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# Deuteron magnetic resonance probe of the D<sub>2</sub>-He potential energy surface

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Measurements of the nuclear magnetic resonance (NMR) longitudinal relaxation time  $T_1$  have been carried out for D<sub>2</sub>-He gas mixtures at temperatures of 293 and 220 K for two concentrations of D<sub>2</sub> in He and the results extrapolated linearly to infinite dilution at each temperature. Full quantum close-coupled scattering calculations have also been carried out for an *ab initio* D<sub>2</sub>-He interaction potential. The agreement found between measured and calculated relaxation times is excellent at 293 and good at 220 K. Based on the level of agreement found between theory and experiment, it can be concluded that the molecular hydrogen-helium *ab initio* potential energy surface employed in the present D<sub>2</sub>-He calculations as well as in earlier H<sub>2</sub>-He calculations [J. Chem. Phys. **81**, 5275 (1984)] represents well the effects of both the spin-rotation and combined dipolar/quadrupolar intramolecular interactions, which dominate the spin relaxation, respectively, of protons and deuterons in the hydrogen isotopes. At the same time, the present results indicate that the disagreement found earlier [J. Chem. Phys. **92**, 5907 (1990)] between calculated and measured deuteron  $T_1$  values for HD-He mixtures must arise from the specific nature of the HD-He potential energy surface.

## I. INTRODUCTION

The temperature dependence of the relaxation of nuclear spin magnetizations in H<sub>2</sub>-He and HD-He gaseous mixtures, as characterized by the longitudinal relaxation time  $T_1$  in the "extreme narrowing" or "linear density dependence" regime, has been shown<sup>1,2</sup> to be very sensitive to the anisotropic components of the potential energy of interaction between helium and the isotopes of molecular hydrogen. Indeed, of the five anisotropic interaction potentials proposed during the past 15 years,<sup>3-6</sup> only that of Ref. 5 has provided satisfactory agreement with accurate experimental results for H<sub>2</sub>-He mixtures.<sup>1</sup> In order to provide a more extensive test of this potential surface, experimental values of  $(T_1/\rho)_{\text{lin}}^\infty$ , the slope of a plot of  $T_1$  vs amagat density  $\rho$ , extrapolated to infinite dilution of the hydrogen isotope in helium, were obtained as functions of temperature for relaxation of both the proton and deuteron magnetizations.<sup>2</sup> The calculated temperature dependence of  $(T_1/\rho)_{\text{lin}}^\infty$  for the protons in HD-He mixtures was in extremely good agreement with the experimentally determined temperature dependence. However, the agreement between calculated and measured temperature dependencies for relaxation of the deuteron magnetization in HD-He mixtures was of poorer quality and could be termed semiquantitative. The reason for the lack of fully quantitative agreement between the calculated and measured deuteron relaxation times is not obvious.

Two possible explanations were tentatively suggested in Ref. 2. Both are associated with the fact that the proton and deuteron relaxations are dominated by different mechanisms.

On the one hand, proton relaxation in HD gas, especially at higher temperatures, is largely determined by the spin-rotation intramolecular relaxation mechanism, with the relaxation arising from the dipolar intramolecular coupling playing a relatively minor role. On the other hand, the deuteron relaxation in HD gas is dominated by the quadrupolar and dipolar relaxation mechanisms, with the spin-rotation intramolecular coupling playing a minor role, even at room temperature. Moreover, a large contribution to the deuteron relaxation derives from the quadrupolar intramolecular interaction, which makes no contribution to the proton relaxation. One possible explanation would therefore be that the quadrupolar coupling constant  $\omega_q$  in HD has been determined inaccurately. As we have pointed out in Ref. 2, however, this would require a change of approximately 5% in its value. Such an error in the determination of  $\omega_q$  is highly unlikely. A second possible explanation originates with the observation that the spin-rotation relaxation mechanism is associated with the collisional reorientation of the rotational angular momentum  $\mathbf{J}$ , while the dipolar and quadrupolar relaxation mechanisms are associated with the effects of reorientation collisions on the microscopic second rank tensor polarization  $\overline{\mathbf{J}\mathbf{J}}/(4J^2 - 3)$ . There is now evidence that the corresponding reorientation effective collision cross sections probe different aspects of the anisotropic components of the potential energy surface.<sup>7</sup>

Relaxation of the deuteron spin magnetization in gaseous D<sub>2</sub> is strongly dominated by the combined dipolar

and quadrupolar relaxation mechanisms. Since the intermolecular interaction between D<sub>2</sub> and He is identical to that between H<sub>2</sub> and He within the Born–Oppenheimer approximation, with only the collision dynamics changed because the reduced mass of the D<sub>2</sub>–He colliding pair and the rotational constant of D<sub>2</sub> are different, a combined theoretical–experimental study of deuteron relaxation in D<sub>2</sub>–He mixtures will show whether scattering calculations made using the hydrogen–helium potential energy surface given in Ref. 5 provide a correct description not only of the proton relaxation in H<sub>2</sub>–He mixtures,<sup>1</sup> but also of the deuteron relaxation in D<sub>2</sub>–He mixtures. If the original potential energy surface agrees with the relaxation of the spin magnetization in both homonuclear cases, then the transformation of the potential surface to the heteronuclear case must be the source of the discrepancy between the calculated and observed deuteron relaxation in the HD–He mixtures. The present paper thus represents a combined theoretical and experimental study of the temperature dependence of the deuteron relaxation in D<sub>2</sub>–He mixtures.

The experimental techniques are discussed in Sec. II, after which the experimental results are presented. A detailed theoretical description of the relaxation of the spin magnetization is given in Sec. III, along with a brief outline of the nature of the calculations. Our theoretical results are presented and their comparison with experiment is made in Sec. IV. Finally, a summary of our findings and conclusions is found in Sec. V.

## II. EXPERIMENTAL TECHNIQUES AND RESULTS

The deuterium spin–lattice relaxation time ( $T_1$ ) measurements were carried out using a phase-coherent, pulsed nuclear magnetic resonance (NMR) spectrometer. The instrument incorporates a wide-band, transistorized 300 W transmitter and a narrow-band GaAs FET preamplifier tuned to the nuclear resonance frequency. The spectrometer was used in conjunction with an Oxford Instruments 8.5 T superconducting magnet; the corresponding deuteron resonance frequency is 55.6 MHz. The data acquisition was via a Nicolet Explorer digital oscilloscope interfaced to an IBM PC. The computer was programmed for automatic temperature control and data acquisition.

The deuterium gas was obtained from MSD Isotopes, with stated isotopic purity of 98%. The helium gas was from Matheson of Canada Inc. and had a stated purity of 99.995%. The gas mixtures were prepared in a 1 ℓ stainless steel cylinder; partial pressure measurements were used to determine the mixture ratios. Two mixtures, containing 8.9% and 17.9% D<sub>2</sub>, respectively, were prepared for the experiments.

The gas samples were contained in a glass cylinder 4 cm long and 2 cm in diameter. The solenoidal radiofrequency coil was wrapped directly onto the glass cylinder. The sample chamber was connected, via a 1/8 in. copper tube, to a mercury manometer or Texas Instruments pressure gauge, which had been calibrated against a dead-weight balance. The sample pressures were known to within ±1%.

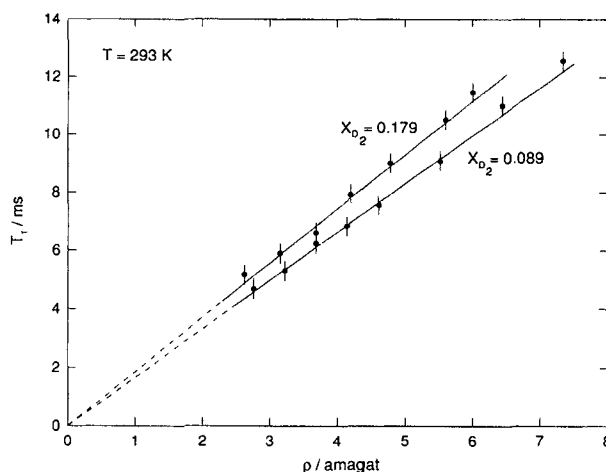


FIG. 1. Dependence of the mixture longitudinal relaxation time  $T_1$  on the mixture amagat gas density  $\rho$  for temperature  $T=293$  K—8.9% (open disks); 17.9% (solid disks).

The NMR probe was designed so that the sample chamber was surrounded by a thick-walled copper container whose temperature was electronically regulated to  $\pm 0.1$  °C over the course of the data acquisition for a  $T_1$  measurement. A copper–constantan thermocouple, located near the sample, was used to record the actual sample temperature, which was thereby known to within  $\pm 0.5$  °C. The copper container could be pressurized, so that measurements with sample pressures up to 10 atm could be made without destroying the glass sample holder.  $T_1$  measurements were made at two temperatures, namely, 220 and 293 K, and at pressures from 2.75 to 8 atm.

The  $T_1$  measurements were carried out using the phase-alternated, inversion-recovery (PAIR) sequence of Demco *et al.*<sup>8</sup> For each  $T_1$  determination, the amplitude of the free-induction decay signal, following the  $\pi/2$  pulse in the  $\pi$ – $\tau$ – $\pi/2$  sequence, was sampled for 15 values of the pulse separation  $\tau$ . For all experiments, the recovery of the nuclear magnetization to equilibrium could be represented, to within experimental error, by a single exponential function, so that a unique  $T_1$  value could be determined in each case.

For densities lying between 1 and 50 amagats,  $T_1$  can be expressed as

$$T_1 = a\rho + b\rho^2, \quad (2.1)$$

in which the coefficients  $a$  and  $b$  give the contributions from binary and ternary collision processes, respectively. It is the temperature dependence of the coefficient  $a$  that is of interest for the present study. Although the contribution to spin relaxation from ternary collisions may, in principle, be non-negligible, it is not expected to represent more than a small percentage of that associated with binary collisions over the range of mixture densities for which data were taken. Indeed, as can be seen from Fig. 1, showing the experimental results at 293 K,  $T_1$  is very nearly a linear function of the amagat density  $\rho$ .

The data obtained are listed in Table I. Values of  $a$  were determined from the data by linear extrapolation as

TABLE I. Measured values of  $T_1$  at 220 and 293 K.

Concentration of D <sub>2</sub>	220 K		293 K	
	$\rho$ (amagat)	$T_1^*$ (ms)	$\rho$ (amagat)	$T_1^*$ (ms)
17.9%	2.20	4.96	2.62	5.17
	2.45	5.22	3.15	5.91
	3.06	6.35	3.68	6.62
	3.60	7.29	4.20	7.93
	4.31	8.53	4.78	9.01
8.9%			5.60	10.52
			6.00	11.47
	3.67	5.74	2.76	4.69
	4.29	6.98	3.22	5.30
	4.98	7.80	3.68	6.24
	5.51	8.69	4.14	6.85
	6.12	10.24	4.60	7.55
	7.35	11.84	5.52	9.09
			6.44	11.00
			7.34	12.55

\*All data have error bars of  $\pm 0.35$  ms.

the intercepts of  $T_1/\rho$  vs  $\rho$  plots; they are given in Table II. The values of  $(T_1/\rho)_{\text{lin}}^\infty$  were determined by linear extrapolation as the intercepts of plots of  $a$  vs deuterium concentration. These values are also provided in Table II as the “infinite dilution” entries. They are the sought after experimental numbers and they are plotted in Fig. 2, along with the theoretical predictions.

### III. THEORETICAL DESCRIPTION AND CALCULATIONS

All molecular gases whose constituent nuclei have nonzero nuclear spins will show relaxation of the nuclear spin magnetizations. Although both intermolecular and intramolecular relaxation mechanisms contribute in general to these relaxations, the time scales upon which they operate are about five to six orders of magnitude different. Intramolecular relaxations take place on microsecond or millisecond time scales, while intermolecular relaxations take place on second to kilosecond time scales. As a consequence, whenever intramolecular relaxation mechanisms are operative, they dominate, and it normally suffices to consider them exclusively.

Because the bond length in D<sub>2</sub> is very short, as in H<sub>2</sub>, both the spin-rotation and dipolar (spin-spin) relaxation

TABLE II. Values of  $a$  deduced from  $T_1$  measurements as a function of  $\rho$ .

Concentration (% D <sub>2</sub> )	Temperature (K)	$a$ (ms amagat <sup>-1</sup> )
17.9	220	$1.81 \pm 0.06$
	293	$1.86 \pm 0.12$
8.9	220	$1.57 \pm 0.07$
	293	$1.66 \pm 0.04$
Infinite dilution	220	$1.33 \pm 0.15$
	293	$1.46 \pm 0.10$

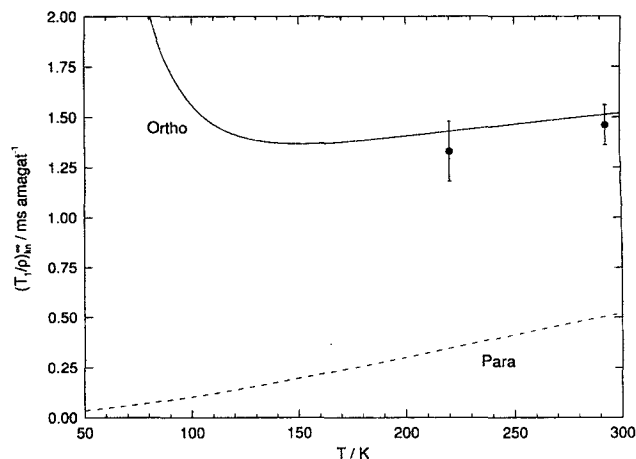


FIG. 2. Temperature dependence of  $(T_1/\rho)_{\text{lin}}^\infty$  for D<sub>2</sub> in He. Calculated result for the *o*D<sub>2</sub>-He interaction (solid curve); calculated result for the *p*D<sub>2</sub>-He interaction (dashed curve); experimental results (solid disks).

mechanisms make important contributions to the deuteron relaxation in D<sub>2</sub>. Spin-rotation relaxation is, however, significantly less important, since the spin-rotation coupling constant for D<sub>2</sub> is 13 times smaller than that for H<sub>2</sub>. Moreover, the spin-1 deuteron has a large intramolecular interaction between the deuteron electric quadrupole moments and the gradient of the electric field at the nuclear sites. Relaxation associated with this intramolecular coupling is termed “quadrupolar relaxation.”

Molecular deuterium differs from molecular hydrogen in that both the *para* and *ortho* modifications show nuclear spin relaxation since both spin-symmetry modifications possess nonzero total nuclear spins. There is also an important difference between *para* and *ortho* deuterium insofar as nuclear spin relaxation is concerned, in that the total nuclear spin angular momentum operator  $\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_2$  is sharp (i.e.,  $I=1$  is a good quantum number) for the *para* modification, while for the *ortho* modification, the total nuclear spin quantum numbers  $I=2$  and  $I=0$  are not good quantum numbers, since both the dipolar and quadrupolar interactions couple the two spin manifolds. The final expression for the longitudinal relaxation time should, of course, reflect this coupling.

The spin-rotation interaction Hamiltonian  $\mathcal{H}_{\text{sr}}$  is given by

$$\mathcal{H}_{\text{sr}} = -\hbar\omega_{\text{sr}}^{\text{D}} \mathbf{I} \cdot \mathbf{j}, \quad (3.1)$$

in which  $\hbar\mathbf{I}$  is the total nuclear spin angular momentum of the D<sub>2</sub> molecule,  $\hbar\mathbf{j}$  is the molecular rotational angular momentum, and  $\omega_{\text{sr}}^{\text{D}}$  is the intramolecular spin-rotation coupling constant for the deuteron (D).

The dipolar and quadrupolar intramolecular Hamiltonians (apart from their so-called “high-frequency” terms<sup>9</sup>) are proportional to the irreducible tensor operator  $\overline{\mathbf{j}\mathbf{j}}/(4j^2 - 3)$ , in which  $\overline{\mathbf{j}\mathbf{j}}$  is a second rank symmetric traceless tensor operator, with Cartesian components given by  $(\overline{\mathbf{j}\mathbf{j}})_{\alpha\beta} = \frac{1}{2}j_{\alpha}j_{\beta} + \frac{1}{2}j_{\beta}j_{\alpha} - \frac{1}{3}j^2\delta_{\alpha\beta}$  and  $j^2 = \mathbf{j} \cdot \mathbf{j}$  is a (commuta-

tive) scalar operator, with eigenvalues  $j(j+1)$ . According to this argument, we can write the combined dipolar and quadrupolar intramolecular interaction Hamiltonians as

$$\begin{aligned}\mathcal{H}_{dq} &= \mathcal{H}_d + \mathcal{H}_q \\ &= \hbar\omega_d^D \overline{\mathbf{I}_1 \mathbf{I}_2} : \overline{\mathbf{j} \mathbf{j}} :_{4j^2-3} - \hbar\omega_q^D (\overline{\mathbf{I}_1 \mathbf{I}_1} + \overline{\mathbf{I}_2 \mathbf{I}_2}) : \overline{\mathbf{j} \mathbf{j}} :_{4j^2-3},\end{aligned}\quad (3.2)$$

in which  $\omega_d^D$  is the dipolar coupling constant and  $\omega_q^D = eqQ/\hbar$  is the quadrupolar coupling constant, with  $e$  the charge of the electron,  $q$  the electric field gradient along the molecular axis, and  $Q$  the nuclear quadrupole moment.

In molecular deuterium, the quadrupolar and dipolar contributions to the intramolecular Hamiltonian cannot be disentangled in spin-relaxation experiments, and should be treated together. For  $pD_2$ , the total nuclear spin  $\mathbf{I}$  is sharp, so that the dipolar second rank irreducible spin tensor  $\overline{\mathbf{I}_1 \mathbf{I}_2}$  and the two quadrupolar second rank irreducible spin tensors  $\overline{\mathbf{I}_1 \mathbf{I}_1}$  and  $\overline{\mathbf{I}_2 \mathbf{I}_2}$  can be projected onto the second rank irreducible tensor  $\overline{\mathbf{I} \mathbf{I}}$  to give the combined dipolar/quadrupolar coupling Hamiltonian<sup>10</sup>

$$\mathcal{H}_{dq} = -\hbar\omega_{dq}^D \overline{\mathbf{I} \mathbf{I}} : \overline{\mathbf{j} \mathbf{j}} :_{4j^2-3}, \quad (3.3)$$

with the combined dipolar/quadrupolar coupling  $\omega_{dq}^D$  represented by the effective scalar operator

$$\omega_{dq}^D = \frac{3}{2} \frac{\omega_q^D}{I_1(2I_1-1)} \left( 1 - \frac{4\mathbf{I}_1^2 + \mathbf{I}^2}{4\mathbf{I}^2 - 3} \right) + \frac{\omega_d^D(4\mathbf{I}_1^2 + \mathbf{I}^2)}{4\mathbf{I}^2 - 3}. \quad (3.4a)$$

For  $pD_2$  we have  $I_1 = I = 1$ , so that  $\omega_{dq}^D$  can be replaced by

$$\omega_{dq}^D(\text{para}) = -\frac{3}{2}\omega_q^D + 2\omega_d^D. \quad (3.4b)$$

The longitudinal spin-lattice relaxation time  $T_1$  is expressed in Chap. 11 of Ref. 11 as

$$T_1^{-1} = \mathbf{b} \mathbf{b} : \int_0^\infty d\tau K^R(\tau), \quad (3.5)$$

in which  $\mathbf{b}$  is a unit vector in the direction of the constant applied magnetic field and  $K^R(\tau)$  represents a relaxation kernel in the rotating frame given by

$$K^R(\tau) = \frac{3}{\langle \mathbf{I}^2 \rangle} \langle \mathcal{L}_{\text{intra}} \mathbf{I} | \exp[-\tau(\mathcal{R} + i\mathcal{L}_{jR})] \mathcal{L}_{\text{intra}} \mathbf{I} \rangle. \quad (3.6)$$

In this expression,  $\mathcal{L}_{\text{intra}}$  is a commutator (super) operator defined in terms of  $\mathcal{H}_{\text{intra}} \equiv \mathcal{H}_{\text{sr}} + \mathcal{H}_{dq}$

$$\mathcal{L}_{\text{intra}} \cdots \equiv \frac{1}{\hbar} [\mathcal{H}_{\text{intra}}, \cdots]_-, \quad (3.7)$$

while  $\mathcal{R}$  is the binary collision (super)operator, and  $\mathcal{L}_{jR} \cdots \equiv (\omega_j - \omega_I) [\mathbf{b} \cdot \mathbf{j}, \cdots]_-$ , with  $\omega_j$  and  $\omega_I$  the precession frequencies associated with rotational angular momentum and individual nuclear spins, arises<sup>12</sup> from the transformation to the rotating frame. Finally, the angular brackets represent an equilibrium ensemble average for the specific spin modification under consideration.

Substitution of Eq. (3.6) into Eq. (3.5), with  $\mathbf{b}$  defining the  $z$  direction, gives the basic working expression for the calculation of the longitudinal relaxation time  $T_1$  as

$$\begin{aligned}T_1^{-1} &= \frac{3}{\langle \mathbf{I}^2 \rangle} \int_0^\infty \langle \mathcal{L}_{\text{intra}} \mathbf{I}_z | \exp[-\tau(\mathcal{R} + i\mathcal{L}_{jR})] \\ &\quad \times \mathcal{L}_{\text{intra}} \mathbf{I}_z \rangle d\tau.\end{aligned}\quad (3.8)$$

For molecular hydrogen, in which only the *ortho* spin modification has a nonzero total nuclear spin, this equation leads directly to the expressions given in Ref. 11. For molecular deuterium, the expression for  $T_1$  for the *para* modification (which behaves analogously to *ortho* hydrogen) can be obtained directly from the expressions in Ref. 11 simply by replacing the coupling constants  $\omega_{\text{sr}}^H$  and  $\omega_d^H$  by the corresponding values  $\omega_{\text{sr}}^D$  and  $\omega_{dq}^D$  for the  $pD_2$  molecule. For *ortho* deuterium, however, more care has to be taken because the dipolar and quadrupolar interactions discussed above couple the  $I=2$  and  $I=0$  total spin manifolds. The spin-rotation intramolecular Hamiltonian does not couple the *ortho* spin states  $I=2$  and  $I=0$ , and as a consequence, the spin-rotation contribution to the nuclear spin relaxation again directly follows the treatment given in Ref. 11. Determination of the correct expression for combined dipolar/quadrupolar relaxation begins by writing the two intramolecular interaction Hamiltonians in terms of spherical components, after which it is possible to separate the kernel into two factors, one of which depends solely on the nuclear spin states, while the other contains the effect of molecular collisions on the rotational states. The nuclear spin-dependent factor can be evaluated using the full six-fold basis set of coupled pair states for the  $I=2$  and  $I=0$  spin manifolds. A somewhat lengthy calculation of spin angular momentum traces leads to an expression which has ultimately the same structure as that given for molecular hydrogen, but in this case, the coupling constant  $\omega_{dq}^D$  (*ortho*) must be interpreted to be given by the expression

$$(\omega_{dq}^D)^2 = \frac{12}{5} (\omega_d^D)^2 - \frac{6}{5} \omega_d^D \omega_q^D + \frac{9}{4} (\omega_q^D)^2. \quad (3.9)$$

Since the experiments reported here have been carried out under extreme-narrowing conditions, we shall present only theoretical expressions appropriate to this regime. In each case ( $pD_2$ -He and  $oD_2$ -He), the basic relaxation equation can be written as the sum of two terms—one representing the spin-rotation contribution, the other representing the combined dipolar/quadrupolar contribution. Thus, we have

$$\left( \frac{\rho}{T_1} \right)_{\text{lin}}^\infty = \left( \frac{\rho}{T_1} \right)_{\text{lin, sr}}^\infty + \left( \frac{\rho}{T_1} \right)_{\text{lin, dq}}^\infty, \quad (3.10)$$

in which the two components are given by

$$\left( \frac{\rho}{T_1} \right)_{\text{lin, sr}}^\infty = \frac{2}{3} \frac{(\omega_{\text{sr}}^D)^2}{L_0 \langle v \rangle} \mathbf{d}^{(1)\dagger} \cdot \langle \sigma_V \rangle^{-1} \cdot \rho \cdot \mathbf{d}^{(1)} \quad (3.11a)$$

and

$$\left(\frac{\rho}{T_1}\right)_{\text{lin}, dq}^{\infty} = \frac{(\omega_{dq}^D)^2}{L_0 \langle v \rangle} \mathbf{d}^{(2)T} \cdot \langle \sigma_T \rangle^{-1} \cdot \rho \cdot \mathbf{d}^{(2)}. \quad (3.11b)$$

In these expressions,  $L_0 = 2.689 \times 10^{25} \text{ m}^{-3}$  is Loschmidt's number,  $\langle v \rangle = (8kT/\pi\mu)^{1/2}$  is the mean relative velocity for a colliding D<sub>2</sub>-He pair with reduced mass  $\mu$ , and the population matrix  $\rho$  is diagonal, with the  $j$ th element being the fractional population per state associated with the  $j$ th rotational manifold. The matrices  $\langle \sigma_V \rangle$  and  $\langle \sigma_T \rangle$  contain the state-to-state reorientation effective collision cross sections, averaged over a Boltzmann distribution of translational energies, associated with the respective irreducible first rank tensor (or vector) operator  $\mathbf{j}$ , and the second rank tensor operator  $\overline{\mathbf{j}\mathbf{j}}/(4j^2-3)$ , while  $\mathbf{d}^{(1)}$  and  $\mathbf{d}^{(2)}$  are vectors whose  $j$ th elements are reduced matrix elements of  $\mathbf{j}$  and  $\overline{\mathbf{j}\mathbf{j}}/(4j^2-3)$ , respectively, in the Edmonds' convention.<sup>13</sup> They are given by

$$d_j^{(1)} = [j(j+1)(2j+1)]^{1/2} \quad (3.12)$$

and

$$d_j^{(2)} = \left[ \frac{j(j+1)(2j+1)}{6(2j-1)(2j+3)} \right]^{1/2}. \quad (3.13)$$

In each case, the summations are to be made over the appropriate rotational states associated with the deuterium spin modifications, i.e., odd rotational states for  $p\text{D}_2$  and even rotational states for  $o\text{D}_2$ . From Eqs. (3.4) and (3.9), it is also clear that the only difference between the *ortho* and *para* relaxation rates for pure quadrupolar relaxation lies in the rotational averages required in Eqs. (3.11). This conclusion has also been reached earlier by Bloom *et al.*<sup>14</sup>

Values of  $c_{\text{sr}}^D = \omega_{\text{sr}}^D/2\pi$ ,  $d_M' = \omega_d^D/(15\pi)$ , and  $eqQ/h$  have been obtained by Code and Ramsey<sup>15</sup> for  $p\text{D}_2$  in its  $j=1$  rotational state and for  $o\text{D}_2$  in its  $j=2$  rotational state from their molecular beam magnetic resonance experiments. If we assume that all  $p\text{D}_2$  molecules have the same values for the intramolecular coupling constants as those found for  $j=1$ , and if we use these values in Eqs. (3.1) and (3.4), we obtain  $\omega_{\text{sr}}^D(\text{para}) = 0.0551 \text{ Mrad/s}$ , and  $\omega_{dq}^D(\text{ortho}) = -2.379 \text{ Mrad/s}$ . If we similarly assume that all  $o\text{D}_2$  molecules have the same values for the intramolecular coupling constants as those obtained by Code and Ramsey for  $j=2$  molecules, and if we use these values in Eqs. (3.1) and (3.9), we obtain  $\omega_{\text{sr}}^D(\text{ortho}) = 0.0549 \text{ Mrad/s}$  and  $\omega_{dq}^D(\text{ortho}) = 2.063 \text{ Mrad/s}$ . It is clear from the values of  $\omega_{\text{sr}}^D$  and  $\omega_{dq}^D$  that nuclear spin relaxation in both  $p\text{D}_2$  and  $o\text{D}_2$  is completely dominated by the combined dipolar/quadrupolar relaxation mechanism, and that the combined dipolar/quadrupolar relaxation itself can be associated primarily with the quadrupolar relaxation mechanism.

We have seen from our previous H<sub>2</sub>-He and HD-He work<sup>1,2</sup> that the only potential energy surface that gives quantitative agreement with the proton relaxation in both H<sub>2</sub>-He and HD-He mixtures is the one derived from the *ab initio* calculations of Meyer *et al.*<sup>5(a)</sup> by Köhler and Schaefer<sup>5(b),5(c)</sup> and referred to in short by us as the KS surface. In the present study, we have focused solely on the

KS surface and its predictive powers for nuclear spin relaxation in D<sub>2</sub>-He mixtures. Close-coupled, or coupled-channel (CC) quantum collisional calculations have been carried out using the MOLSCAT package<sup>16</sup> for the scattering of D<sub>2</sub> (treated as a rigid rotor with bond distance 1.447 bohr) against He. We have employed the numerical grids of Legendre components of the potential given in Table I of Ref. 5(c). As in our earlier study for HD-He, we have not carried out vibrational averaging over the D<sub>2</sub> vibrational wave functions for the full stretching-dependent potential surface, since the cross sections governing nuclear spin relaxation have not been found to be sensitive to the stretching dependence<sup>17</sup> and are similarly not expected to be sensitive to small changes<sup>18</sup> in the polarizability of the hydrogen isotopes.

In order to obtain the longitudinal relaxation time for a bulk gas mixture at a specified temperature, it is necessary to calculate the required energy-dependent (binary collision) effective cross sections over a range of collision energies, or equivalently, total energies as in the present calculations, sufficient to allow accurate evaluation of thermally averaged effective cross sections of the type that appear in Eqs. (3.11) to be made. Scattering calculations have therefore been carried out in the present case for 17 total energies for  $o\text{D}_2$ -He collisions, ranging from a lowest total energy of 200 cm<sup>-1</sup> to a highest total energy of 3500 cm<sup>-1</sup>, and for 18 total energies for  $p\text{D}_2$ -He scattering, ranging from a lowest total energy of 100 cm<sup>-1</sup> to a highest total energy of 3500 cm<sup>-1</sup>.

For  $o\text{D}_2$ -He collisions, the effective cross sections  $\sigma_V(j',j)$  and  $\sigma_T(j',j)$  are identically zero for total energies less than or equal to the  $j=2$  threshold energy 182.652 cm<sup>-1</sup>. For  $p\text{D}_2$ -He collisions, the cross sections vanish for total energies less than or equal to the  $j=1$  threshold energy 60.884 cm<sup>-1</sup>. Since the interaction potential for D<sub>2</sub> with He is too shallow to support orbiting resonances near the threshold energies, the energy dependence of  $\sigma_V$  and  $\sigma_T$  for  $p\text{D}_2$ -He and  $o\text{D}_2$ -He is obtained quite reliably from scattering calculations performed at total energies greater than or equal to 100 and 200 cm<sup>-1</sup>, respectively. In all calculations, sufficient partial waves have been included to ensure fully converged results for all state-to-state reorientation cross sections up to and including  $j=6$  ( $o\text{D}_2$ ) and 5 ( $p\text{D}_2$ ). Values of  $(T_1/\rho)_{\text{lin}}^{\infty}$  have been calculated for temperatures ranging from 50 up to 300 K.

#### IV. COMPARISON BETWEEN THEORY AND EXPERIMENT

Figure 2 shows the present experimental and theoretical results for the infinite-dilution limits of deuteron relaxation in D<sub>2</sub>-He mixtures. The solid curve represents  $(T_1/\rho)_{\text{lin}}^{\infty}$  for  $o\text{D}_2$ -He mixtures, while the dashed curve represents  $(T_1/\rho)_{\text{lin}}^{\infty}$  for  $p\text{D}_2$ -He mixtures. Notice that the relaxation times for the nuclear spin magnetizations for the *ortho* and *para* modifications differ considerably. At 100 K,  $(T_1/\rho)_{\text{lin}}^{\infty}$  is a factor of 14.8 times longer for  $o\text{D}_2$ -He than it is for  $p\text{D}_2$ -He, while at 200 and 300 K, the corresponding factors are 4.6 and 2.9, respectively. The differences

TABLE III. Calculated values of  $(T_1/\rho)_{\text{lin}}^\infty$  for *o*D<sub>2</sub>-He and *p*D<sub>2</sub>-He.

<i>T</i> (K)	$(T_1/\rho)_{\text{lin}}^\infty$ (ms amagat <sup>-1</sup> )	
	<i>o</i> D <sub>2</sub> -He	<i>p</i> D <sub>2</sub> -He
50	7.40	0.036
60	3.90	0.048
70	2.61	0.061
80	2.03	0.075
90	1.73	0.090
100	1.56	0.105
110	1.46	0.122
120	1.41	0.140
130	1.38	0.158
140	1.37	0.177
150	1.37	0.197
160	1.37	0.217
170	1.38	0.238
180	1.38	0.259
190	1.39	0.281
200	1.41	0.303
210	1.42	0.325
220	1.43	0.347
230	1.44	0.370
240	1.45	0.392
250	1.46	0.414
260	1.48	0.436
270	1.49	0.458
280	1.50	0.479
290	1.51	0.500
293	1.51	0.506
300	1.52	0.521

between the nuclear spin relaxation times for the two modifications are essentially due to *p*D<sub>2</sub> having  $j=1$  in its rotational ground state, while *o*D<sub>2</sub> has  $j=0$  in its rotational ground state. The intramolecular interactions (3.1) and (3.2) vanish for  $j=0$ , so that molecules in the  $j=0$  rotational state make no contribution to intramolecular relaxation of the nuclear spin magnetization in *o*D<sub>2</sub>. Thus, only those molecules in rotational states  $j=2,4,\dots$  contribute to relaxation of the nuclear spin magnetization of *o*D<sub>2</sub> on the time scale of the present experiments, with their contributions weighted according to Eqs. (3.11) by respective fractional populations. This effect has already been discussed in detail for nuclear spin relaxation in HD-He mixtures.<sup>2</sup>

The relaxation times for *p*D<sub>2</sub> and *o*D<sub>2</sub> differ significantly (see Table III), with *o*D<sub>2</sub> relaxing at least three times more slowly than *p*D<sub>2</sub> at all temperatures below 300 K. Furthermore, there is twice as much *o*D<sub>2</sub> as *p*D<sub>2</sub> in the high-temperature “frozen-out” equilibrium *n*D<sub>2</sub> used in the experiments. Finally, there is a 5:1 ratio in the intensities of the signal strengths from *o*D<sub>2</sub> and *p*D<sub>2</sub> molecules. When all these properties are taken into consideration, it is clear that only the relaxation of the *o*D<sub>2</sub> spin modification is observable experimentally under present conditions, so that direct comparison can be made with the relaxation times calculated for *o*D<sub>2</sub> infinite dilution mixtures.

Agreement between theory and experiment is good at 220 K, with the calculated value of  $(T_1/\rho)_{\text{lin}}^\infty=1.43$  ms/amagat being 7.5% higher than the experimental value 1.33 ms/amagat, but lying within the  $\pm 0.15$  ms/amagat

error bar; the level of agreement is considerably improved at 293 K, with the calculated value of 1.51 ms/amagat being only 3% higher than the experimental value 1.46 ms/amagat and lying well within the  $\pm 0.10$  ms/amagat error bar. The overall agreement between theory and experiment lies between that found earlier for the proton and deuteron relaxations in HD-He mixtures; it is considerably better than that obtained for the deuteron relaxation, yet not quite as good as that obtained for the proton relaxation. There is no systematic difference as was found for the deuteron relaxation in HD-He mixtures. The general theoretical trend can be seen from Fig. 2.

We have assumed in our calculations that the dipolar and quadrupolar coupling constants  $\omega_d^D$  and  $\omega_q^D$  for a given spin modification are independent of rotational state. This is not quite true, since these quantities depend on averages of the inverse cube  $r^{-3}$  of the intramolecular separation over the D<sub>2</sub> vibrational wave functions. Such an averaging procedure introduces a weak  $j$  dependence into these coupling constants (which is, however, smaller than 1%). Such subtle changes in the intramolecular coupling constants would not likely account for the remaining differences presently seen between the theoretical and experimental values of  $(T_1/\rho)_{\text{lin}}^\infty$ .

A D<sub>2</sub> molecule in the total spin state with  $I=2$  possesses not only a net magnetic dipole moment, but also a net magnetic octupolar moment. These magnetic multipole moments will each relax via the intramolecular and intermolecular interactions and, since their tensor ranks differ by two, their relaxations will, in general, be coupled. Our present calculations have dealt explicitly with the independent relaxation of the magnetic dipole moment and have ignored any contribution to the net relaxation of the dipolar magnetization associated with coupling to the relaxation of the magnetic octupolar magnetization. A detailed discussion of the influence of the relaxation of the octupolar magnetization on the relaxation of the dipolar magnetization for gaseous *o*D<sub>2</sub> can be found in Ref. 19 (see also Ref. 14 and Abragam<sup>20</sup>). The arguments given there apply equally well to magnetic relaxation in mixtures of *o*D<sub>2</sub> with noble gases. In particular, it has been shown in Ref. 19 that the magnetic octupolar moment plays a role in the relaxation of the nuclear magnetization only if cross relaxation between the dipolar and octupolar spin reservoirs exists. Moreover, it has been shown in Ref. 19 (see also Ref. 21) that in the gas phase, the cross-relaxation time vanishes under the conditions of extreme narrowing that apply to all measurements presently being reported.

## V. SUMMARY AND CONCLUSIONS

The present study was undertaken in order to help answer certain questions raised in an earlier study of the proton and deuteron spin relaxation times in HD-He mixtures.<sup>2</sup> Proton relaxation in HD is strongly dominated by the intramolecular spin-rotation interaction, while deuteron spin relaxation is strongly dominated by the intramolecular dipolar and quadrupolar interactions, especially the latter. Since theory and experiment were in excellent agree-



ment for the temperature dependence of the proton longitudinal relaxation times both in H<sub>2</sub>-He and HD-He mixtures, while they were in significant disagreement at all temperatures for the deuteron longitudinal relaxation time in HD-He mixtures, one specific question which arose was whether or not the vector intramolecular (or spin-rotation) interaction and the second rank tensorial intramolecular interactions governing relaxation of the (spin) magnetization probe different aspects of the anisotropy of the hydrogen isotope-helium intermolecular interaction. For temperatures exceeding 100 K spin-rotation relaxation plays a dominant role in nuclear spin relaxation in H<sub>2</sub>-He mixtures. Because calculations using the *ab initio* anisotropic intermolecular interaction potential of Ref. 5 are fully consistent with spin relaxation measurements in H<sub>2</sub>-He mixtures, and because the D<sub>2</sub>-He intermolecular interaction is identical to the H<sub>2</sub>-He interaction, a combined experimental-theoretical study of deuteron spin relaxation in D<sub>2</sub>-He mixtures (dominated by the second rank tensorial intramolecular interactions) was therefore expected to shed light on this question.

For the reasons given above, we have carried out NMR measurements of the deuteron longitudinal (or "spin-lattice") relaxation time  $T_1$  in gaseous mixtures of  $nD_2$  and He at temperatures of 220 and 293 K. Measurements were made on two  $nD_2$ -He mixtures, one with 8.9% D<sub>2</sub> in He and the other with 17.9% D<sub>2</sub> in He. The results obtained for these two mixtures were then extrapolated linearly to infinite dilution of D<sub>2</sub> in He to obtain values of  $(T_1/\rho)_{\text{lin}}^\infty$ . These values were then compared with values of  $(T_1/\rho)_{\text{lin}}^\infty$  calculated for the  $oD_2$ -He interaction, since only the signal from the  $oD_2$  component of the mixture is experimentally observed.

A systematic deviation of the type seen for the deuteron relaxation in HD-He mixtures<sup>2</sup> has not been observed for D<sub>2</sub>-He mixtures. We have found very good agreement between the calculated and measured longitudinal relaxation time for  $oD_2$  in He both at 293 and at 220 K. It should be noted that the spin-rotation intramolecular interaction plays an extremely small role in the relaxation of the deuteron magnetization in  $oD_2$  because  $\omega_{\text{sr}}^D$  is only 2.66% the size of  $\omega_{\text{dq}}^D$ , and the coupling constants enter quadratically in the corresponding expressions for the (independent) contributions to the longitudinal relaxation time. Thus, the level of agreement found between theory and experiment in the present study allows us to conclude that the Köhler-Schaefer hydrogen-helium potential energy surface provides a good description of the effects of reorientation collisions upon the relaxation of the deuteron spin magnetization by second rank tensor intramolecular interactions. Relaxation of the proton spin magnetization in  $oH_2$  has significant contributions from both the spin-rotation and dipolar interactions (since  $\omega_{\text{sr}}^H$  is 13.2% of  $\omega_{\text{d}}^H$ ). Indeed, spin-rotation relaxation becomes dominant at higher temperatures, since the spin-rotation interaction energy is proportional to  $j$ . The agreement found in the present study between theory and experiment for intramolecular relaxation of the deuteron spin magnetization in  $nD_2$ -He mixtures, taken together with the excellent agree-

ment between theory and experiment found earlier<sup>1</sup> for intramolecular relaxation of the proton magnetization in  $oH_2$ -He mixtures, allows us to conclude that close-coupled scattering calculations based on the Köhler-Schaefer hydrogen-helium potential energy surface accurately represent the reorientation effective cross sections  $\mathfrak{S}(0100|A)_{A-\text{He}}$  and  $\mathfrak{S}(0200|A)_{A-\text{He}}$ , with  $A=H_2$  and  $D_2$  that determine the intramolecular relaxation of the nuclear spin magnetizations of H<sub>2</sub> and D<sub>2</sub> in their binary mixtures with He. Consequently, it appears that the systematic deviation noted between the calculated and measured deuteron relaxation times in a previous study<sup>2</sup> on HD-He mixtures is most likely associated with some feature of the original H<sub>2</sub>-He potential surface that is not probed by relaxation of the spin magnetizations in the homonuclear isotopomers. The HD-He quantum scattering calculations will have to be reexamined to test this conclusion, with greater attention being paid to the specific forms of the radial coefficients, especially those for the odd Legendre polynomials that appear in the Legendre expansion of the HD-He intermolecular interaction.

It can also be seen from the results obtained in the present study that there are additional experiments that could usefully be undertaken. In particular, it would be useful to carry out measurements of longitudinal nuclear spin relaxation in  $nD_2$ -He mixtures for a series of lower temperatures, spanning the temperature range 50–250 K. Such measurements at lower temperatures are especially desirable, since it should be possible to detect simultaneously relaxation of both the *para* and *ortho* magnetizations, as has been observed by Hardy<sup>22</sup> for pure D<sub>2</sub>. Furthermore, it would be interesting to carry out measurements for mixtures of pure  $oD_2$  and  $pD_2$  with He to remove any uncertainty in the interpretation of the experimental data. Finally, it would be interesting to extend the measurements of  $T_1$  in  $oD_2$ -He mixtures to (lower) densities, where extreme-narrowing conditions no longer apply, so that the role of cross coupling between the relaxations of the dipolar and octupolar magnetizations can be studied.

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