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Ortho-to-para conversion in solid tritium. I. Theoretical models

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Reliable theoretical models developed to calculate the intrinsic ortho-to-para conversion rate in orientationally ordered solid H_2 are used to estimate the conversion rate in solid T_2. Since the Debye energy is larger than the rotational energy difference between the $J=1$ level and the ground state $J=0$, both the single-phonon transition probability and the transition probability due to the Raman effect must be taken into account. These additional intrinsic processes are treated here, but are found to be too weak to account for the experimentally observed rates. The single-phonon conversion rate due to unpaired electron spins in the solid is obtained for both localized and mobile spins. The conversion rate due to mobile unpaired electron spins is large enough to account for the experimental data if the atom density is of order 10^{18} atoms per cm^3.

I. INTRODUCTION

The subject of ortho-to-para conversion in hydrogen and its isotopes has been studied for decades. Both the intrinsic conversion process (the process applicable in a pure solid) and the catalyzed process due to paramagnetic impurities such as O_2 dissolved in the hydrogen have been extensively treated. This phenomenon, in the solid phase, is of particular current technological interest because it bears directly on the possibility of producing samples of DT (deuterium tritide) with high polarizations of both species of nuclear spins. Although extensive theoretical work has been done on solid H_2 and some theoretical work has been done on solid D_2, to date, there has been no theoretical work on ortho-to-para conversion in solid T_2. This study has been motivated by recent experimental determinations of the ortho-to-para conversion rate in solid T_2 presented in the following paper. In brief, these NMR experiments find that the rate is temperature dependent and has a peak near 11 K. The magnitude of the conversion rate at the peak is about 150 times larger than that of intrinsic conversion in solid H_2.

The most recent work on solid H_2 by Berlinsky and Hardy[1] provides an excellent guide to the intrinsic $J=1$ to $J=0$ conversion process in all the solid hydrogen isotopes as they clearly display the dependence of the conversion rate on the rotational energy difference, E_{10}, and the Debye temperature, Θ_D. Furthermore, the agreement between their calculated rate (for an orientationally disordered system) and the observed experimental values is very impressive (and reassuring). In addition, details of the effects of conversion on nuclear-spin populations in the orientationally ordered state, where $m_j=0$, seem to be borne out by their own experiments.[2]

Under high pressures, the Debye temperature of solid H_2 increases. Experiments on the ortho-to-para conversion rate by Pedroni *et al.*,[3] as a function of pressure, revealed enhanced rates that could not be explained on the basis of two-phonon processes. A calculation by Berlinsky[4] of the one phonon conversion rate in H_2, with density as a parameter, satisfactorily explained these observed large rates.

The situation in solid D_2 is not nearly so satisfactory. The first systematic measurements of the $J=1$ (para-D_2) to $J=0$ (ortho-D_2) rate were done by Grenier and White[5] for samples with high enough $J=1$ concentration to be orientationally ordered (below some specific temperature). However, their $J=1$ concentration was still low enough that the samples must be considered alloys. In the experiments, it was not established that the conversion rate was independent of temperature nor $J=1$ concentration. There was also some scatter in the experimental data (as is to be expected). The theory, revised to include a more correct value for the Debye temperature, only roughly agreed with the data.

In D_2, the theoretical situation is quite a bit more complicated than in H_2. For instance in solid H_2, the rotational energy difference expressed in temperature units (E_{10}/k) is 170 K and thus is larger than the Debye temperature of about 120 K (at low densities). This completely eliminates a single-phonon conversion process as well as the two-phonon Raman process. The dominant process is then a two-phonon process where the sum of the energies of the two phonons equals the rotational energy difference. The process is the only one considered by Berlinsky and Hardy and it produces a temperature-independent rate in good agreement with experiment. Actually their calculation is done in the zero-temperature limit but if this restriction were relaxed, the calculated rate would still be essentially independent of temperature in the solid region below 14 K. In D_2 (or in T_2), both the single-phonon process and the two-phonon Raman process are energetically possible adding to the complexity of the calculation. The original work on D_2 used the wrong Debye temperature and concluded that the single-phonon process was also impossible there.[6] This has been modified in the more recent calculations.[7] In D_2, the effects of the electric quadrupole interaction cannot be ignored, adding yet another term into the calculation. An additional complication also arises in D_2 that is not present in H_2 or T_2. This comes from the fact that some of the $J=0$ molecules ($\frac{5}{6}$ of them) have nuclear spins ($I=2$) and can contribute the magnetic field gradient necessary for nuclear-spin conversion. This complicates the "gain-loss" equation as well. A similar situation arises in the $J=1$ to $J=0$ conversion of small amounts of H_2 in solid HD and to the conversion of T_2 in DT.

Data taken by Milenko and Sibileva[8] on D_2 at 4.2 K give an average conversion rate of 5.3×10^{-4} h^{-1} over a range of $J=1$ concentrations from 33% to 89%. This value agrees very well with the recent measurement of 5.5×10^{-4} h^{-1} by Honig *et al.*[9] where very low $J=1$ concentrations were used. The theoretical value of the conversion rate is a factor of 2–3 too high to account for these two experimental determinations.

In Sec. II, we adapt the Berlinsky and Hardy calculation to the specific situation presented by solid T_2 to calculate the intrinsic conversion rate due to the two-phonon processes, both the ordinary one and the Raman process. In Sec. III, we will present the single-phonon conversion rate for the intrinsic process based on the Berlinsky calculation and estimate the total intrinsic conversion rate.

In Sec. IV, we will treat $J=1$ to $J=0$ conversion in the presence of paramagnetic impurities. This problem has also received considerable attention in solid H_2.[10] In addition to considering the impurities as fixed in space, we will consider two cases where the impurities have translational motion and can diffuse through the solid[11] or hop from site to site. By comparing these calculations to the recent experimental measurements of the ortho-to-para conversion rate in solid T_2, it is possible to estimate the concentration of atoms needed.

II. INTRINSIC TWO-PHONON PROCESSES

The magnetic dipole-dipole interaction between the "central" ortho molecule and a near-neighbor ortho molecule is written in terms of the four intermolecular interactions of the spin-$\frac{1}{2}$ nuclei:

$$H_{ss}=\left[\frac{24\pi}{5}\right]^{1/2}\sum_{p,\delta,s}\frac{4\mu_p^2}{|r_\delta+r_s-r_p|^3}\times\sum_{m,n}C(112;m,n)i_{\delta,s}^{m}i_p^{n}\times[Y_2^{m+n}(\Omega_{\delta,s,p})]^* . \tag{1}$$

A similar expression can be written for the magnetic coupling with the rotational magnetic moment of the neighboring molecule but in H_2 this contributes only 2.5% of the rate so we will neglect it here. Berlinsky and Hardy assume a low-temperature limit applies to the phonon occupation probabilities and also use the fact that $E_{10}>E_D$ (where E_{10} is the energy separation of the $J=1$ and $J=0$ levels and E_D is the Debye energy) in choosing the limits for their integrals.

One of the goals of Berlinsky and Hardy was to calculate the rate for each of the magnetic substates, M, in order to demonstrate the effect of ortho-to-para conversion on the NMR line shape in the orientationally ordered state. We are interested in the overall conversion rate, the average over the individual rates. Accordingly, to simplify the calculation, we sum over the magnetic substates immediately to obtain the overall net rate, R_n,

$$R_n=\frac{1}{3}\sum_M R_{ss}^M=\frac{44}{21\pi}A^2\frac{\gamma_{ss}^2}{\hbar}\left[\frac{\rho}{R_0}\right]^2 g^{(2)}x_1 , \tag{2}$$

where ρ is the bond length in the molecule (0.75 Å for all the hydrogens), R_0 is the nearest-neighbor distance in the solid, A^2 is a pure number, where x_1 is the concentration of $J=1$ molecules, and γ_{ss} and $g^{(2)}$ are defined below:

$$(44/21\pi)A^2=9.048\times10^4 , \tag{3a}$$

$$\gamma_{ss}^2=(\mu_p^2/R_0^3)^2 , \tag{3b}$$

$$g^{(2)}=\frac{18}{E_D}\left[\frac{\hbar^2}{2MR_0^2E_D}\right]^2\eta^{(2)} . \tag{3c}$$

The quantity $\eta^{(2)}$, an integral, must be evaluated for different limits than those used by Berlinsky and Hardy since $E_D>E_{10}$ for either T_2 or D_2. The sum over the twelve nearest neighbors in an hcp (or fcc) lattice introduces a factor $12x_1$ into Eq. (2). In the work of Berllinsky and Hardy, the concentration was so high that x_1 can be taken equal to unity. In general, however, x_1 is a variable and must be included to obtain the correct rate equation for conversion. Another difference between this calculation and that of Berlinsky and Hardy is that we have included all the rotational substates where they only need the contribution from the state $m_J=0$ in the ordered phase. The value of $\eta^{(2)}$ to be used in the above equation is

$$\eta^{(2)}=\frac{1}{2E_{\mathrm{D}}^{2}}\int_{E_{10}}^{E_{10}} d\varepsilon_2(E_{10}+\varepsilon_2)(E_{10}-\varepsilon_2)\{1-j_0[\pi(E_{10}+\varepsilon_2)/\varepsilon_0]\}\{1-j_0[\pi(E_{10}-\varepsilon_2)/\varepsilon_0]\}$$
$$\times\{n[(E_{10}+\varepsilon_2)/2]+1\}\{n[(E_{10}-\varepsilon_2)/2]\}\ . \tag{4}$$

In this equation, ε_0 is defined to be $E_D(\pi/3)^{1/3}$. The phonon factor, n, in the above equation is $n(\varepsilon)=[\exp(\varepsilon/kT)-1]^{-1}$. Since the spherical Bessel functions in Eq. (4) can be expressed as simple trigonometric functions, the integrals are easy to evaluate. At $T=0$, the phonon factors, n, vanish so

$$\eta^{(2)}(T=0)=\frac{1}{b^3}\left[\tfrac{2}{3}a^3-2a-\frac{a}{2}\cos(2a)+\tfrac{5}{4}\sin(2a)\right], \tag{5}$$

with $a=b(E_{10}/E_D)\approx b/2$ where $b=2.1876$. For H_2, at zero pressure and temperature, using $E_D=120$ K, Berlinsky and Hardy obtained for the net rate, R_n, the value 1.67% per hour.

The value of $\eta^{(2)}$ depends on the choice of E_D. In Fig. 1, we plot $\eta^{(2)}(T=0)$, as given above, as a function of E_D from 90 to 130 K, the expected range for T_2, although the proper value to use is not known. Even in H_2, different experiments tend to favor different values of E_D. We will use the value $E_D=117$ K in our calculations, mainly for simplicity, as this makes $2E_{10}=E_D$. With $E_D=117$ K, we plot $\eta^{(2)}(T)$ for the approximate temperature range covered by the experiments on T_2 in Fig. 2. It can be seen from the weak temperature dependence obtained here that Berlinsky and Hardy were perfectly justified in ignoring any temperature dependence in their theory of the ordered state ($T<3$ K) and using just the value $\eta^{(2)}(T=0)$.

The other two-phonon process possible in D_2 or T_2 (but not in H_2), since $E_{10}<E_D$, is the Raman process. The only factor in Eq. (2) that is changed is the function $g^{(2)}$ which becomes

$$g^{(R)}=\frac{36}{E_D}\left[\frac{\hbar^2}{2MR_0^2E_D}\right]^2\eta^{(R)}, \tag{6}$$

where

$$\eta^{(R)}=\frac{1}{2E_D^2}\int_{E_{10}}^{2ED-E_{10}} d\varepsilon_1(\varepsilon_1^2-E_{10}^2)\{1-j_0[\pi(\varepsilon_1+E_{10})/\varepsilon_0]\}\{1-j_0[\pi(\varepsilon_1-E_{10})/\varepsilon_0]\}$$
$$\times\{n[(\varepsilon_1+E_{10})/2]+1\}\{n[(\varepsilon_1-E_{10})/2]+1\}\ . \tag{7}$$

This integral was evaluated numerically. In Fig. 3, with $E_D=117$ K and x_1 equal to unity, we show the net intrinsic conversion rate in solid T_2 for both the two-phonon processes. In T_2, the sum of the direct two-phonon process and the Raman process would represent the entire two-phonon contribution; however, in D_2, quadrupole effects, not taken into account here, must be included to give the total two-phonon rate. At 10 K, the sum of the two-phonon rates in T_2, multiplied by 3.6×10^5 to convert to percent per hour, is equal to 2.5×10^{-3} percent per hour for $x_1=1$, about 3 orders of magnitude smaller than the intrinsic rate due to ordinary two-phonon processes in H_2.

The large difference between the two-phonon conversion rate in H_2 and that in T_2 arises from two effects. The mass difference accounts for a factor of 10 in the rates since the rate is inversely proportional to the square of the mass. The second effect reflects the difference in the integrated area of the two-phonon density of states. The conversion rate is roughly proportional to this quantity. The ratio of the integrated two-phonon density of states in T_2 to that in H_2 is 7.4×10^{-3} so that the product of these two "reduction factors" is 10^3.

As a final application of the Berlinsky and Hardy approach, we calculated the ortho-to-para conversion rate for low concentrations of ortho-H_2 in HD. Only the two-phonon process was considered since $E_{10}>E_D$. At low concentration, each ortho-H_2 molecule is surrounded by twelve nearest-neighbor HD molecules which pro-

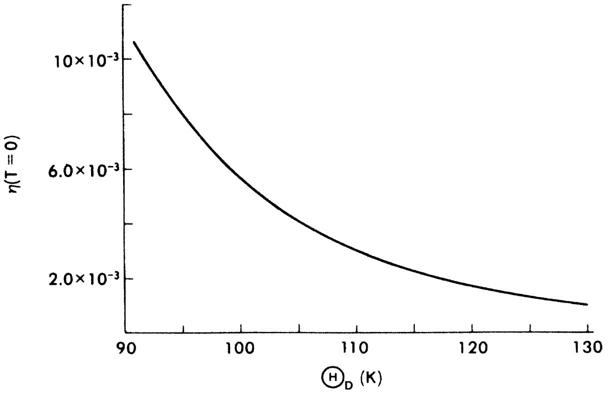

FIG. 1. The dependence of $\eta^{(2)}$ for the ordinary two-phonon process is plotted as a function of the Debye temperature. The energy E_{10}/k is taken equal to 58.5 K.

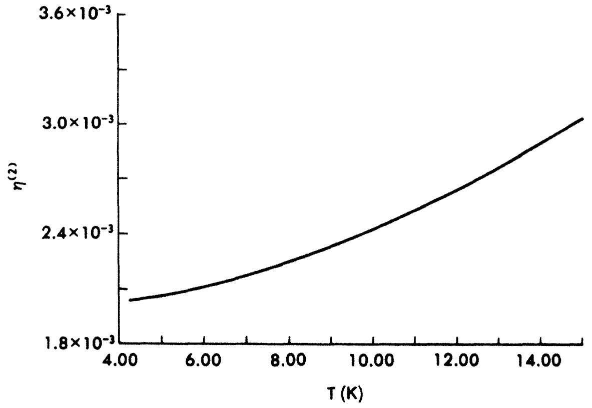

FIG. 2. The dependence of $\eta^{(2)}$ is plotted as a function of temperature taking the Debye temperature to be 117 K.

duces an exponential decay of the concentration. The calculated value of the conversion rate is 0.55% per hour which compares favorably with the rough estimate from experiment of 0.45% per hour.[12]

III. THE ONE-PHONON CONVERSION RATE

The same formalism set up by Berlinsky and Hardy for the two-phonon calculation can be used to calculate the intrinsic conversion rate due to a single-phonon process. They were apologetic in their original work for using the Debye phonon spectrum but they pointed out that the two-phonon Debye spectrum resembles rather closely the two-phonon density of states calculated by Mertens and Biem.[13]

In a subsequent calculation of the single-phonon conversion rate by Berlinsky,[4] he avoided using the Debye approximation by calculating numerically a one-phonon spectral function. One of his goals was to compare his calculation with the conversion rate data of Pedroni *et al.*[3] Their data covered densities in solid H_2 that ranged from ρ_0 to $1.7\rho_0$ where ρ_0 is the zero-pressure density making the Debye approximation very questionable. For the single-phonon process considered below, the density is ρ_0 and we will use the Debye approximation even though the single-phonon density of states in D_2 or T_2 may not be accurately described by the Debye spectrum.

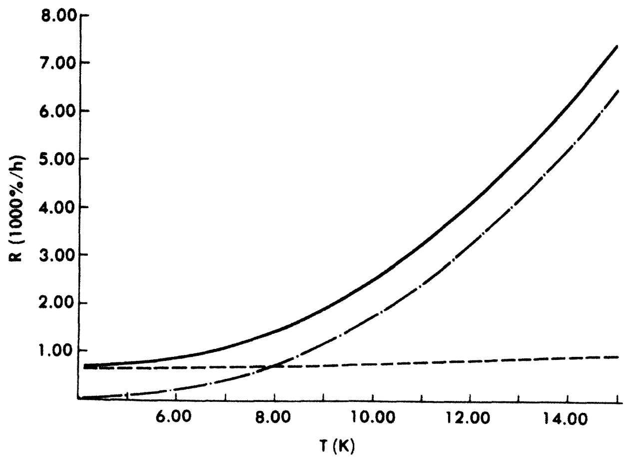

FIG. 3. The two-phonon Raman rate is plotted (dots) as a function of temperature along with the ordinary two-phonon intrinsic rate (dashes). The solid line represents the sum of the two-phonon intrinsic rates for solid T_2.

The important details of the single-phonon calculation are given in the paper by Berlinsky.[4] We take a simplified approach and make the Debye approximation. The calculation itself is straightforward and the net rate for the single-phonon process can be put in a form similar to Eq. (2):

$$R_n=\tfrac{1}{3}\sum_M R_{ss}^M=\frac{3}{5\pi}A^2\frac{\gamma_{ss}^2}{\hbar}\left[\frac{\rho}{R_0}\right]^2 g^{(1)}x_1\ , \qquad (8)$$

where γ_{ss}, ρ, and R_0 have their previous meaning and

$$g^{(1)}=\frac{6}{E_D}\left[\frac{\hbar^2}{2MR_0^2E_D}\right]^2\eta^{(1)}\ , \qquad (9a)$$

$$A^2=(560\pi)^2(\tfrac{2}{105})\ . \qquad (9b)$$

In this case, using $b=(\pi/\sqrt{2})(3/\pi)^{1/3}$, however, $\eta^{(1)}$ has the very simple form (for $2E_{10}=E_D$)

$$\eta^{(1)}=\frac{E_{10}}{E_D}\left[1-\frac{\sin[2b(E_{10}/ED)]}{2b(E_{10}/E_D)}\right]\approx\frac{1}{2}\left[1-\frac{\sin b}{b}\right]$$

$$=0.3136\ . \qquad (10)$$

The expressions developed here can be applied to the calculation of the part of the conversion rate in solid D_2 that is due to dipole-dipole interactions. Choosing a para-D_2 molecule as the central molecule, we obtain a contribution to the rate,

$$(12x)R_{pp}=(3.14\times10^{-4}\ \mathrm{h}^{-1})x\ ,$$

from the para-D_2 near neighbors where x is the concentration of para-D_2. The contribution from near-neighbor ortho-D_2 molecules is

$$12(1-x)(\tfrac{5}{6})R_{po}=(4.70\times10^{-4}\ \mathrm{h}^{-1})(1-x)\ .$$

The total contribution to the rate from the dipole-dipole interaction is the sum of these two terms. At very low para-D_2 concentrations, the calculated rate of $4.70\times10^{-4}\ \mathrm{h}^{-1}$ is lower than the comparable estimate of Motizuki[7] but is nearly in agreement with the *total* rate measured by Honig *et al.*[9] The use of the Debye approximation in the calculation, plus neglect of the quadrupole-quadrupole terms (taken into account by Motizuki), renders any more detailed comparison meaningless.

For solid T_2, the net rate for the one-phonon process, at zero temperature, has the value

$$R_n=(4.114\times10^{-6}\ \mathrm{s}^{-1})x_1=(1.481\%\ \text{per h})x_1\ . \qquad (11)$$

To include temperature dependence, one simply has to multiply Eq. (11) by the phonon factor, $n(E_{10})+1$. This contribution is significantly larger than the sum of the rates for the intrinsic two-phonon processes. Thus in our discussion that follows, we will neglect the two-phonon contributions in comparison to the single-phonon term, even when we treat conversion due to unpaired electron spins in the solid.

IV. CONVERSION DUE TO UNPAIRED ELECTRON SPINS

A. Localized electron spins

The single-phonon calculation for the intrinsic conversion rate can be modified to predict the conversion rate of the central molecule due to an unpaired electron spin positioned a distance R from it. In this case, there is no sum over nearest neighbors that produced the factor $12x_1$ present in the intrinsic conversion rates. Instead, the calculated rate for one unpaired spin must be multiplied by the probability of finding an unpaired electron spin at position R and then summed over R. The net rate for this process, using only the single-phonon calculation, will be designated R_{sa} where

$$R_{sa}=\frac{1}{3}\sum_{M} R_{sa}^{M}=\frac{3}{64}\left[\frac{3}{5\pi}\right] A^{2}\frac{\gamma_{sa}^{2}}{\hbar}\left[\frac{\rho}{R_0}\right]^{2} g^{(1)}c_a\ , \qquad (12)$$

where A^2 and $g^{(1)}$ have the same meaning as in Eqs. 9(a) and 9(b), and

$$\gamma_{sa}^{2}=(\gamma_s\gamma_a\hbar^{2}/4R_0^{3})\ , \qquad (13)$$

with γ_a being the electron-spin gyromagnetic moment. In the previous expressions for the net rates, we must replace the factor $12x_1$ by the probability of finding an electron spin a distance R from the central molecule. Roughly, this can be done by multiplying the rate for one-electron spin by the concentration of such spins, c_a, as has been done in Eq. (12). Making this replacement, we can evaluate the conversion rate for solid T_2 using for R_0 the near-neighbor distance for molecules and then scaling the final result by the factor $(R_0/R)^{10}$ to allow R to be a variable. This evaluation yields

$$R_{sa}=(0.0735\ \mathrm{s}^{-1})c_a(R_0/R)^{10}=c_a\Omega_0\ . \qquad (14)$$

This equation, simple though it may be, is difficult to apply. The difficulties arise because of the sensitivity of the result to R (power 10) and the presence of the factor c_a. It is usually very difficult to know either R or the electron-spin concentration with any precision.

B. Electron spins with translational motion

If the electron spins are capable of moving through the background of stationary molecules, the magnetic field (and associated field gradient) they produce becomes time dependent itself and can be treated in the framework used for perturbations that are stationary, random functions of time. There appears to be (at least) two distinct mechanisms for moving electron spins to produce ortho-to-para conversion: (1) the time-dependent magnetic field gradient is supplied by the *phonons*, the *hopping* of the electron spin serving only to carry it from one conversion site to another; and (2) the time-dependent magnetic field gradient is supplied by the translational motion of the spin, no coupling with the phonons being required.

For the first case where the essential time dependence is supplied by the coupling with the phonons, the conversion rate, R, in the low-concentration limit, can be written simply as[14]

$$R=\frac{cz\Omega_0\Gamma}{z\Omega_0+\Gamma}\ . \qquad (15)$$

In this expression, c denotes the concentration of unpaired electron spins, Γ is the rate for an electron spin to hop to a single neighboring site, z is the number of neighboring sites, and Ω_0 is the conversion rate for a single molecule next to an electron spin. The product $c\Omega_0$ was calculated in the preceding section, Eq. (14). If we use the large interstitial position as the site occupied by the electron spins in between hops to nearby interstitial positions, $R=R_0/\sqrt{2}$, and the fact that there are six such interstitial positions for the central molecule makes $z=6$. This leads to a value of $z\Omega_0=14.1\ \mathrm{s}^{-1}$.

The expression for the rate given by Eq. (15) has the feature that there is a peak in the rate. The two extreme limits have simple interpretations. When the hopping rate is large compared to $z\Omega_0$, the net rate (R) depends just on the product $cz\Omega_0$. In the other extreme, where the hopping is slow, the net rate is equal to the product $c\Gamma$. For diffusing atoms of H in H_2, Leach and Fitzsimmons[15] obtain results that indicate that the atom concentration, c_a, depends on τ, if atoms are being produced at a steady rate, due to recombination that depends on the atom motion. Assuming $c\propto\Gamma^{-1/2}$, the maximum rate is obtained when $\Gamma=z\Omega_0$. The concentration at the peak in the rate will thus depend on $(z\Omega_0)^{-1/2}$.

The second mechanism for conversion, where the time-dependent gradient is due to moving electron spins, also yields an expression for the rate that has a peak. The detailed contribution to the conversion rate from *moving* electron spins where the time-dependent magnetic field gradient comes from the translational motion is given in the Appendix. There the dipolar interaction between the unpaired electron spin and the nearby nuclear spins on a molecule with total spin $I=1$ is treated perturbatively as a stationary, random function of time.[16] Since only the magnetic field gradient is effective in converting nuclear spins from the triplet state to the singlet state, H_{sa} is expanded to first order in the separation of the two atoms in the central molecule. The time-dependent nature of the interaction that arises from the translational motion of the electron spin is expressed by assuming a single exponential correlation function. The final result for the rate contains the Fourier transform of the correlation function, $j(\omega)$, where

$$j(\omega)=\frac{2\tau}{1+\omega^{2}\tau^{2}}\ , \qquad (16)$$

where τ is the translational correlation time.

In terms of this definition, as shown in the Appendix, the conversion rate can be written as

$$R_{sa}=(2.04\times10^{12})c_a\left[\frac{R_0}{R}\right]^8 j(\omega)\ \mathrm{s}^{-1}\ , \tag{17}$$

where R is the distance from the unpaired electron spin to the center of the molecule. Again by assuming $c_a \propto \tau^{1/2}$, we find that the peak rate occurs when $\omega^2\tau^2=3$. If we use the large interstitial position in the hcp lattice to obtain $R=R_0/\sqrt{2}$, we obtain for the peak rate,

$$(R_{sa})_{\max}=(2.83\times10^{13})(c_a/\omega)\ \mathrm{s}^{-1}\ . \tag{18}$$

The question concerning what value of ω to use in this expression is an interesting one. The most obvious choice for an ortho-to-para transition is $\omega=\omega_{10}$ since $\hbar\omega_{10}$ is the energy that must be removed for a $J=1$ to $J=0$ transition in the gas phase. If this choice is made, use of the experimentally observed peak rate ($\approx 8\times10^{-4}$ s^{-1} at 11 K) gives $n_a\approx 7\times10^{18}$ atoms per cm^3.

A second, and less obvious, choice for ω is the NMR Larmor frequency, ω_0, since $\hbar\omega_0$ is the energy that must be removed from the nuclear-spin system alone in an ortho-to-para transition. Golovin and Buyanov[17] suggested this choice for *surface* catalysis of H_2 where they conclude that interactions with the surface break the symmetry between the two atoms in the molecule so that they are no longer equivalent (the restriction of the Pauli principle does not apply). Since the ortho and para labels no longer apply, the rotational levels of the molecules are equal so that only nuclear-spin energy must be removed to convert the triplet-spin state to the singlet-spin state. While there is no such surface present in bulk T_2 solid, it is not unreasonable to assume that large strains are produced on neighboring molecules by an atom in an interstitial site. A sufficiently large strain would hinder the rotation of the ortho molecules to the extent that J would not be a good quantum number. If this interpretation is correct, then the atom density at the peak in the rate is $n_a=1.7\times10^{14}$ atoms per cm^3 (for a Larmor frequency of 30 MHz). The peak rate should then depend on Larmor frequency but this effect is *not observed experimentally.* However, the idea that the rotational energy levels for a molecule near an atom may be significantly altered should not be dismissed.

The mechanism where the time dependence is supplied by the phonons but hopping carries the atom from site to site (the hopping model) requires that the atom density at the peak in the rate be $n_a=3.6\times10^{18}$ atoms per cm^3, just a factor of 2 below the estimate obtained where the motion of the atom supplies the time dependence (the ballistic model) with $\omega=\omega_{10}$. While only a direct measurement of the concentration of unpaired spins can illuminate the details of the conversion process in solid T_2, an analysis given in the following paper concludes that the hopping model provides the more correct description of the T_2 results and reconciles those experimental results with previous measurements of the atom recombination coefficient in H_2 and the equilibrium atom density in D_2 doped with T_2.

V. CONCLUSIONS

The approach used by Berlinsky and Hardy to successfully calculate the intrinsic ortho-to-para conversion rate, at zero temperature, in orientationally ordered ortho-H_2 and that used by Berlinsky to predict the pressure dependence of the H_2 conversion rate, has been adapted here to calculate the intrinsic ortho-to-para conversion rate in solid tritium. Since the Debye energy in tritium is larger than the rotational energy difference between the excited rotational level, $J=1$, and the ground state, $J=0$, two processes not possible in solid H_2 at zero pressure contribute to the conversion rate in solid T_2. These processes are the single-phonon process and the two-phonon Raman process. Both are taken into account here. It is concluded that the single-phonon intrinsic process dominates both of the two-phonon processes in solid T_2. However, the sum of all the intrinsic processes is much too small to account for the recently observed conversion rates in solid T_2.

The conversion rate due to unpaired electron spins, using only the single-phonon process, is calculated, again using the approach of Berlinsky. For unpaired electron spins that are fixed in position, the number of such spins that would be required to explain the peak conversion rates in solid T_2 is excessive. At the lowest temperature (6.4 K) of the experiment, where the rates are lower, this calculation may in fact be the correct one to use as it requires of the order of 10^{20} spins per cm^3 to give the observed rate. At 6.4 K, this number of spins is reasonable but it is not reasonable at 11.4 K where the peak rate is observed. To account for this peak rate, it is proposed that the unpaired electron spins are hopping or translating through the background of molecules and that the peak rate occurs when the correlation time for hopping or translation is comparable to ω^{-1}, where ω is different for the different mechanisms. By computing the maximum rate for this process and equating it to the experimental value, it is estimated that between 3×10^{18} and 7×10^{18} spins per cm^3 would produce the observed rate at 11.4 K if the gas-phase rotational levels are correct for the solid.

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APPENDIX

Using time-dependent perturbation theory, the transition probability per unit time from state α to state β, $W_{\alpha\beta}$ is

$$W_{\alpha\beta}=\frac{1}{\hbar^2}\int_0^t \langle\alpha\,|\,H_{sa}(t')\,|\,\beta\rangle\langle\beta\,|\,H_{sa}(t)\,|\,\alpha\rangle\exp[i\omega_{\alpha\beta}(t'-t)]dt'+\text{c.c.} \tag{A1}$$

where $H_{sa}(t)$ is the time-dependent dipole-dipole interaction between the nuclear spins in the central molecule and the electron spin on an atom. The energy difference between the initial and final states, $\hbar\omega_{\alpha\beta}$, depends on the details of the interactions in the solid. The correlation function, $G_{\alpha\beta}$ is defined as

$$G_{\alpha\beta}(t,t')=\langle\alpha\,|\,H_{sa}(t')\,|\,\beta\rangle\langle\beta\,|\,H_{sa}(t)\,|\,\alpha\rangle\ . \tag{A2}$$

If the perturbation is a stationary, random function of time, then the correlation function only depends on the time interval, $t-t'=\tau$, so it can be written

$$G_{\alpha\beta}(t,t')=G_{\alpha\beta}(\tau)\ . \tag{A3}$$

It is customary to introduce the reduced correlation functions,

$$g_{\alpha\beta}(\tau)=G_{\alpha\beta}(\tau)/G_{\alpha\beta}(0)\ , \tag{A4}$$

and their Fourier transforms, $j(\omega)$.

The conversion rate, R, can be written

$$R=\sum_{\alpha,\beta} W_{\alpha\beta}P_\alpha\ , \tag{A5}$$

where P_α is the probability of finding the system in the initial state. Substitution of Eqs. (A1)–(A4) into Eq. (A5) yields

$$R=\frac{1}{\hbar^2}\sum_{\alpha,\beta} G_{\alpha\beta}(0)P_\alpha j(\omega_{\alpha\beta})\ , \tag{A6}$$

where the actual integration limits in Eq. (A1) are approximated by setting them equal to $\pm\infty$. The calculation is now separated into two parts: a time-independent matrix element and the Fourier transform of a reduced correlation function.

The time-independent dipole-dipole interaction between the nuclear spins and the electron spin, H_{sa}, can be written as

$$H_{sa}=A\gamma_{sa}\left[\frac{\rho}{R}\right]\sum_{\mu,\nu,m} C(112;\mu,\nu)C(213;\mu+\nu,m)$$

$$\times(i_1^\mu-i_2^\mu)i_a^\nu Y_1^m(\Omega_P)$$

$$\times[Y_3^{\mu+\nu+m}(\Omega_a)]^*\ , \tag{A7a}$$

$$A=40\pi(\tfrac{6}{35})^{1/2}\ , \tag{A7b}$$

$$\gamma_{sa}=\frac{1}{4}\frac{\gamma_p\gamma_e}{R^3}\hbar^2\ , \tag{A7c}$$

where i_a^ν is the electron spin on the atom and R is the distance between the central molecule (center) and the atom.

The calculation of the matrix element is similar to that done for the one-phonon process except here we take the random average over the atom orientation, $\langle\,|\,Y_3^{\mu+\nu+m}(\Omega_a)\,|^2\rangle=(1/4\pi)$. The conversion rate is found to be

$$R=\frac{1}{18}\frac{21}{64\pi^2}\frac{A^2}{\hbar^2}\gamma_{sa}^2\left[\frac{\rho}{R}\right]^2 j(\omega)\ . \tag{A8}$$

After numerical evaluation appropriate for solid T_2, we obtain

$$R=(2.045\times10^{12})\left[\frac{R_0}{R}\right]^8 j(\omega)\ , \tag{A9}$$

where R_0 is the nearest-neighbor distance between molecules.

Finally, to evaluate the Fourier transform of the reduced correlation function, we make the crude but convenient assumption that the reduced correlation function is of the form

$$g(\tau)=\exp(-\,|\,\tau\,|\,/\tau_c) \tag{A10}$$

where τ_c is the correlation time. The Fourier transform of the reduced correlation function becomes

$$j(\omega)=\frac{2\tau_c}{1+\omega^2\tau_c^2}\ ,$$

leading to the final expression for the rate:

$$R=(2.045\times10^{12})\left[\frac{R_0}{R}\right]^8\left[\frac{2\tau_c}{1+\omega^2\tau_c^2}\right]\ . \tag{A11}$$

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