2). Agreement between theory and experiment is quite good for T_2 and quite reasonable for T_1.

At room temperature, it should be sufficient to include, in addition to the $j=1$ level, the $j=3$ and $j=5$ levels, giving rise to a three-level collisionally decoupled system (see, however, Ref. 23). If this is done, Eqs. (4.5) and (4.6) reduce to

$$1/\tau' = 0.236nH^{(0)},\quad 1/\tau'' = 0.131nH^{(0)}\,, \tag{4.10}$$

which gives the value 0.553 for the ratio τ'/τ''. This result shows that there is not a strong temperature dependence of the ratio of the correlation times. The influence of the ratio τ'/τ'' will have its maximal effect at low densities where T_1 passes through its minimum while at higher densities (in the region where $T_1 = T_2$) Eqs. (4.1) and (4.2) can be approximated as

$$1/T_1 = 1/T_2 \simeq \tfrac{1}{21}\, d^2\tau''\left[1+34.0\,(c/d)^2(\tau'/\tau'')\right]. \tag{4.11}$$

From this equation and the result $T_1 = 1$msec at 10 amagat, given by Lalita, Bloom, and Noble,[15] $H^{(0)}$ can be calculated to be

$$H^{(0)} = 1.418\times 10^{9}\ \mathrm{sec^{-1}\,amagat^{-1}} = 5.27\times 10^{-11}\ \mathrm{cm^3\,sec^{-1}}\,. \tag{4.12}$$

This leads to a value of $\sigma_{H_2}^{(0)} = 3.15$ Å^2, to be compared with the value $\sigma_{H_2}^{(0)} = 10.8$ Å^2 at 77 K [obtained from Eq. (4.9) and the value $p_1 = 0.495$].

V. DISCUSSION

From the value of $H^{(0)}$ obtained from Eq. (4.9) and Eqs. (2.15) and (2.16) for $j=1$, the cross sections $\sigma\left(\begin{smallmatrix}0100\\0100\end{smallmatrix}\right)_{o\text{-}H_2}$ and $\sigma\left(\begin{smallmatrix}0200\\0200\end{smallmatrix}\right)_{o\text{-}H_2}$ are found to have the values 2.89 and 1.73 Å^2, respectively. From this latter value and Fig. 2, the cross sections $\sigma\left(\begin{smallmatrix}0200\\0200\end{smallmatrix}\right)$ for all other homonuclear hydrogen isotope modifications may be read off, assuming $\sigma_{D_2}^{(0)}/\sigma_{H_2}^{(0)}$ to be the same as at 300 K. These results are collected in Table VI. A partial check on these values may be had by calculating $\sigma_0\left(\begin{smallmatrix}1200\\1200\end{smallmatrix}\right)$ at 77 K from these values using the last of the equations in Table I and the value of $\sigma\left(\begin{smallmatrix}1001\\1001\end{smallmatrix}\right)$ at 77 K [which may itself be calculated from $\sigma\left(\begin{smallmatrix}1001\\1001\end{smallmatrix}\right)$ as found in Sec. III by using the expression in Table II and the tables of Ω^* integrals given by Hirschfelder, Curtiss, and Bird[18]]. Hermans *et al.*[38] have also obtained $\sigma_0\left(\begin{smallmatrix}1200\\1200\end{smallmatrix}\right)$ from their measurements on the transverse thermal conductivity effect at low temperatures. Their values, obtained at 85 K, are given in the final column of Table VI. The agreement is seen to be reasonable.

Although the value extracted for $\sigma\left(\begin{smallmatrix}0200\\0200\end{smallmatrix}\right)$ from the room-temperature T_1 measurements should not have exactly the same value as that found from SB measurements, it should be close. Using the fact that $\sigma\left(\begin{smallmatrix}0200\\0200\end{smallmatrix}\right)_{n\text{-}H_2} = 0.103\,\sigma_{H_2}^{(0)}$ at room temperature, a value of $\sigma\left(\begin{smallmatrix}0200\\0200\end{smallmatrix}\right)_{n\text{-}H_2}$ of 0.32 Å is obtained from the T_1 data, to be compared with the value $\sigma\left(\begin{smallmatrix}0200\\0200\end{smallmatrix}\right)_{n\text{-}H_2}$

$= (0.47 \pm 0.05)$ Å found from the thermomagnetic torque measurements.[25] Similarly, $\sigma\binom{0100}{0100}_{o\text{-}H_2} = 0.50$ Å^2 which should be compared with the value 0.608 Å obtained by Gioumousis[39] in an analysis of the room-temperature T_1 data of Johnson and Waugh.[40]

Two final applications of the present theory can be made. These are to a calculation of the cross section entering into depolarized Rayleigh light-scattering measurements and to a calculation of the self-diffusion coefficient for n-H_2. In the first case, Hess[16] has shown that the cross section determining the half-width at half-height of the depolarized Rayleigh line in light-scattering experiments in gases is given by

$$\sigma_{\mathrm{DPR}} = \left(\frac{1}{j^2+j-\frac{3}{4}}[\vec{\mathrm{J}}]^{(2)}:,\ \mathcal{R}_0[\vec{\mathrm{J}}]^{(2)}\frac{1}{j^2+j-\frac{3}{4}}\right) \times \left\langle \frac{2}{3}\frac{j(j+1)}{j^2+j-\frac{3}{4}}\right\rangle_0^{-1} . \tag{5.1}$$

Under the same assumptions as were made in the previous section, this may be expressed as

$$\sigma_{\mathrm{DPR}} = 4\left\langle\frac{j(j+1)(4j+4j-7)}{(2j-1)(2j+3)}\right\rangle_0 \left\langle\frac{j(j+1)}{(2j-1)(2j+3)}\right\rangle_0^{-1} \sigma^{(0)}_{H_2} . \tag{5.2}$$

For $n-H_2$ at 300 K, it is found that $\sigma_{\mathrm{DPR}} = 0.152\sigma^{(0)}_{H_2}$. From this and the previously determined value of $H^{(0)}$, σ_{DPR} is found to be 0.48 Å^2. The only experimental value presently available in the literature is that of Cooper *et al.*,[41] who found σ_{DPR} to be (0.77 ± 0.15) Å^2. These two results are in strong disagreement. Recently, however, the depolarized Rayleigh light-scattering experiments have been carefully redone by Gupta.[42,43] In this study, Gupta was able to show that there had been significant extraneous contributions to the width of the depolarized line from three sources, viz., photomultiplier dark counts, parasitic scattering of laser light by the cell, and polarized Rayleigh light-scattering from the gas. When these were eliminated, the true depolarized Rayleigh linewidth yielded a value of σ_{DPR} of 0.495 Å^2, in very good agreement with the value calculated above.

The self-diffusion coefficient in a gas is given by

$$D_0 = \frac{kT}{\langle v_{\mathrm{rel}}\rangle_0\, \rho\sigma'\binom{1000}{1000}} , \tag{5.3}$$

where ρ is the mass density and $\sigma'\binom{1000}{1000}$ is the cross section governing self-diffusion. The prime indicates that only that part of the collision integral not containing the variables of the collision partner is retained. [$\sigma\binom{1000}{1000}$ is zero because "1000" represents a summational invariant.] It has been shown in Ref. 7 that in the absence of energetically inelastic collisions $\sigma'\binom{1000}{1000}$ is related to $\sigma\binom{1001}{1001}$ by

$$\sigma'\binom{1000}{1000} = \sigma\binom{1001}{1001} , \tag{5.4}$$

from which the self-diffusion coefficient is given as

$$D_0 = \frac{kT}{\langle v_{\mathrm{rel}}\rangle_0\, \rho\sigma\binom{1001}{1001}} . \tag{5.5}$$

For n-H_2 at room temperature and 1 atm, $kT = 4.14 \times 10^{-14}$ erg, $\rho = 9.03 \times 10^{-5}$ g cm^{-3}, $\langle v_{\mathrm{rel}}\rangle_0 = 2.48 \times 10^5$ cm sec^{-1}, and $\sigma\binom{1001}{1001} = 14.1$ Å^2, so that $D_0 = 1.31$ cm^2 sec^{-1} which should be compared with the value $D_0 = 1.34$ cm^2 sec^{-1} measured by Harteck and Schmidt.[44]

The results obtained in this paper can be summarized as follows: (i) The approximations used to obtain Eqs. (2.5), (2.9), and (2.10) for the reorientation cross sections for the homonuclear hydrogen isotopes, viz., the distorted wave Born approximation and the neglect of inelastic collisions, have been shown to be good. (ii) The good agreement found between $\sigma\binom{0200}{0200}$ calculated using only transport data and that obtained by using the g factor as determined from molecular-beam experiments gives a particular indication that collisions between two hydrogen molecules may be treated as nearly classical in the same sense as was done in Refs. 6 and 7 for heavy diatomic molecules. (iii) Ratios of reorientation collision cross sections may be obtained as functions of temperature, using only the distorted-wave Born

TABLE VI. Predicted values of $\sigma\binom{0200}{0200}$ and $\sigma_0\binom{1200}{1200}$ in Å^2.

Gas	$\sigma\binom{1001}{1001}$ (at 300 K; from λ_0, η_0)	$\sigma\binom{1001}{1001}$ (at 77 K; predicted[a])	$\sigma\binom{0200}{0200}$ (at 77 K; calculated)	$\sigma_0\binom{1200}{1200}$ (at 77 K; calculated)	$\sigma_0\binom{1200}{1200}$ (at 85 K; measured[b])
p-H_2	13.2	18.1 ± 1.8	1.68	20.0 ± 1.8	(15)
n-H_2	14.1	19.3 ± 1.9	1.73	21.3 ± 1.9	(18)
o-D_2	13.4	18.3 ± 1.8	3.67	22.6 ± 1.8	20 ± 5
n-D_2	13.4	18.3 ± 1.8	3.56	22.4 ± 1.8	18 ± 4

[a] An error of 10% has been assumed for approximating the spherical interaction potential by a Lennard-Jones 6-12 potential.

[b] Reference 38. The values in brackets are rather uncertain. For the last two entries an error of ~ 25% has been assumed.

approximation and the neglect of inelastic collisions. At 300 K, reasonable agreement has been found between theory and experiments on the SB effects, NMR, depolarized Rayleigh light-scattering, and sound absorption measurements.[45]

APPENDIX

The defining relations and explicit expressions for the quantities $\Omega(j,k,l)$, $\alpha_j^{(k)}$, and $\mu(j,k,l)$ entering into Eq. (2.4) are given in this Appendix. $\Omega(j,k,l)$ is defined in terms of Cartesian (3-j)-tensors as[43]

$$\Omega(j,k,l) \equiv \underline{\mathrm{T}}(\bar{j},\bar{k},\bar{l})\,\underline{\mathrm{T}}(\bar{j},\bar{k},\bar{l}) \quad , \tag{A1}$$

where a bar over an index (which denotes an irreducible set of indices) means that this set has to be contracted with the corresponding set in the adjacent (3-j) tensor. Coope[46] has given an explicit form for $\Omega(j,k,l)$ as

$$\Omega(j,k,l) = \frac{(J+1)!\;(J-2j)!\;(J-2k)!\,(J-2l)!}{(2j)!\,(2k)!\,(2l)!} \times \begin{cases} 1, & J \text{ even} \\ 2, & J \text{ odd} \end{cases} \tag{A2}$$

with $J=j+k+l$.

The $\alpha_j^{(k)}$ are defined by[7]

$$\langle \hat{r} | \mathcal{P}_j [\vec{\mathrm{J}}]^{(k)} \mathcal{P}_j | \hat{r}' \rangle \equiv \alpha_j^{(k)} [\hat{r}]^{(j)} \odot^j \underline{\mathrm{T}}(j,k,j) \odot^j [\hat{r}']^{(j)} \quad , \tag{A3}$$

where $\hat{r}$ and $\hat{r}'$ are unit vectors and $\mathcal{P}_j$ is the projection operator onto the subspace of constant j. The explicit form of $\alpha_j^{(k)}$ has been shown to be[7]

$$\alpha_j^{(k)} = \frac{2^j(2j+1)!!\,(2j-1)!!}{4\pi(2j-k)!}\, i^k \begin{cases} (\frac{1}{2})^{k/2} \quad , & k \text{ even} \\ (\frac{1}{2})^{(k+1)/2} \quad , & k \text{ odd} \end{cases} \quad . \tag{A4}$$

Finally, the $\mu(j,k,l)$ are defined by

$$\int d\hat{r}\,[\hat{r}]^{(j)}[\hat{r}]^{(k)}[\hat{r}]^{(l)} \equiv \mu(j,k,l)\,\underline{\mathrm{T}}(j,k,l) \quad , \tag{A5}$$

so that $\mu(j,k,l)$ is explicitly given by[7]

$$\mu(j,k,l) = 4\pi \frac{j!\,k!\,l!}{(J+1)!!\,(\frac{1}{2}J-j)!\,(\frac{1}{2}J-k)!\,(\frac{1}{2}J-l)!} \quad ,$$

$$\text{if } J=j+k+l \text{ is even;}$$

$$\mu(j,k,l) = 0, \text{ if } J \text{ is odd.} \tag{A6}$$

The required (6-j) symbols have been given by Edmonds[19] as

$$\begin{Bmatrix} 2 & j & j \\ 2 & j & j \end{Bmatrix} = \frac{3[2j^2(j+1)^2 - 13j(j+1) + 21] - 2j^2(j+1)^2}{(2j-1)(2j+1)(2j+3)j(j+1)} \tag{A7}$$

and

$$\begin{Bmatrix} 2 & j & j \\ 1 & j & j \end{Bmatrix} = -\frac{j^2+j-3}{j(j+1)(2j+1)} \quad . \tag{A8}$$

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Hyperfine and Zeeman Interactions in the Metastable, $c\,^3\Pi_u$, State of H_2[†]

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The magnetic hyperfine and g_F constants were calculated for the $c\,^3\Pi_u(1s, 2p)$ metastable state of H_2 using wave functions determined from the optimal-double-configuration model. The hyperfine constants differ by as much as 24% from previous values obtained using a single-configuration electronic wave function. The hyperfine constants are $a = 21.98$ MHz, $b = 471.14$ MHz, $c = 59.37$ MHz, $d = -12.87$ MHz, where a and b are the orbital interaction of the electron with the nucleus and the Fermi contact interaction, respectively, and c and d arise from the dipolar interaction of electron and nucleus. With these values for the hyperfine constants, along with the experimental fine-structure splittings and a matrix-diagonalization procedure, the g_F values were calculated and found to be in better agreement with experiment than the earlier theoretical values.

I. INTRODUCTION

Some experimental evidence as to the existence of the metastable state, $c\,^3\Pi_u(1s, 2p)$, of molecular hydrogen was first reported by Lichten[1] on the basis of a molecular-beam time-of-flight experiment, and the first vibrational level of this electronic state was firmly established to be metastable by Lichten[2] with a magnetic-resonance molecular-beam experiment. The fine structure in the $N = 2$ rotational state of parahydrogen has been measured by Lichten,[3] and the fine-hyperfine splittings have been determined experimentally for the $N = 1$ rotational state of orthohydrogen by Brooks *et al.*[4] The theory of the fine-structure splitting in the metastable state was first worked out by Fontana[5] who used the united-atom approximation and found good agreement with experiment. However, Chiu[6] found an error of a factor of 2 too small in his expression for the spin-spin interaction, and when this is properly accounted for the simple united-atom approximation fails. The fine-structure constants have been calculated by Chiu[7] using a simple single-configuration wave function that is a linear combination of a Heitler-London-type wave function and an ionic type. She obtained fair agree-