PHYSICAL REVIEW B VOLUME 8, NUMBER 1 1 JULY 1973

Para- to Ortho-Hydrogen Conversion on Magnetic Surfaces

K. G. Petzinger*† and D. J. Scalapino*
Department of Physics, University of California, Santa Barbara, California 93106
(Received 26 January 1973)

We have calculated the rate of para- to ortho-hydrogen conversion when the transition occurs in a physically-adsorbed-gas surface layer above a magnetic substrate. The conversion rates for surfaces with dilute, random, paramagnetic surface sites and for surfaces with a regular lattice of magnetic sites are considered separately. Absolute rates in terms of physical parameters are obtained for a variety of different physical situations.

I. INTRODUCTION

The first calculation for the rate of catalysis of the transition between para- and ortho-states of molecular hydrogen was carried out by Wigner[1] in 1933. In Wigner's theory the catalytic agents were taken to be paramagnetic atoms or molecules introduced into otherwise pure gaseous hydrogen. He showed that the inhomogeneous magnetic-dipole field of an impurity could couple to the proton magnetic moments of the H_2 molecule in such a way as to cause transitions between the para- and ortho-states. Many authors have applied Wigner's calculation with modification to the case of catalysis in the presence of a paramagnetic surface in contact with gaseous H_2.[2,3] However, until the recent work of Ilisca and Legrand[4] there existed no general theoretical treatment of heterogeneous conversion. Our work is similar in approach to that of Ref. 4, but differs in specifics. Ilisca and Legrand considered a model in which the H_2 molecules diffuse and rotate in the plane of the surface. Their integration technique and approximations lead to rather complicated expressions for the correlation functions, and they do not give an expression for the absolute rate. We have treated a model in which the spins rotate freely in three dimensions[5] and considered a variety of translational modes and substrates. Our integration and approximation procedures differ in such a way that we obtain relatively simple absolute expressions for the rates in several different physical situations.

Because of the complicated nature of the surfaces on which many experiments have been done, it has not been possible to treat each in detail. Rather we have sought to identify the dominant physical processes responsible for the conversion and to parametrize them in a way amenable to calculation.

In Sec. II we begin by examining the manner in which a static inhomogeneous magnetic field is able to cause transitions between singlet and triplet states of two nonrotating protons. Following this we introduce the dynamics appropriate to the conversion process for molecules physiadsorbed on a magnetic substrate. The formalism of first-order time-dependent perturbation theory is employed to directly calculate the transition rate in terms of molecular spin and rotation matrix elements and correlations involving substrate spins and molecular motion on the surface. Group-theoretical matrix-element theorems are employed to derive selection rules governing the transition.

In Sec. III we consider some specific cases of the general formalism developed in Sec. II. First we calculate the transition rate in the case that the surface contains a dilute random array of paramagnetic centers. The three cases treated specifically correspond to molecular motion appropriate to (i) a two-dimensional Maxwell–Boltzmann gas, (ii) diffusion parallel to the surface, and (iii) motion simply on and off the surface.

Second, we examine the conversion rate over a dense regular lattice of spins. If the exchange coupling is comparable to the rotational energy differences, the dynamics of the spins influences the conversion rate. In addition, spatial correlations of the spins can affect the rate. We illustrate the effect of changes in the spatial spin correlations by calculating the temperature dependence of the conversion rate near a ferromagnetic or antiferromagnetic critical point of the substrate. Fairly general arguments are given for the prediction that the temperature derivative of the rate should scale as the surface magnetic specific heat.

In Sec. IV we discuss and summarize the major conclusions which precede.

II. GENERAL FORMULATION

Before calculating the para-ortho ($p \leftrightarrow o$) transition rate in detail, it is worthwhile to discuss the underlying physics of the transition and to identify the physical mechanism of conversion.

If we ignore high-energy vibrational states, the nuclear wave function of a hydrogen molecule consists of two parts, for the spin and rotation, respectively. Taking the z axis as the axis of quantization, there are four spinors corresponding to one singlet state and three triplet states:

$$\chi_s = (1/\sqrt{2})\,|\uparrow\downarrow - \uparrow\downarrow\rangle\ , \quad I=0 \tag{1}$$

$$\chi_t^{(1)} = |\uparrow\uparrow\rangle,\quad \chi_t^{(0)} = (1/\sqrt{2})|\uparrow\downarrow + \uparrow\downarrow\rangle,\quad \chi_t^{(-1)} = |\downarrow\downarrow\rangle\ ,\quad I = 1\ .$$

Note that these are coherent states of protons physically separated by the internuclear distance $b = 0.74$ Å. The relative phase of the two components of the singlet state is important. This state is clearly antisymmetric under interchange of the two protons, and hence the Pauli principle requires the rotational wave function to be symmetric. The rotational quantum number l must be even. Similarly the triplet spin states are symmetric under interchange, and are associated with odd-l values. Molecules in even-l states are known as para- and those in odd-l states as ortho-.

For three-dimensional free rotation, the Hamiltonian for the molecule is simply

$$\begin{aligned} \mathcal{H}_{\text{Rot}} &= BL^2 = Bl(l+1), \\ B &\sim 86\ {}^\circ\text{K} \sim 1.13\times 10^{13}\ \text{rad/sec}. \end{aligned} \tag{2}$$

Hence the spin symmetry leads to a large energy splitting of the para- and ortho-states. To cause a transition this energy must be either supplied or absorbed by a perturbation. As we shall later find, for conversion which proceeds through paramagnetic surface ions, the dominant source or sinks of energy are twofold: (i) the kinetic energy of the molecule, and (ii) the energy of the surface electronic spin system.

The perturbation which causes the p ⟷ o transition is the time-dependent inhomogeneous magnetic field near a paramagnetic surface. Some insight into the conversion process may be had if we first consider the simpler problem of finding the evolution in time of a singlet state of two protons exposed to a static inhomogeneous magnetic field. We locate the two protons at positions $\vec{r}_1$ and $\vec{r}_2$ in the presence of magnetic fields $\vec{H}_1$ and $\vec{H}_2$, respectively. The Hamiltonian of the system is

$$\mathcal{H} = -\vec{\mu}_1\cdot\vec{H}_1 - \vec{\mu}_2\cdot\vec{H}_2 \tag{3}$$

and the singlet state evolves according to

$$\chi_s(t) = e^{-i\mathcal{H}t}\chi_s(0). \tag{4}$$

By a power-series expansion of the exponential in Eq. (4) and using the special properties of the Pauli matrices we have

$$e^{-i\mathcal{H}t} = \left(\cos\omega_1 t + i\,\sin\omega_1 t\,\frac{\vec{\sigma}_1\cdot\vec{H}_1}{|\vec{H}_1|}\right) \times\left(\cos\omega_2 t + i\sin\omega_2 t\,\frac{\vec{\sigma}_2\cdot\vec{H}_2}{|\vec{H}_2|}\right), \tag{5}$$

where ω_i is the precession frequency of the ith proton in its local field. To simplify Eq. (5) we use the fact that $e^{-i\mathcal{H}t}$ will act on a singlet state, and hence

$$(\vec{\sigma}_1 + \vec{\sigma}_2)\,\chi_s = 0\ . \tag{6}$$

Thus replacing $\vec{\sigma}_2$ by $-\vec{\sigma}_1$ and further noting that $(\vec{\sigma}_1\cdot\vec{H}_1)(\vec{\sigma}_1\cdot\vec{H}_2) = \vec{H}_1\cdot\vec{H}_2 + i\vec{\sigma}_1\cdot(\vec{H}_1\times\vec{H}_2)$ we have

$$\begin{aligned} e^{-i\mathcal{H}t}\chi_s = \Bigg(&\cos\omega_1 t\cos\omega_2 t + \sin\omega_1 t\sin\omega_2 t\cos\gamma + i\sin\omega_1 t\cos\omega_2 t\,\frac{(\vec{\sigma}_1\cdot\vec{H}_1)}{|\vec{H}_1|} \\ &- i\sin\omega_2 t\cos\omega_1 t\,\frac{(\vec{\sigma}_1\cdot\vec{H}_2)}{|\vec{H}_2|} + i\sin\omega_1 t\sin\omega_2 t\,\frac{\vec{\sigma}_1\cdot(\vec{H}_1\times\vec{H}_2)}{|\vec{H}_1|\,|\vec{H}_2|}\Bigg)\chi_s, \end{aligned} \tag{7}$$

where γ is the angle between the fields $\vec{H}_1$ and $\vec{H}_2$. Since $\vec{\sigma}_1\chi_s$ always produces one of the three triplet states, the amplitude of the singlet state is just the sum of the first two terms of Eq. (7). The probability at time t of still being in the singlet state is this amplitude squared, and hence the probability of conversion into any of the three triplet states is

$$\begin{aligned} P_t(t) &= 1 - [\cos\omega_1 t\cos\omega_2 t + \sin\omega_1 t\sin\omega_2 t\cos\gamma]^2 \\ &= \sin^2(\omega_1-\omega_2)t + \sin^2\tfrac{1}{2}\gamma\sin 2\omega_1 t\sin 2\omega_2 t \\ &\quad + \sin^2\gamma\sin^2\omega_1 t\sin^2\omega_2 t\ . \end{aligned} \tag{8}$$

From this it is clear that the p ⟷ o conversion will depend on differences in the precession of the two protons in an inhomogeneous magnetic field.

The general expression (8) contains two effects which can be analyzed separately by looking at two limiting cases.

Case 1. The magnitudes of the fields $\vec{H}_1$ and $\vec{H}_2$ are different, but they point in the same direction ($\gamma = 0$). Then,

$$P(t) = \sin^2(\omega_1-\omega_2)t\ . \tag{9}$$

Case 2. The fields $\vec{H}_1$ and $\vec{H}_2$ have the same magnitude ($\omega_1 = \omega_2 = \omega$), but they point in different directions:

$$P_t(t) = \sin^2 2\omega t\sin^2\tfrac{1}{2}\gamma + \sin^4\omega t\sin^2\gamma. \tag{10}$$

In the first case the differing *rates* of precession about the same axis dephase the singlet state. In the second case, although the rates of precession are identical, the *axes* of precession are inclined to one another, which results in similar dephasing. The general case contains both of these effects. Note that a constant static field leads to no transitions at all because the two nuclear spins precess at exactly the same rate around the same axis.

Physical processes equivalent to the above, are responsible for p ⟶ o conversion near surfaces containing paramagnetic ions as the source of the inhomogeneous field. The oscillatory time dependence in Eq. (8) is a consequence of ignoring the dynamic processes required to supply or absorb the large energy of the transition for a real molecule. This will be modified when such processes are introduced as we now proceed to do.

For a real physical system it is not possible to find the explicit time dependence of the para- and ortho-states of molecules physiadsorbed at the gas-solid interface. Neither is it desirable since experiments are designed not to measure such details, but rather the rate at which a nonequilibrium ratio of para- and ortho-molecules relaxes back to the appropriate equilibrium concentration. The formalism most suited to our purpose is a direct calculation of this rate constant through time-dependent perturbation theory.

The zero-order Hamiltonian of the system consists of two commuting terms for the H_2 molecule and electronic spin system, respectively:

$$\mathcal{H}_0 = \mathcal{H}_{\mathrm{mol}} + \mathcal{H}_{\mathrm{spin}} \quad . \tag{11}$$

The molecular Hamiltonian we take to have three parts involving rotation, translation, and binding to the surface:

$$\mathcal{H}_{\mathrm{mol}} = BL^2 + P^2/2M + V(R) \; . \tag{12}$$

In addition to binding the molecule to the surface, $V(R)$ influences the rotational motion and movement along the surface as well.[6] $\mathcal{H}_{\mathrm{spin}}$ includes terms for exchange coupling between the local moments and surface anisotropy. Additional stochastic forces due, for example, to the interactions of either spins or molecules with lattice vibrations are also present. These will be treated in a somewhat *ad hoc* fashion since it is not fruitful to enlarge $\mathcal{H}_0$ to include phonons and their interactions. The approximations used to treat such effects will be detailed later.

The para-ortho transitions proceed through the time-dependent inhomogeneous magnetic fields of the electronic spins. We locate these spins at lattice sites $\vec{R}_j$ and write

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\mathrm{int}} \; , \tag{13}$$

where

$$\mathcal{H}_{\mathrm{int}} = -\mu_p [\vec{I}_1 \cdot \vec{H}(\vec{r}_1) + \vec{I}_2 \cdot \vec{H}(\vec{r}_2)] \; . \tag{14}$$

The coordinates $\vec{r}_1$ and $\vec{r}_2$ are those of the two protons in the molecule, μ_p is the proton magnetic moment, and $\vec{H}(\vec{r})$ is the dipole field due to the electronic spins:

$$\begin{aligned}\vec{H}(r) = \sum_j \frac{\mu_S}{|\vec{R}_j - \vec{r}|^5} \{ \vec{S}_j \, |\vec{R}_j - \vec{r}|^2 \\ - 3(\vec{R}_j - \vec{r})[\vec{S}_j \cdot (\vec{R}_j - \vec{r})] \} \; .\end{aligned} \tag{15}$$

Here μ_S is equal to the effective-spin g value times the Bohr magneton.

To simplify later calculation, it is desirable to separate $\mathcal{H}_{\mathrm{int}}$ into two parts:

$$\begin{aligned}\mathcal{H}_{\mathrm{int}} = -\tfrac{1}{2} \mu_p \{ (\vec{I}_1 + \vec{I}_2) \cdot [\vec{H}(\vec{r}_1) + \vec{H}(\vec{r}_2)] \\ + (\vec{I}_1 - \vec{I}_2) \cdot [\vec{H}(\vec{r}_1) - \vec{H}(\vec{r}_2)] \} \; .\end{aligned} \tag{16}$$

The first term has no matrix elements between ortho- and para-states since it is a function of the total nuclear spin $\vec{I} = \vec{I}_1 + \vec{I}_2$. The second term has matrix elements only between ortho- and para-states, so we may restrict our consideration to it in calculating the transition rate.

As noted earlier, it is only the spatial inhomogeneity of $\vec{H}(\vec{r})$ which leads to conversion, so that it is useful to expand $\vec{H}(\vec{r}_1) - \vec{H}(\vec{r}_2)$ in a Taylor series about the molecular center of mass $\vec{r}$. Defining $\vec{b} \equiv \vec{r}_1 - \vec{r}_2$ as the vector distance between the two protons we have

$$\begin{aligned}\vec{H}(\vec{r}_1) - \vec{H}(\vec{r}_2) = \vec{b} \cdot \vec{\nabla} \vec{H}(\vec{r}) \\ + \frac{2}{3!} \left(\frac{\vec{b}}{2} \right) \left(\frac{\vec{b}}{2} \right) \left(\frac{\vec{b}}{2} \right) : \vec{\nabla} \vec{\nabla} \vec{\nabla} \vec{H}(\vec{r}) + \cdots \; .\end{aligned} \tag{17}$$

The expansion parameter above is roughly $(b/2R)^2$ where R is some average distance from molecule to local spin. Thus successive approximations converge quite rapidly. In practice we will keep only the leading term, but it is useful to note some group-theoretical properties of the full expansion before dropping the others.

Equation (17) is an expansion of the dipole field in terms of contracted spherical tensors of rank $\omega = 2, 4, 6, \ldots$. To illustrate, consider the dominant first term $(\vec{\nabla} \vec{H})_{ij} = \partial H_i / \partial x_j$ is the second-rank Cartesian tensor which may be written as the direct sum of scalar, spherical-vector, and spherical-second-rank-tensor components. However, both the scalar and vector components vanish since $\vec{\nabla} \cdot \vec{H} = 0$ and $\vec{\nabla} \times \vec{H} = 0$. Thus $\vec{\nabla} \vec{H}$ is a pure second-rank spherical tensor. Defining $D^{\pm} = \partial / \partial x \pm i \partial / \partial y$, $D^z = \partial / \partial z$, and $H^{\pm} = H_x \pm i H_y$, the five components are

$$\begin{aligned}
T_2^{(2)}(\vec{H}) &= \tfrac{1}{2} D^+ H^+ \; , \\
T_1^{(2)}(\vec{H}) &= -\tfrac{1}{2} (D^+ H^z + D^z H^+) \quad , \\
T_0^{(2)}(\vec{H}) &= \sqrt{\tfrac{2}{3}} \left(D^z H^z - \tfrac{1}{4} D^+ H^- - \tfrac{1}{4} D^- H^+ \right) \quad , \\
T_{-1}^{(2)}(\vec{H}) &= \tfrac{1}{2} (D^- H^z + D^z H^-) \quad , \\
T_{-2}^{(2)}(\vec{H}) &= \tfrac{1}{2} D^- H^- \quad .
\end{aligned} \tag{18}$$

Similarly, it is easily shown that the vanishing curl and divergence of $\vec{H}$ imply that the fourth-rank Cartesian tensor $\vec{\nabla} \vec{\nabla} \vec{\nabla} \vec{H}$ has only nine nonvanishing linearly independent components which transform under rotation as a pure fourth-rank spherical tensor. Analogous reasoning on higher-order terms leads to the identification of pure sixth-, eighth-, etc., rank spherical tensors.

The (scalar) interaction Hamiltonian may then be expanded as

$$\mathcal{H}_{\text{int}} = -\frac{\mu_p}{2}\Big[(\vec{\mathrm{I}}_1 - \vec{\mathrm{I}}_2)\vec{\mathrm{b}} : \vec{\nabla}\vec{\mathrm{H}} + \frac{1}{4!}(\vec{\mathrm{I}}_1 - \vec{\mathrm{I}}_2)\vec{\mathrm{b}}\vec{\mathrm{b}}\vec{\mathrm{b}} \vdots \vec{\nabla}\vec{\nabla}\vec{\nabla}\vec{\mathrm{H}} + \cdots\Big] . \quad (19)$$

The significance of Eq. (19) is twofold. First, it isolates (to the left of the contraction sign) the portions of the interaction referring to molecular spin and rotation states; and (to the right of the contraction sign) the portions of the interaction pertaining to the electronic spin system. This greatly simplifies the calculation of matrix elements of the former. Second, even though the tensors $(\vec{\mathrm{I}}_1 - \vec{\mathrm{I}}_2)\vec{\mathrm{b}}$ and $(\vec{\mathrm{I}}_1 - \vec{\mathrm{I}}_2)\vec{\mathrm{b}}\vec{\mathrm{b}}\vec{\mathrm{b}}$, for example, have components which transform as scalars, vectors, etc., only the second-rank-spherical-tensor components, in the first case, and the fourth-rank-spherical-tensor components, in the second case, are contracted with nonvanishing tensors of the electronic-spin system. This fact enables us to develop group-theoretical selection rules for the transitions caused by successive terms in the expansion.

If we consider molecular eigenstates of total angular momentum $\vec{\mathrm{J}} = \vec{\mathrm{L}} + \vec{\mathrm{I}}$, we can apply the Wigner-Eckart theorem to identify the possible transitions caused by each succeeding term of the expansion. The resulting selection rules are sketched in Fig. 1 for the lowest few J values and for the lowest rank tensors. Thus, independent of any approximation made by dropping higher-order terms in Eq. (19), the total transition rate between $l = 0$ and $l = 1$ states may be found by keeping only the first term of the expansion. To calculate the rate between $l = 2$ and $l = 1$ states we need only the first two terms of the expansion, etc.

As our first approximation to the full interaction we drop all but the leading term of Eq. (19). We form the second-rank spherical tensor $\vec{\mathrm{b}}(\vec{\mathrm{I}}_1 - \vec{\mathrm{I}}_2)$ with components

$$\begin{aligned}
T_2^{(2)}(\vec{\mathrm{b}}\,\vec{\mathrm{I}}) &= \tfrac{1}{2} b^+ I^+ ,\\
T_1^{(2)}(\vec{\mathrm{b}}\,\vec{\mathrm{I}}) &= -\tfrac{1}{2}(b^+ I^z + I^+ b^z) ,\\
T_0^{(2)}(\vec{\mathrm{b}}\,\vec{\mathrm{I}}) &= \sqrt{\tfrac{2}{3}}(b^z I^z - \tfrac{1}{4} b^+ I^- - \tfrac{1}{4} b^- I^+) , \qquad (20)\\
T_{-1}^{(2)}(\vec{\mathrm{b}}\,\vec{\mathrm{I}}) &= \tfrac{1}{2}(b^- I^z + b^z I^-) ,\\
T_{-2}^{(2)}(\vec{\mathrm{b}}\,\vec{\mathrm{I}}) &= \tfrac{1}{2} b^- I^- ,
\end{aligned}$$

where $b^{\pm} \equiv b_x \pm i b_y$ and $\vec{\mathrm{I}} \equiv \vec{\mathrm{I}}_1 - \vec{\mathrm{I}}_2$. The truncated interaction Hamiltonian then becomes

$$\mathcal{H}_{\text{int}} \approx -\tfrac{1}{2}\mu_p \sum_{\mu=-2}^{+2} (-1)^{\mu}\, T_{\mu}^{(2)}(\vec{\mathrm{b}}\,\vec{\mathrm{I}})\, T_{-\mu}^{(2)}(\vec{\mathrm{H}}) . \quad (21)$$

Apart from statistical factors appropriate to the molecule, the standard Golden Rule expression for the para-to-ortho conversion rate is

$$\lambda = \frac{2\pi}{\hbar}\frac{1}{Z}\sum_{k,n,n'} e^{-\beta E_n} \left| \langle p, n | \mathcal{H}_{\text{int}} | O_k n' \rangle \right|^2 \delta(E_i - E_f) . \quad (22)$$

By n and n' we denote states of molecular translation and electronic spin, while p and O_k refer only to molecular spin and rotation states. E_i and E_f are the initial and final energies of the entire system, E_n is the energy of state n, and $Z = \sum_n e^{-\beta E_n}$. Because of the complexity of $\mathcal{H}_{\text{int}}$ it is more convenient to express Eq. (22) in terms of time-dependent correlation functions. Writing

$$\begin{aligned}
\delta(E_i - E_f) &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} e^{i(E_i - E_f)t/\hbar}\, dt\\
&= \frac{1}{2\pi\hbar}\int_0^{\infty} dt\, e^{i(E_i - E_f)t/\hbar} + \text{c.c.} , \qquad (23)
\end{aligned}$$

we have, in the usual way,

$$\lambda = \frac{\hbar^{-2}}{Z}\sum_{k,n,n'} e^{-\beta E_n}\int_0^{\infty} \langle p, n | e^{i\mathcal{H}_0 t/\hbar}\mathcal{H}_{\text{int}}\, e^{-i\mathcal{H}_0 t/\hbar} | O_k n' \rangle \times \langle O_k n' | \mathcal{H}_{\text{int}} | p, n \rangle\, dt + \text{c.c.} \quad (24)$$

The intermediate states in Eq. (24) are product states involving nuclear spin and rotation, molecular translation, and electronic spin. Extracting the time dependence due to $\mathcal{H}_{\text{rot}}$, using the fact that a complete set of molecular translation states and electronic spin states is represented by $|n'\rangle\langle n'|$, and using the explicit form of $\mathcal{H}_{\text{int}}$, we have

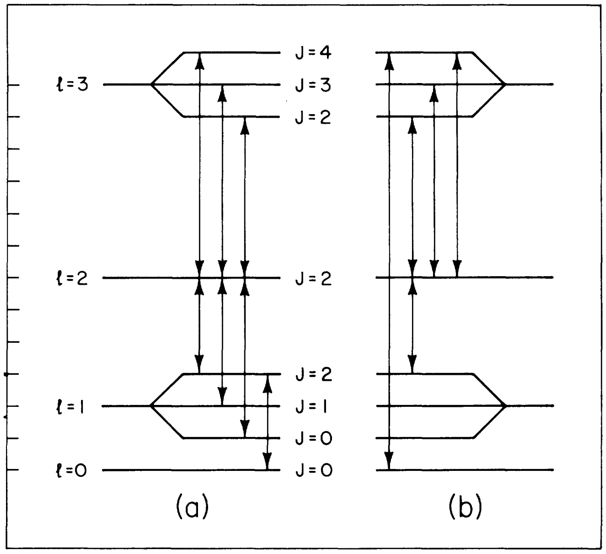

FIG. 1. Allowed para-ortho transitions due to successive terms in the expansion of the interaction, Eq. (19). (a) Rank $\omega = 2$ tensor, (b) rank $\omega = 4$ tensor. The energy splittings for different J values have been exaggerated for clarity.

$$\lambda=\left(\frac{\mu_p}{2\hbar}\right)^2\int_0^\infty dt\,e^{i\omega_{op}t}\sum_k\sum_{\mu=-2}^{+2}\left|\langle p|\,T_\mu^{(2)}(\vec{\mathrm{b}}\,\vec{\mathrm{I}})|O_k\rangle\right|^2$$

$$\times\langle T_\mu^{(2)*}(\vec{\mathrm{H}},t)T_\mu^{(2)}(\vec{\mathrm{H}},0)\rangle+\mathrm{c.c.}\qquad(25)$$

Further simplification of Eq. (25) is impossible without specific assumptions regarding the para- and ortho-molecular states. Because of the potential $V(R)$ the adsorbed molecules are perturbed from the eigenstates of a free rotor appropriate to the gas phase. The extent and nature of this perturbation depend upon the details of surface geometry.[6] Here, in calculating matrix elements we will approximate the rotational eigenstates by their free-rotation forms but treat the rotational energy differences $\hbar\omega_{op}$ as parameters which may vary from their free-space values.[6]

The molecular spin and rotation matrix elements can be evaluated in straightforward fashion. As illustrative, consider the $l=0\rightarrow l'=1$ transition. Then,

$$\sum_k\left|\langle p|\,T_\mu^{(2)}(\vec{\mathrm{b}}\vec{\mathrm{I}})|O_k\rangle\right|^2$$

$$=(-1)^\mu\langle p|T_\mu^{(2)}(\vec{\mathrm{b}}\,\vec{\mathrm{I}})T_{-\mu}^{(2)}(\vec{\mathrm{b}}\,\vec{\mathrm{I}})|p\rangle\,,\qquad(26)$$

since the set of $l'=1$ ortho-states is a complete set in so far as matrix elements of $T_\mu^{(2)}(\vec{\mathrm{b}}\,\vec{\mathrm{I}})$ are concerned. Only the scalar portion contributes and this is independent of μ:

$$(-1)^\mu T_\mu^{(2)}(\vec{\mathrm{b}}\,\vec{\mathrm{I}})T_{-\mu}^{(2)}(\vec{\mathrm{b}}\vec{\mathrm{I}})=\tfrac{1}{9}\,b^2(I_1^2+I_2^2-2\vec{\mathrm{I}}_1\cdot\vec{\mathrm{I}}_2)$$

$$=\tfrac{1}{9}\,b^2(\tfrac{3}{2}-2\vec{\mathrm{I}}_1\cdot\vec{\mathrm{I}}_2)\,.\qquad(27)$$

In the para-state $\vec{\mathrm{I}}_1\cdot\vec{\mathrm{I}}_2=-\frac{3}{4}$, and hence

$$\sum_k\left|\langle l=0|T_\mu^{(2)}(\vec{\mathrm{b}}\,\vec{\mathrm{I}})|O_k\rangle\right|^2=\tfrac{1}{3}b^2\,.\qquad(28)$$

For other sums of matrix elements the same method can be used because of the $\Delta l=\pm1$ selection rule. It is then straightforward to derive the general expression

$$\sum_{m_l,m_{l'},m_{I'}}\left|\langle lm_l|T_\mu^{(2)}(\vec{\mathrm{b}}\,\vec{\mathrm{I}})|l'm_{l'},m_{I'}\rangle\right|^2\equiv k_{ll'}b^2\,,\qquad(29)$$

where $k_{ll'}=\frac{1}{6}(l+l'+1)$.

The final factor entering the transition rate is the correlation function $\langle T_\mu^{(2)*}(\vec{\mathrm{H}},t)\,T_\mu^{(2)}(\vec{\mathrm{H}},0)\rangle$. The field $\vec{\mathrm{H}}$ and its gradients which appear in the above tensor operators is that due to all electronic spins both on or below the surface. However, the magnitude of the contribution from a spin a distance R away from the molecule falls off as R^{-4}. Further, in the correlation function above, this factor is squared, so that the range of the interaction is actually quite short. We thus approximate that the dominant portion of the transition rate is due only to the first surface layer of paramagnetic ions, and neglect the contribution of ions deeper in the bulk.

The explicit tensor operators are

$$T_2^{(2)}(\vec{\mathrm{H}})=\sum_j\frac{\mu_S}{2}\left(\frac{-6a^+S_j^+}{a^5}+\frac{15(\vec{\mathrm{S}}_j\cdot\vec{a})(a^+)^2}{a^7}\right),$$

$$T_{-2}^{(2)}(\vec{\mathrm{H}})=T_2^{(2)*}(\vec{\mathrm{H}}),$$

$$T_1^{(2)}(\vec{\mathrm{H}})=\sum_j 3\mu_S\left(\frac{a^+S_j^z+S_j^+a^z}{a^5}-\frac{5a^+a^z(\vec{\mathrm{S}}_j\cdot\vec{\mathrm{a}})}{a^7}\right),\qquad(30)$$

$$T_{-1}^{(2)}(\vec{\mathrm{H}})=-T_1^{(2)*}(\vec{\mathrm{H}}),$$

$$T_0^{(2)}(\vec{\mathrm{H}})=-\sum_j\mu_S\sqrt{\tfrac{3}{2}}\left[\frac{6a^zS_j^z}{a^5}+\frac{3(\vec{\mathrm{S}}_j\cdot\vec{\mathrm{a}})}{a^5}\left(1-\frac{5(a^z)^2}{a^2}\right)\right],$$

where $\vec{\mathrm{a}}\equiv\vec{\mathrm{R}}_j-\vec{\mathrm{r}}$ is the vector distance between the jth surface spin and the molecule. It becomes convenient to introduce a two-dimensional Fourier transform in Eq. (30). This is easily accomplished by the replacement

$$\sum_j T_\mu^{(2)}(\vec{\mathrm{S}}_j,\vec{\mathrm{R}}_j-\vec{\mathrm{r}})\rightarrow\sum_{j,\vec{\mathrm{a}}}T_\mu^{(2)}(S_j,\vec{\mathrm{a}})\,\delta_{R_j-\vec{\mathrm{r}}-\vec{\mathrm{a}}}$$

$$=\frac{1}{N}\sum_{\vec{\mathrm{q}}}\sum_{\vec{\mathrm{a}},j}e^{i\vec{\mathrm{q}}\cdot(\vec{\mathrm{R}}_j-\vec{\mathrm{r}}-\vec{\mathrm{a}})}T_\mu^{(2)}(\vec{\mathrm{S}}_j,\vec{\mathrm{a}})\,,\qquad(31)$$

where the functions $T_\mu^{(2)}(\vec{\mathrm{S}}_j,\vec{\mathrm{R}}_j-\vec{\mathrm{r}})$ are given by Eqs. (30). N is the number of equivalent lattice sites on the surface, and is not necessarily equal to the number of paramagnetic sites. The set of vectors $\vec{\mathrm{a}}=(a_x,a_y,z)$ defines the distances from molecule to local spin within which the dipole interaction is considered effective.

Since each tensor operator in Eqs. (30) is linear in the spin operators we may write

$$T_\mu^{(2)}(\vec{\mathrm{S}}_j,\vec{\mathrm{a}})\equiv\vec{\mathrm{S}}_j\cdot\vec{\beta}_\mu(\vec{\mathrm{a}})\,,\qquad(32)$$

where the $\vec{\beta}_\mu(\vec{\mathrm{a}})$ are spatial form factors for the dipole interaction. Inserting this definition into Eq. (31) we have

$$\sum_j T_\mu^{(2)}(\vec{\mathrm{S}}_j,\vec{\mathrm{R}}_j-\vec{\mathrm{r}})=\frac{1}{N}\sum_{\vec{\mathrm{q}}}\sum_{\vec{\mathrm{a}},j}e^{i\vec{\mathrm{q}}\cdot(\vec{\mathrm{R}}_j-\vec{\mathrm{r}}-\vec{\mathrm{a}})}\vec{\mathrm{S}}_j\cdot\vec{\beta}_\mu(\vec{\mathrm{a}})$$

$$=\sum_{\vec{\mathrm{q}}}e^{-i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}}[\vec{\mathrm{S}}_{\vec{\mathrm{q}}}\cdot\vec{\beta}_\mu(\vec{\mathrm{q}})]\,,\qquad(33)$$

where

$$\vec{\mathrm{S}}_{\vec{\mathrm{q}}}\equiv(1/N)\sum_j e^{i\vec{\mathrm{q}}\cdot\vec{\mathrm{R}}_j}\vec{\mathrm{S}}_j\,,$$

$$\vec{\beta}_\mu(\vec{\mathrm{q}})\equiv\sum_{\vec{\mathrm{a}}}\vec{\beta}_\mu(\vec{\mathrm{a}})\,e^{-i\vec{\mathrm{q}}\cdot\vec{\mathrm{a}}}\,.\qquad(34)$$

Thus the time-dependent correlation function becomes

$$\langle T_\mu^{(2)*}(\vec{\mathrm{H}},t)T_\mu^{(2)}(\vec{\mathrm{H}},0)\rangle$$

$$=\sum_{\vec{\mathrm{q}},\vec{\mathrm{q}}'}\langle e^{-i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}(t)}e^{i\vec{\mathrm{q}}'\cdot\vec{\mathrm{r}}(0)}\rangle$$

$$\times\langle[\vec{\mathrm{S}}_{\vec{\mathrm{q}}}(t)\cdot\vec{\beta}_\mu(\vec{\mathrm{q}})]^*\vec{\mathrm{S}}_{\vec{\mathrm{q}}'}(0)\cdot\vec{\beta}_\mu(\vec{\mathrm{q}}')\rangle$$

$$= \sum_{\vec{q}} \langle e^{-i\vec{q}\cdot[\vec{r}(t)-\vec{r}(0)]}\rangle \langle [\vec{S}_{\vec{q}}(t)\cdot\vec{\beta}_\mu(\vec{q})]^* \vec{S}_{\vec{q}}(0)\cdot\vec{\beta}_\mu(\vec{q})\rangle \ . \tag{35}$$

In writing Eq. (35) we have adopted a random-phase approximation, so that

$$\langle e^{-i\vec{q}\cdot\vec{r}(t)} e^{i\vec{q}'\cdot\vec{r}(0)}\rangle = \delta_{\vec{q}\vec{q}'} \langle e^{-\vec{q}\cdot[\vec{r}(t)-\vec{r}(0)]}\rangle$$

and

$$\langle S^*_{\vec{q}} S_{\vec{q}'}\rangle = \delta_{\vec{q}\vec{q}'} \langle S^*_{\vec{q}} S_{\vec{q}}\rangle \ .$$

This is rigorously true for a homogeneous surface, but is otherwise true only in an average sense.

The two factors of Eq. (35) are, respectively, correlation functions involving the translational motion of the molecule and the dynamics of the electronic spin system. In the latter the form factors guarantee that only correlations involving the same spin component survive:

$$\langle [\vec{S}_{\vec{q}}(t)\cdot\vec{\beta}_\mu(\vec{q})]^* \vec{S}_{\vec{q}}(0)\cdot\vec{\beta}_\mu(\vec{q})\rangle = \sum_i \langle S^i_{-\vec{q}}(t) S^i_{\vec{q}}(0)\rangle \,|\beta^i_\mu(\vec{q})|^2 \ , \tag{36}$$

where $i = x, y, z$. Our expression for the transition rate between the para-state with orbital angular momentum l and the ortho-states with orbital angular momentum l' is finally

$$\lambda_{ll'} = k_{ll'}(\mu_p b/2\hbar)^2 \int_0^\infty dt \sum_{\vec{q}} \langle e^{-i\vec{q}\cdot[\vec{r}(t)-\vec{r}(0)]}\rangle \times \sum_i \langle S^i_{-\vec{q}}(t) S^i_{\vec{q}}(0)\rangle \sum_\mu |\beta^i_\mu(\vec{q})|^2 e^{i\omega_{l'l}t} + \text{c.c.} \tag{37}$$

Here ω_{op} has been replaced by the difference in energy between the l' and l orbital states which we denote by $\omega_{l'l}$. Equation (37) is the central result of this section. Before applying it in detail we pause to identify the possible forms of the time-dependent correlation functions.

Consider the correlation function involving molecular position. There are two appropriate limits. If the molecule moves over the surface essentially as in a two-dimensional gas, $\vec{r}(t) = \vec{r}(0) + \vec{v}t$, where $\vec{v}$ is a thermal velocity of motion parallel to the surface. Averaging the spatial correlation function over a two-dimensional Maxwellian velocity distribution we find the simple result

$$\langle e^{-i\vec{q}\cdot[\vec{r}(t)-\vec{r}(0)]}\rangle = e^{-q^2\bar{v}^2t^2} \ , \tag{38}$$

where $\bar{v}$ is the rms thermal velocity $(2kT/M)^{1/2}$.

On the other hand, if the molecule is found preferentially at certain surface sites, random phonon collisions can cause it to execute a kind of random walk from site to site across the surface. The exponential can be expanded, and for a Gaussian random process the higher moments $\langle[\vec{r}(t)-\vec{r}(0)]^n\rangle$ can be related to the second moment $\langle[\vec{r}(t)-\vec{r}(0)]^2\rangle$. Resumming the series we have

$$\langle e^{-i\vec{q}\cdot[\vec{r}(t)-\vec{r}(0)]}\rangle = e^{-Dq^2t} \ , \tag{39}$$

where D is the diffusion constant. One additional factor which can enter is the surface lifetime. In that case the molecule executes a "lossy random walk" with an additional probability that stochastic forces will eject it from the surface into the surrounding gas. Calling this lifetime τ we have

$$\langle e^{-i\vec{q}\cdot[\vec{r}(t)-\vec{r}(0)]}\rangle = e^{-t/\tau} e^{-Dq^2t} \ . \tag{40}$$

A similar correction can be applied to Eq. (38).

The spin-spin correlation is discussed most readily in limits appropriate to (i) a dilute random array of uncoupled moments and (ii) a regular array of exchange coupled moments. In the former case the spin dynamics is governed by the spin-lattice relaxation time T_1:

$$\langle S^i_{-\vec{q}}(t) S^i_{\vec{q}}(0)\rangle = (N_s/N^2)\tfrac{1}{3}S(S+1)e^{-t/T_1} \ , \tag{41}$$

where N_s is the number of spins. In the latter case the possibility of spin waves exists, and these can produce a kind of resonant transition probability.[7] This arises when $\langle S_{-\vec{q}}(t)S_{\vec{q}}(0)\rangle \approx e^{-i\omega(q)t}\langle S_{-\vec{q}}S_{\vec{q}}\rangle$, where $\omega(q)$ is a spin-wave energy $\approx \omega_{ll'}$.

In any case Eq. (37) makes clear that there exist two means to supply the necessary energy for the conversion—the translational motion across the surface or away from it, and the dynamics of the spin system. Which of these is more important depends on the particular temperature and the substrate under consideration.

III. APPLICATION

With this formalism, we proceed to calculate the conversion rate appropriate to the two cases of a dilute number of paramagnetic spins and of a dense regular lattice of exchange coupled spins.

A. Dilute Concentration of Paramagnetic Centers

Here we consider a surface in the x-y plane containing N_s paramagnetic impurities sufficiently diluted so that each impurity separately affects molecules in its vicinity. Then the spin correlation function is given by Eq. (41) and the rate of conversion from Eq. (37) is

$$\lambda_{ll'} = k_{ll'} \frac{N_s}{N}\left(\frac{\mu_p b}{2\hbar}\right)^2 \frac{1}{3}S(S+1)\int_0^\infty dt\, e^{i\omega_{l'l}t} e^{-t/T_1} \times \frac{1}{N}\sum_{\vec{q}} \langle e^{i\vec{q}\cdot[\vec{r}(t)-\vec{r}(0)]}\rangle \sum_{i=x,y,z} \sum_{\mu=-2}^{2} |\beta^i_\mu(\vec{q})|^2 + \text{c.c.} \tag{42}$$

Essentially the only factor which has not been specified in some limit is the sum of form factors. If the molecular motion across the surface proceeds in a continuous manner, governed either by diffusion or by a Maxwellian velocity distribution, we can evaluate these form factors in the limit of continuous $\vec{a}$. Then,

$$\beta^i_\mu(\vec{q}) = \sum_{\vec{a}} e^{-i\vec{q}\cdot\vec{a}}\beta^i_\mu(\vec{a}) \rightarrow L^{-2}\iint d^2\vec{a}\, e^{-i\vec{q}\cdot\vec{a}}\beta^i_\mu(\vec{a}) , \tag{43}$$

where L^2 is the area of a unit cell of the surface. If we define the angles made by $\vec{q}$ and $\vec{a}$ with respect to a fixed x axis as ϕ' and ϕ, respectively, we have

$$\beta^i_\mu(\vec{q}) = L^{-2}\int_0^{2\pi} d\phi \int_0^\infty a\, da\, e^{-iqa\cos(\phi-\phi')}\, \beta^i_\mu(\vec{a}) . \tag{44}$$

The integrals can all be carried out exactly, yielding the remarkably simple results

$$\begin{aligned}
\vec{\beta}_2(\vec{q}) &= -\frac{i\pi\mu_s}{L^2} q^2 e^{-qz} e^{2i\phi'} (\cos\phi', i\sin\phi', -i) , \\
\vec{\beta}_{-2}(\vec{q}) &= \vec{\beta}_2^*(\vec{q}) , \\
\vec{\beta}_1(\vec{q}) &= \frac{2\pi\mu_s}{L^2} q^2 e^{-qz} e^{i\phi'} (\cos\phi', i\sin\phi', -i) , \\
\vec{\beta}_{-1}(\vec{q}) &= \vec{\beta}_1^*(\vec{q}) , \\
\vec{\beta}_0(\vec{q}) &= \frac{i2\pi\mu_s}{L^2} (\tfrac{3}{2})^{1/2} q^2 e^{-qz} (\cos\phi', i\sin\phi', -i) .
\end{aligned} \tag{45}$$

Hence,

$$\sum_i \sum_{\mu=-2}^{2} |\beta^i_\mu(\vec{q})|^2 = 2\left(\frac{4\pi\mu_s}{L^2}\right)^2 q^4 e^{-2qz}. \tag{46}$$

The short range of the interaction is indicated by the factor of q^4 and the exponential dependence on z. With this result we can perform rate calculations appropriate to the different kinds of molecular motion on the surface.

As the first example we allow the molecule to move in accord with a two-dimensional Maxwellian velocity distribution at temperature T. Then the conversion rate becomes

$$\lambda_{ll'} = k_{ll'} \frac{N_s}{N}\left(\frac{\mu_p b}{2\hbar}\right)^2 \frac{2}{3} S(S+1)\int_0^\infty dt\, e^{i\omega_{l'l}t} \times \frac{1}{N}\sum_{\vec{q}} \langle e^{-i\vec{q}\cdot\vec{v}t}\rangle \left(\frac{4\pi\mu_s}{L^2}\right)^2 q^4 e^{-2qz} + \text{c.c.}, \tag{47}$$

where we ignore both the surface lifetime and the spin-lattice relaxation time as small compared to $\omega_{ll'}$. The bracket around the factor for translational motion now indicates an average over the velocity distribution.

We take the appropriate continuum limit so that in polar coordinates

$$\frac{1}{N}\sum_{\vec{q}} \rightarrow \left(\frac{L}{2\pi}\right)^2 \int_0^{2\pi} d\phi' \int_0^{q_c} q\, dq, \tag{48}$$

where q_c is a cutoff wave vector. Performing the angular average we have

$$\frac{1}{2\pi}\int_0^{2\pi} d\phi\, \langle e^{-i\vec{q}\cdot\vec{v}t}\rangle = \frac{1}{2\pi}\int_0^{2\pi} d\phi'\, \langle e^{iqvt\cos\phi'}\rangle = \langle J_0(qvt)\rangle . \tag{49}$$

The time integration in Eq. (47) yields

$$\int_0^\infty dt \cos\omega_{l'l}t\, \langle J_0(qvt)\rangle = \langle \theta(qv - \omega_{l'l})/[(qv)^2 - \omega^2_{l'l}]^{1/2}\rangle, \tag{50}$$

where $\theta(x)$ is the unit-step function.

The average over velocity can now be carried out:

$$\left\langle \frac{\theta(qv - \omega_{l'l})}{[(qv)^2 - \omega^2_{l'l}]^{1/2}} \right\rangle = \frac{2}{\bar{v}^2}\int_{\omega_{l'l}/q}^\infty \frac{v\, dv\, e^{-v^2/\bar{v}^2}}{[(qv)^2 - \omega^2_{l'l}]^{1/2}} = \frac{\sqrt{\pi}}{q\bar{v}} e^{-\omega^2_{l'l}/q^2\bar{v}^2}. \tag{51}$$

Thus our final expression for the transiton rate becomes

$$\lambda_{ll'} = \lambda F(\alpha), \tag{52}$$

with

$$\lambda = \frac{2\pi}{\hbar}\frac{N_s}{N}\frac{S(S+1)}{3}\left(\frac{\mu_b\mu_s}{z^3}\right)^2 \left(\frac{b}{L}\right)^2 \frac{1}{2B} \tag{53}$$

and

$$F(\alpha) = \frac{\sqrt{\pi}}{4!}\alpha\int_0^{2q_c z} dx\, x^4 e^{-x} e^{-4\alpha^2/x^2}. \tag{54}$$

Here B is the rotational energy given in Eq. (2) and α is the dimensionless parameter $\omega_{l'l}(z/\bar{v})$. Taking the cutoff wave vector so that $2q_c z = 6$, the numerical results obtained for $F(\alpha)$ are plotted in Fig. 2.

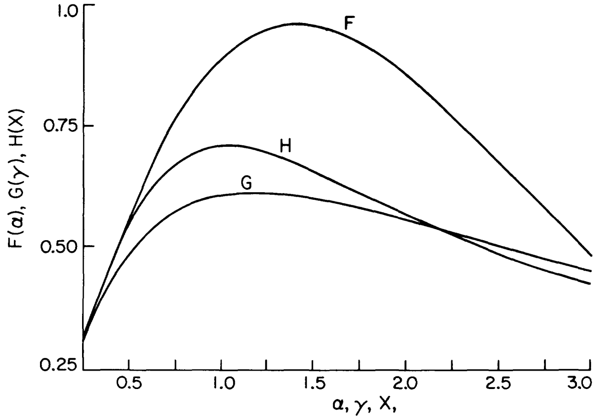

FIG. 2. Spectral weight functions $F(\alpha)$, $G(\gamma)$, and $H(x)$ vs α, γ, and x, respectively. $F(\alpha)$ is a measure of the dipole-gradient power spectrum for a two-dimensional Maxwell–Boltzmann H_2 gas with $\alpha = \omega z(M/2kT)^{1/2}$. $G(\gamma)$ is the power spectrum for diffusive motion with $\gamma = \omega z^2/4D$, and $H(x)$ is the spectrum for motion controlled by a surface lifetime τ with $x = \omega\tau$.

If the characteristic time of passage $z/\bar{v}$ is long compared to $\omega_{ll'}^{-1}$, then $\alpha \gg 1$ and

$$F(\alpha) \approx \alpha^4 e^{-3\alpha^{2/3}}. \tag{55}$$

In the vicinity of $\alpha \approx 1$, there is a broad maximum and for $\alpha \ll 1$,

$$F(\alpha) \approx \sqrt{\pi}\, \alpha\, . \tag{56}$$

For the $l = 0$ to $l' = 1$ transition and an assumed value of $z \approx 2$ Å, the peak in $F(\alpha)$ occurs for $T \sim 1200$ K. Since this value is proportional to $(\omega_{10}/z)^2$, it is sensitive to the energy-level spacings of the para- and ortho-states as well as to the effective distance of approach z. It is possible that the surface potentials could be such that the temperature of the peak is in fact considerably reduced. For example, if the rotational motion were hindered to two-dimensional rotation, then the peak for the $l = 0$ and $l' = 1$ transition would occur at room temperature. The remarks following Eq. (39) are appropriate here.

Consider now a second case in which the molecular motion is diffusion dominated. If we neglect the surface lifetime and spin-lattice relaxation,

$$\lambda_{ll'} = k_{ll'} \frac{N_s}{N} \left(\frac{2\pi \mu_s \mu_s}{\hbar} \right)^2 \left(\frac{b}{L} \right)^2 \frac{2}{3}\, S(S+1)$$
$$\times \int_0^\infty dt\, e^{i\omega_{l'l}t} \int_0^{q_c} \frac{dq}{2\pi}\, q^5 e^{-2qz} e^{-Dq^2t} + \text{c.c.} \tag{57}$$

Carrying out the time integration, we can write this in the same form as Eq. (52):

$$\lambda_{ll'} = \lambda G(\gamma). \tag{58}$$

In this case,

$$G(\gamma) = \frac{4^4}{3} \gamma \int_0^{q_c z/2} dy\, \frac{y^7 e^{-4y}}{y^4 + \gamma^2} \tag{59}$$

and $\gamma \equiv \omega_{l'l} z^2/4D$. Figure 2 shows a plot of $G(\gamma)$ obtained by numerical integration using the same cutoff $q_c z = 3$ as before. At high temperature, $\gamma \ll 1$ and

$$G(\gamma) \approx 0.318\gamma. \tag{60}$$

The transition rate then exhibits a negative temperature coefficient proportional to D^{-1}. At low temperatures,

$$G(\gamma) \approx 0.315\gamma^{-1} \tag{61}$$

and the transition rate decreases as the diffusion coefficient. A maximum occurs for $\gamma \sim 1$.

As the final possibility for molecular motion on the surface, we consider the case in which only the surface lifetime is important. The molecule executes no motion other than its hop on and off the surface. Then Eq. (37) reduces to

$$\lambda_{ll'} = \frac{\lambda}{48} \int_0^{2q_c z} dx\, x^5 e^{-x} \operatorname{Re} \int_0^\infty dt\, e^{i\omega_{l'l}t} e^{-t/\tau}$$
$$= \lambda H(\omega_{l'l} \tau_s), \tag{62}$$

with

$$H(x) = 1.40[x/(1 + x^2)]. \tag{63}$$

H is plotted in Fig. 2. It exhibits the same type of resonant behavior found for F and G. The transition rate peaks when $\tau = \omega_{l'l}^{-1}$. Thus an extremely short surface lifetime is required for maximum conversion efficiency. In general we expect $\tau > \omega_{l'l}^{-1}$, so that

$$\lambda_{ll'} \approx 1.4\lambda/\omega_{l'l}\tau. \tag{64}$$

Note that in each of the three cases considered the spin-lattice relaxation lifetime has not appeared—the spin system has been considered to be static. Unless $T_1 \lesssim 10^{-13}$ sec, it can safely be ignored in comparison with $\omega_{ll'}$. To the authors' knowledge no experimental dependence of the p→o rate on the spin-lattice relaxation time T_1 has ever been observed[8] which is consistent with the physical expectation that T_1 is long compared to $\omega_{ll'}^{-1}$.

In order to obtain the absolute para-ortho conversion rate, we consider the case in which the rate determining step is the rate of conversion on the surface. Assuming that there is a rapid internal thermalization of the individual para- and ortho-surface-state manifolds, the rate equations describing the relaxation of the nonequilibrium surface concentrations of para-δN_p and ortho-δN_0 have the simple forms

$$\frac{d}{dt} \delta N_p = -[\lambda_{01} + (\lambda_{21} + \lambda_{23}) e^{-\beta\hbar\omega_2} + (\lambda_{43} + \lambda_{45}) e^{-\beta\hbar\omega_4} + \cdots] \delta N_p / z_p$$
$$+ [(\lambda_{10} + \lambda_{12}) e^{-\beta\hbar\omega_1} + (\lambda_{34} + \lambda_{32}) e^{-\beta\hbar\omega_3} + \cdots] \delta N_0 / z_0 \tag{65}$$

and

$$\frac{d}{dt} \delta N_0 = -\frac{d}{dt} \delta N_p\, . \tag{66}$$

Here we are treating the H_2 molecules as freely rotating in three dimensions and taking $\hbar\omega_l = Bl(l+1)$.

The para- and ortho-partition functions have the standard form

$$z_p = 1 + 5e^{-\beta\hbar\omega_2} + 9e^{-\beta\hbar\omega_4} + \cdots,$$
$$z_0 = 3e^{-\beta\hbar\omega_1} + 7e^{-\beta\hbar\omega_3} + \cdots. \tag{67}$$

The physical interpretation of Eq. (65) is straightforward. The first term takes into account the thermal occupation and transition rate out of all of the para-states, while the second term describes in a similar way the rate of transitions out of the ortho-states and hence into the para-manifold. The degeneracy factors $(2l+1)$ which one expects in the numerator are already included in our definition of $\lambda_{ll'}$; see Eq. (29).

Combining the rate equations gives

$$\frac{d}{dt}(\delta N_p - \delta N_0) = -k(\delta N_p - \delta N_0), \tag{68}$$

with the absolute rate constant given by

$$\frac{k}{\lambda} = \frac{H(\omega_{10}\tau)}{Z_p} + \frac{[H(\omega_{10}\tau)+H(\omega_{21}\tau)]e^{-\beta\omega_1}}{Z_0} + \frac{[H(\omega_{21}\tau)+H(\omega_{32}\tau)]e^{-\beta\omega_2}}{Z_p}\cdots. \tag{69}$$

Here H is appropriate for the case in which the surface lifetime τ controls the dynamics. For free motion or diffusion F or G should be used in place of H.

In order to determine the temperature dependence of the absolute rate given by Eq. (69) we must include the temperature dependence of τ. As a simple parametrization we will assume that τ has the activated form

$$\tau\omega_{10} = a e^{b/t}. \tag{70}$$

Here t is the temperature measured in units of the temperature separation of the lowest para-ortho states (for free rotation $t = \frac{1}{172}T$). The parameter ω_{10}/a represents an effective vibrational frequency of the H_2 molecule perpendicular to the surface. For physical adsorption we expect that the effective vibrational frequency ω_{10}/a is of order 10^{13}, so that a is of order 1. The parameter b is a measure of the surface activation energy. A value $b=1$ corresponds to a surface activation energy of order 350 cal/mole. In computation we have allowed b to vary from 1 to 5.

When the effective vibration frequency ω_{10}/a is larger than ω_{10} $(a<1)$ the peak in the spectral density $H(\omega)$ moves from above ω_{10} at low temperatures to below ω_{10} at higher temperatures. This causes the conversion rate from $l=0$ to $l'=1$ to increase with temperature at low temperatures, reach a maximum at an intermediate temperature where $\tau\omega_{10} \sim 1$, and then decrease as the temperature is further increased. This can also come about simply by the variation in thermal population of the various states even if a >1. At higher temperatures the relative population of the $l'=1$ state decreases, and the spectral weight $H(\omega)$ can be sufficiently weak for the higher transitions that dk/dT becomes negative. Thus both negative and positive temperature coefficients for conversion are possible.

For $a=1$ and $b=1$, the successive contributions to k/λ obtained from the first three terms in Eq. (69) are plotted in Fig. 3 versus the reduced temperature. We see that over this temperature range (43–430 K), the first few terms dominate. In Fig. 4, results for various values of the parameters a and b are given. It seems likely that $a>1$ for most physical situations.

In a similar way, we have parameterized the diffusion constant as

$$\omega_{10} z^2/D = a' e^{b'/t}. \tag{71}$$

Then, using the appropriate values of G in Eq. (69), we have obtained the diffusion results for k/λ given in Fig. 5. We expect that b' will be less than b since the activation energy for diffusion should be less than that for evaporation. We have used values of a' equivalent to those previously used for a. Finally, for the case of free motion, taking $z = 2$ Å and $\bar{v} = (2kT/M)^{1/2}$, we obtained the results for k/λ shown in Fig. 6.

The variety of thermal behavior illustrated for these three dynamic models is further complicated by the variation in the ortho-para spectrum produced by the surface potential. As the rotational motion becomes hindered, the energy splitting and degeneracies can change from the three-dimensional form to two-dimensional and even to one-dimensional form. In addition, it may well be that the local atomic arrangement characteristic of the catalytic sites is such as to locally hinder the motion. One of the important consequences of this hindering is that the relevant para-ortho energy differences are reduced. Thus even if $\omega_{10}\tau \gg 1$ for free rotation, it may be that the hindered frequency $\tilde{\omega}_{10}$ is such that $\tilde{\omega}_{10}\tau \sim 1$. It is just for this

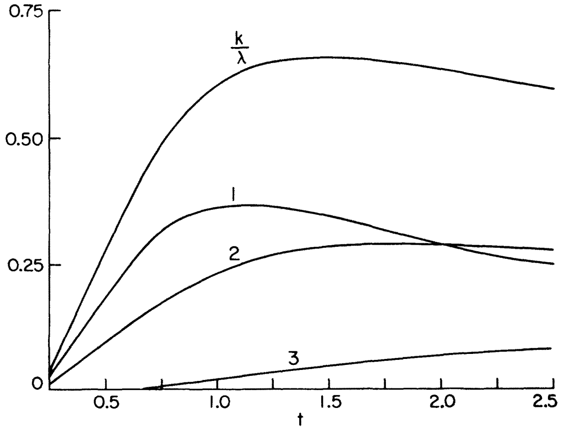

FIG. 3. For $a=1$ and $b=1$, the first three terms contributing to k/λ, Eq. (69), are plotted vs the reduced temperature $t = \frac{1}{172}T$ K. The uppermost curve corresponds to k/λ obtained from the sum of these contributions.

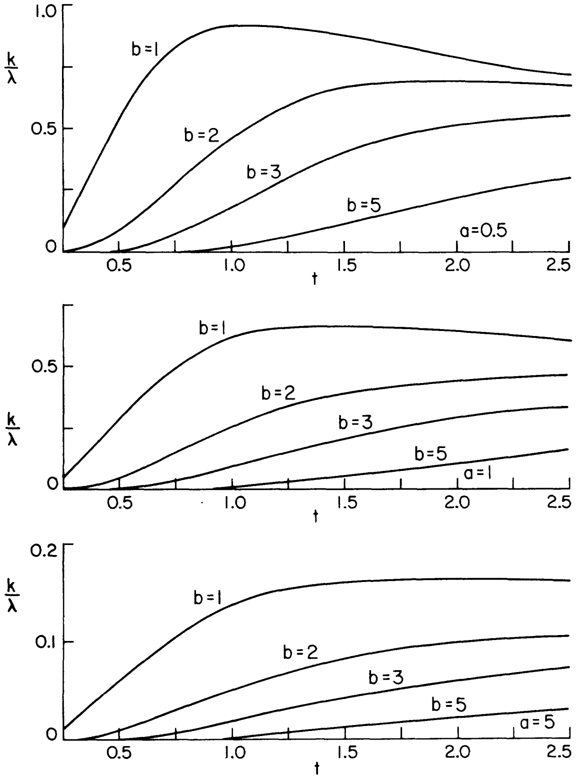

FIG. 4. The normalized conversion rate k/λ vs $t = \frac{1}{172} T$ K for the case in which the surface lifetime $\tau = (a/\omega_{10})e^{b/t}$ controls the dynamics. The value of a is listed just above the t axis and the b values are listed next to the curves.

reason that we have plotted k/λ for a variety of parameters. We hope that it will be possible to use these results to deduce some information about the nature of the catalytic site and the H_2 motion from the experimental temperature dependence of the rate.

The net number of para-H_2 molecules converted to ortho-H_2 molecules per second can be written

$$k(\delta N_p - \delta N_0) = \lambda N_s \delta\theta(k/\lambda). \tag{72}$$

Here we have introduced a coverage fraction $\delta\theta$ which gives the nonequilibrium difference between the ratio of the sites occupied by para-H_2 and ortho-H_2 molecules:

$$\delta\theta = (\delta N_p - \delta N_0)/N. \tag{73}$$

$N = A/L^2$ is the number of possible H_2 sites on an area A of the surface. Taking L and z equal to 2 Å, Eq. (72) gives

$$k(\delta N_p - \delta N_0) = 2\times 10^2\,[\tfrac{1}{3}S(S+1)]N_s\delta\theta(k/\lambda). \tag{74}$$

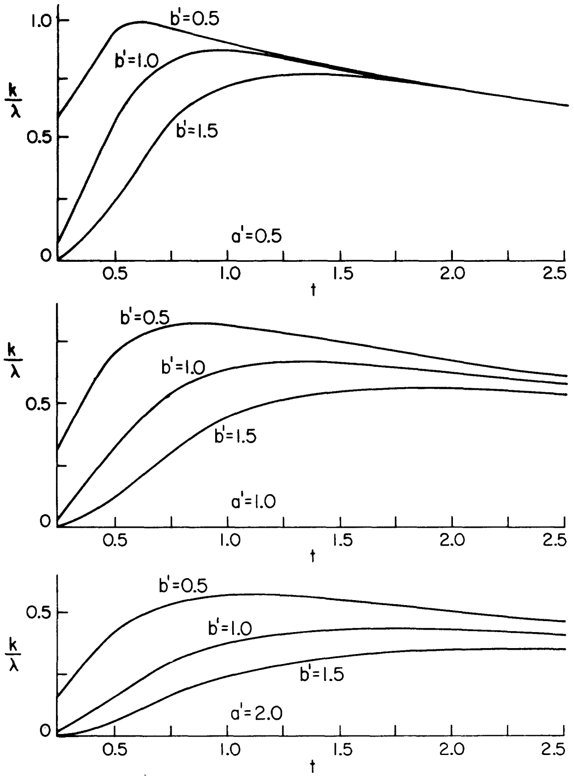

FIG. 5. The normalized conversion rate k/λ vs $t = \frac{1}{172} T$ K for diffusion with $\omega_{10}z^2/D = a'e^{b'/t}$.

For a coverage fraction $\delta\theta$ of order 1%, this corresponds to approximately k/λ conversions per surface impurity spin per second. Thus, to within a factor $\frac{2}{3}S(S+1)$, the ratios k/λ plotted in Figs. 4–6 can be interpreted as the number of conversions per surface-impurity spin per second for a coverage fraction of 1%.

B. Dense Magnetic Lattice Substrate

In a regular lattice of spins, several additional effects of physical interest can influence the conversion rate. First, if the exchange coupling is comparable to $\hbar\omega_{ll'}$, the dynamics of the spin system become important. For example, in the ordered state, Ilisca[7] has pointed out that the energy transfer in p → o conversion can be supplied by the

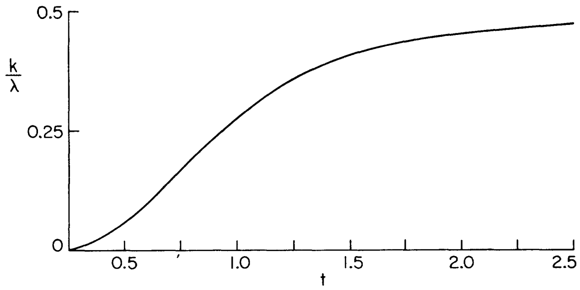

FIG. 6. The normalized conversion rate k/λ vs $t = \frac{1}{172} T$ K for a two-dimensional Maxwell–Boltzmann H_2 gas.

absorption or emission of a spin wave. Secondly, even when the energy transfer comes from the center-of-mass motion of the H_2 molecules, the static spatial correlations of the lattice of spins will affect the conversion rate. Here we briefly discuss the dynamic spin-wave problem using the formalism of Sec. II to obtain an explicit expression for $\lambda_{ll'}$. We then turn to the effects of spatial correlations and examine the conversion rate in the vicinity of the Curie or Néel temperature for the case in which the energy is supplied by translational motion.

Our starting point is again Eq. (37), but for ease of later analysis we adopt a somewhat different approximation for the form factors. Consider the specific case that the molecule sits preferentially above a magnetic site. Because the interaction is of such short range, it is a useful approximation to assume that this site is responsible for all of the catalytic activity. This corresponds to setting $a_x = a_y = 0$, $a_z = z$ in the Fourier transform of $\vec{\beta}_\mu(\vec{a})$.

$$\beta_\mu(\vec{q}) = \sum_{\vec{a}} e^{-i\vec{q}\cdot\vec{a}}\, \vec{\beta}_\mu(\vec{a}) = \vec{\beta}_\mu(\vec{a} = (0, 0, z)). \tag{75}$$

Thus, the form factors are independent of $\vec{q}$, and from Eq. (30) it follows that

$$\begin{aligned} &\vec{\beta}_2(\vec{q}) = 0 = \vec{\beta}_{-2}(\vec{q}), \\ &\vec{\beta}_1(\vec{q}) = (3\mu_s/z^4)(1, i, 0) = \vec{\beta}^*_{-1}(\vec{q}), \\ &\vec{\beta}_0(\vec{q}) = 6\ \sqrt{\tfrac{3}{2}}\ (\mu_s/z^4)(0, 0, 1). \end{aligned} \tag{76}$$

Within this approximation

$$\sum_i \langle S^i_{-\vec{q}}(t) S^i_{\vec{q}}(0)\rangle \sum_\mu |\beta^i_\mu(\vec{q})|^2 = (3\mu_s/z^4)^2 [\langle S^+_{-\vec{q}}(t) S^-_{\vec{q}}(0)\rangle + \langle S^-_{-\vec{q}}(t) S^+_{\vec{q}}(0)\rangle + 6\langle S^z_{-\vec{q}}(t) S^z_{\vec{q}}(0)\rangle], \tag{77}$$

and Eq. (37) reduces to

$$\lambda_{ll'} = k_{ll'}(3\mu_p \mu_s{}^b/2z^4\hbar)^2 \int_0^\infty dt\, e^{i\omega_{ll'}t} \sum_{\vec{q}} \langle e^{-i\vec{q}\cdot[\vec{r}(t)-\vec{r}(0)]}\rangle [\langle S^+_{-\vec{q}}(t) S^-_{\vec{q}}(0)\rangle + \langle S^-_{-\vec{q}}(t) S^+_{\vec{q}}(0)\rangle + 6\langle S^z_{-\vec{q}}(t) S^z_{\vec{q}}(0)\rangle] + \text{c.c.} \tag{78}$$

To treat the translational correlation function in Eq. (78) we first consider the specific limit in which the time dependence of the spin operators is much more rapid than that of the molecular motion. Hence we set $\vec{r}(t) \approx \vec{r}(0)$ and

$$\langle e^{-i\vec{q}\cdot[\vec{r}(t)-\vec{r}(0)]}\rangle \approx 1. \tag{79}$$

We will ignore H_2 surface lifetime effects.

As illustrative of the effects to be expected consider the case of ferromagnetic ordering along the $+z$ direction. An analogous calculation could be carried out for antiferromagnetic ordering with similar results. In the ferromagnetic case the two transverse spin correlations of Eq. (78) correspond, respectively, to single magnon emission and absorption. Notice, however, that the operators $S^{\pm}_{\vec{q}}$ are hybrid operators. They create or destroy a single magnon of wave vector $\vec{q}$ in the x-y plane at z coordinate zero. Therefore, we can represent them in terms of a sum over the Q_z component of the fully Fourier transformed operators $S^{\pm}_{\vec{Q}}$:

$$S^{\pm}_{\vec{q}} = \sum_{Q_z} S^{\pm}_{\vec{Q}}. \tag{80}$$

Introducing an effective surface magnon energy of states $\rho_s(\omega)$ by

$$\sum_{\vec{q}} \int_{-\infty}^{\infty} \langle S^-_{-\vec{q}}(t) S^+_{\vec{q}}(0)\rangle e^{-i\omega t}\, dt = 2S\hbar n(\omega)\, \rho_s(\omega), \tag{81}$$

where $n(\omega)$ is the Bose factor, the transverse contribution to $\lambda_{ll'}$, Eq. (78), reduces to

$$\begin{aligned} (\lambda_{ll'})_\perp = {} & k_{ll'}\pi S(3\mu_p \mu_s b/\hbar z^4)^2 \hbar \\ & \times\{\rho_s(-\omega_{ll'})[1 + n(-\omega_{ll'})] + \rho_s(\omega_{ll'}) n(\omega_{ll'})\}. \end{aligned} \tag{82}$$

This expression will be valid so long as the magnon density of states and the Bose factors vary slowly in comparison with the inverse of characteristic damping times. Note that $\hbar\omega_{ll'}$ is the energy difference between an ortho-state of angular momentum l and para-state of angular momentum l'. If $l > l'$ then $\omega_{ll'}$ is positive, but if $l < l'$ then $\omega_{ll'}$ is negative; and $\rho_s(-|\omega|) \equiv 0$. In the temperature region $kT \gg \hbar|\omega_{ll'}|$ the transition rate can be expressed as

$$(\lambda_{ll'})_\perp \approx [4.5/(S+1)](L/z)^2 kT \rho_s(|\omega_{ll'}|)\lambda. \tag{83}$$

This can exhibit a temperature dependence in ρ_s due to the renormalization of the spin-wave energies as well as the simple linear dependence arising from the increasing number of magnons at high temperature.

In the low-temperature limit $kT \ll \hbar|\omega_{ll'}|$,

$$\begin{aligned} (\lambda_{ll'})_\perp \approx {} & [4.5/(S+1)](L/z)^2 \hbar|\omega_{ll'}| \\ & \times[\rho_s(-\omega_{ll'}) + \rho_s(\omega_{ll'}) e^{-\beta\hbar\omega_{ll'}}]\lambda. \end{aligned} \tag{84}$$

In this case, the conversion requiring magnon absorption falls exponentially as the number of available magnons decreases, while conversion driven by magnon emission becomes relatively insensitive to temperature. However, the latter process is exponentially damped by the fact that relatively few high-energy para-molecules are present at low temperature. This statistical factor is, of course, not contained in Eq. (84).

We conclude by estimating the rate of these magnon-assisted processes. With $z = 2$ Å, $n(\hbar\omega_{ll'}) = 1$, and $\rho_s(\omega_{ll'}) \sim Q/J_{\text{exch}} \approx Q/\hbar\omega_{ll'}$ we find an absolute rate $10^2 QS\,\delta\theta$ sec^{-1} per spin. For $Q \sim 1$, this rate is comparable to that obtained when molecular translation supplies the necessary energy [cf. Eq. (74)]. However, as discussed by Ilisca,[7] if the energy $\hbar\omega_{ll'}$ corresponds to a peak in the magnon density of states, the value of Q can be an order of magnitude or more larger.

Note in addition, that the relative stability of our estimates of the absolute conversion rate should not be taken to imply an expected uniformity of conversion rate for all catalysts. Many of them undoubtedly have material parameters, e.g., D, τ, J_{exch}, which cause them to operate at far below their theoretical maximum efficiency.

Another characteristic effect of a regular lattice of spins on the conversion rate arises from the spatial correlation of the spins. Clearly these spatial correlations will influence the gradient fields probed by the adsorbed H_2 molecules. The time dependence of this field can be due to the dynamics of the spins, as is the case of spin waves, or to the translational motion of H_2. Here we focus on the spatial spin correlation effects near the Curie or Néel point for a material in which the translational motion supplies the energy transfer.

We will use the form factors given in Eq. (76). If, in addition, we ignore the H_2 surface lifetime and assume that the dynamics are described by molecular diffusion, Eq. (39), the conversion rate is

$$\begin{aligned}\lambda_{ll'} &= k_{ll'}\left(\frac{3\mu_p\mu_s b}{2\hbar z^4}\right)^2 \int_0^\infty dt\, e^{i\omega_{ll'}t} \sum_{\vec{q}} e^{-Dq^2 t} \left(\langle S^+_{-\vec{q}} S^-_{\vec{q}}\rangle + \langle S^-_{-\vec{q}} S^+_{\vec{q}}\rangle + 6\langle S^z_{-\vec{q}} S^z_{\vec{q}}\rangle\right) + \text{c.c.} \\ &= k_{ll'}\left(\frac{3\mu_p\mu_s b}{2\hbar z^4}\right)^2 \sum_{\vec{q}} \frac{2Dq^2}{\omega^2_{ll'} + (Dq^2)^2} \left(\langle S^+_{-\vec{q}} S^-_{\vec{q}}\rangle + \langle S^-_{-\vec{q}} S^+_{\vec{q}}\rangle + 6\langle S^z_{-\vec{q}} S^z_{\vec{q}}\rangle\right).\end{aligned} \tag{85}$$

The form factor in Eq. (85) limits the range to $(D/\omega_{ll'})^{1/2}$, which means that the short-range spin correlations dominate and $\lambda_{ll'}$ varies as the surface interaction energy. The temperature derivative of the conversion rate should then be proportional to the magnetic specific heat of the surface. This argument is similar to that originally introduced by Fisher and Langer[8] to explain the temperature dependence of the electrical resistivity of a metallic ferromagnet near T_c. Here, however, the local surface-spin correlations are explored.

It is worthwhile to pursue this somewhat further with a more specific model of molecular translation. Suppose there were a definite array of local surface spins, and the molecular hopping proceeded with a rate p from one site to the next. The discrete lattice counterpart to Eq. (39) is then

$$\langle e^{-i\vec{q}\cdot[\vec{r}(t)-\vec{r}(0)]}\rangle = \exp\left(-pt\sum_{\vec{\delta}}(1 - e^{-i\vec{q}\cdot\vec{\delta}})\right), \tag{86}$$

where $\vec{\delta}$ is a distance to a nearest-neighbor spin. This reduces to the continuum limit as $\vec{\delta} \to 0$ with $D = p\delta^2$. Using this form and neglecting terms of order $(p/\omega_{ll'})^2$ compared to 1 in the denominator we find that

$$\begin{aligned}\lambda_{ll'} = k_{ll'}\left(\frac{3\mu_p\mu_s b}{2\hbar\omega_{ll'} z^4}\right)^2 & 2\sum_{\vec{q}} p \sum_{\vec{\delta}} (1 - e^{-i\vec{q}\cdot\vec{\delta}}) \\ & \times\left(\langle S^+_{-\vec{q}} S^-_{\vec{q}}\rangle + \langle S^-_{-\vec{q}} S^+_{\vec{q}}\rangle + 6\langle S^z_{-\vec{q}} S^z_{\vec{q}}\rangle\right).\end{aligned} \tag{87}$$

The sum over $\vec{q}$ may be done exactly from the definition of the Fourier transform:

$$\lambda_{ll'} = k_{ll'}\left(\frac{3\mu_p\mu_s b}{2\hbar\omega_{ll'} z^4}\right)^2 2p\,\frac{1}{N_s}\sum_{\delta}\sum_{\vec{R}}\left[\left(\langle S^+_R S^-_R\rangle + \langle S^-_R S^+_R\rangle + 6\langle S^z_R S^z_R\rangle\right) - \langle S^+_R S^-_{R+\delta}\rangle - \langle S^-_R S^+_{R+\delta}\rangle - 6\langle S^z_R S^z_{R+\delta}\rangle\right]. \tag{88}$$

In this case the transition rate is seen to involve only autocorrelations and nearest-neighbor pair correlations.

If one spin site is equivalent to any other, and rotational invariance holds (i.e., neglect surface anisotropy) we have the simple result

$$\lambda_{ll'} = k_{ll'}\left(\frac{3\mu_p\mu_s b}{\hbar\omega_{ll'} z^4}\right)^2 \left(\frac{5pN_\delta}{3}\right)\left(\langle\vec{S}_0\cdot\vec{S}_0\rangle - \langle\vec{S}_0\cdot\vec{S}_1\rangle\right)$$

$$= \frac{15}{2\pi}\left(\frac{L}{z}\right)^2 \frac{pN_\delta}{|\omega_{ll'}|}\left(1 - \frac{\langle\vec{S}_0\cdot\vec{S}_1\rangle}{S(S+1)}\right)\lambda, \tag{89}$$

where N_δ is the number of nearest neighbors, $\vec{S}_0$ is the spin operator for a typical site, and $\vec{S}_1$ is the operator for one of its (equivalent) nearest neighbors. We note that even without the assumption of rotational invariance, there will always be a portion of Eq. (88) which can be written in such rotationally invariant form.

The first term of Eq. (89) will have no marked temperature dependence near the critical point since the hopping rate p should not vary substantially. However, if the spin system is governed by Heisenberg exchange, the second term is proportional to the magnetic energy of the surface spins. Neglecting the variation of p the temperature derivative of Eq. (89) near the critical point yields

$$\frac{d\lambda_{ll'}}{dT}=\frac{15}{\pi}\left(\frac{L}{z}\right)^2\frac{p}{|\omega_{ll'}|}\;\frac{\lambda}{J_{\text{exch}}}\;C_s(T),\qquad T\approx T_c\,,T_N \qquad (90)$$

where J_{exch} is the exchange integral and $C_s(T)$ is the surface specific heat per spin. For antiferromagnetic ordering, $J_{\text{exch}} < 0$ and Eq. (90) predicts an increase in the conversion rate as the system orders. For a ferromagnetic transition $J_{\text{exch}} > 0$ and a decrease is indicated.

Although we have obtained this particular result under specific geometrical assumptions regarding the interactions of the molecule with the spin system, we expect that the earlier general arguments concerning the importance of short-range correlations will carry over to more general cases. So long as the diffusion is relatively slow (compared to $\omega_{ll'}$), and the replacement of dynamical short-wavelength spin correlations by static averages is warranted, the conversion rate should reflect the temperature dependence of the surface magnetic specific heat.

IV. CONCLUSION

We have not attempted to explain in detail the wide variety of experimental measurements on the p ⟶ o transition. Our purpose has been rather to explore a framework, based upon a microscopic study of the conversion process, within which experimental results can be interpreted. It is unfortunate that much of the literature is clouded by rather ill-defined theoretical concepts such as, for example, "negative" activation energies. This is perhaps understandable in the light of the great complexity and variety of surface phenomena; however, we have tried to present our treatment in terms of parameters such as $\bar{v}$, τ, D, $\omega_{ll'}$, and z which are hopefully more amenable to measurement and calculation.

In Sec. II we have expanded the interaction Hamiltonian responsible for the transition and developed group-theoretical matrix-element theorems which justify the neglect of all but the first term in the expansion. The Golden Rule of time-dependent perturbation theory has been used to find a general expression [Eq. (37)] for the transition rate in terms of two correlation functions involving the molecular position and the surface spin system. The time dependence of these correlations then determines which contributes more effectively to the rate of conversion. In the limit of dilute, widely separated paramagnetic surface sites we find that the kinetic energy of the molecule governs the transition because spin-lattice relaxation times are generally too long. In the case of a magnetically ordered surface, emission and absorption of spin waves can become rate determinative if J_{exch} is large enough. In addition, spatial spin correlations can play a significant role.

In Sec. III we have investigated three possible types of molecular motion: (i) motion as in a classical two-dimensional Maxwell–Boltzmann gas; (ii) motion governed by diffusion; and (iii) motion simply on and off the surface. We find that under different conditions there can be negative as well as positive temperature coefficient of conversion. These results provide a basis for understanding the activation energies which occur repeatedly in experimental literature. Given the uncertainties in such parameters as $\omega_{ll'}$, z, and D, we estimate an absolute rate of conversion per spin which is comparable to that often encountered experimentally. We believe that it should be possible to use the theory to determine these parameters from the measurements of the p ⟶ o rate.

For magnetically ordered systems we have discussed the phenomenon of resonant conversion due to emission or absorption of spin waves first suggested by Ilisca.[7] For this process to occur with maximum efficiency it is desirable that $J_{\text{exch}} \approx \hbar\omega_{10}$. If $J_{\text{exch}} \ll \hbar\omega_{10}$, resonant conversion is impossible because the spin-wave energies are too low; whereas if $J_{\text{exch}} \gg \hbar\omega_{10}$, the density of magnon states becomes too small. For resonant conversion we regard the molecule as effectively static while the spin dynamics induces the transition. Such a resonant effect is found to exist for both ferromagnetic and antiferromagnetic ordering.

Finally, we have considered the effects to be expected near a magnetic phase transition of the substrate. We have treated this for the case that the energy of conversion arises solely from molecular motion, with the spin system regarded as static. Due to the small range of the interaction Hamiltonian, short-wavelength spin correlations are found to be the most important. This leads to a dependence of the conversion rate $\lambda_{ll'}$ upon the magnetic energy of the surface, and hence a prediction that $d\lambda_{ll'}/dT$ is proportional to the surface specific heat near the critical point.

In conclusion we note that we have ignored molecule-molecule interactions which occur on surfaces of high coverage, and have not considered the effects which an externally applied magnetic field can have on the conversion rate.[9,10] These will be considered in later publications.

ACKNOWLEDGMENTS

The authors wish to thank Professor P. W. Selwood for interesting them in this problem and for numerous discussions and helpful suggestions over the past year. We would also like to acknowledge stimulating conversations with Professor D. Cannell, Professor V. Jaccarino, and R. Bruce.

---

*Research supported by AFOSR under Grant No 71-2007.

†Present address: Department of Physics, College of William and Mary, Williamsburg, Va. 23185.

[1] E. Wigner, Z. Phys. Chem. B **23**, 28 (1933).

[2] L. G. Harrison and C. A. MacDowell, Proc. R. Soc. A **220**, 77 (1953).

[3] A. J. Leffler, J. Chem. Phys. **43**, 4410 (1965).

[4] E. Ilisca and A. P. Legrand, Phys. Rev. B **5**, 4994 (1972).

[5] The method discussed here can be applied to analyze the case of hindered rotation. Results for various degrees of hindering between free three-dimensional rotation and planar two-dimensional rotation will be reported elsewhere.

[6] T. B. MacRury and J. R. Sams, Mol. Phys. **19**, 337 (1970); Mol. Phys. **19**, 353 (1970); Mol. Phys. **20**, 49 (1971); Mol. Phys. **20**, 57 (1971).

[7] E. Ilisca, Phys. Rev. Lett. **24**, 797 (1970); Phys. Lett. A **33**, 247 (1970).

[8] M. E. Fisher and J. S. Langer, Phys. Rev. Lett. **20**, 665 (1968).

[9] P. W. Selwood, J. Catal. **19**, 353 (1970).

[10] P. W. Selwood, J. Catal. **22**, 123 (1971).

PHYSICAL REVIEW B VOLUME 8, NUMBER 1 1 JULY 1973

Anomalous Behavior of the Anisotropy and Linewidth due to Pr in Iron Garnets

E. M. Gyorgy, R. C. Le Craw, A. Rosencwaig, L. G. Van Uitert, R. D. Pierce, R. L. Barns, and E. Heilner
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 16 February 1973)

The contribution of Pr^{3+} in iron garnets to the first-order anisotropy constant and to the microwave loss is highly nonlinear with respect to the Pr^{3+} concentration and is shown to be strongly dependent on the lattice constant. The value of the anisotropy constant per Pr ion goes from -18×10^4 to about $+3\times10^4$ erg/cm^3 as the lattice constant increases from 12.4 to 12.7 Å. The microwave linewidth of $Pr_3ScFe_4O_{12}$ is 21 times narrower than expected from the extrapolation of the low-concentration data of Pr^{3+} in yttrium iron garnet.

The contributions of Pr^{3+} in the iron garnets (IG) to the first-order anisotropy constant K_1 and to the microwave linewidth have been investigated. In each case this contribution is found to be highly nonlinear with Pr content and to be strongly dependent on the lattice constant. To our knowledge this is the first detailed experimental study of the concentration dependence of K_1 and the linewidth in rare-earth garnets. The usual formulation of the expression for the linewidth[1,2] and the anisotropy[3-6] assumes that the rare-earth ions act independently, and consequently the contribution per ion is independent of the concentration. The only substantial deviation from this single-ion approximation previously reported[6] is for the second-order anisotropy constant K_2 at 80 °K of $Y_3Fe_5O_{12}$ with 1-at.% Sm when compared to $Sm_3Fe_5O_{12}$. For pure SmIG K_2 is large and positive, while for the 1-at.% Sm crystal K_2 due to Sm is small and negative. The value of K_1 at 80 °K extrapolated from the Sm-doped yttrium iron garnet (YIG) sample is 25% higher than the value obtained from SmIG. For GdIG, YbIG, and YIG from 4.2 to 300 °K,[6] and for SmIG and EuIG at 300 °K,[7] the single-ion approximation has been shown to give an accurate description of K_1.

The anisotropy constant for the garnets indicated in Fig. 1 was measured at 77 °K using a recording torque magnetometer. To eliminate the growth-induced anisotropy the samples were annealed at 1200 °C for 16 h. The results for K_1 per Pr ion (per formula unit) are plotted in Fig. 1(a) as a function of the Pr content. (The Sc_1 is necessary to obtain Pr_3 in the crystal.) To obtain these results the contribution to K_1 of the host lattice was subtracted from the measured anisotropy. For the series $Pr_xY_{3-x}ScFe_4O_{12}$ and $Pr_xY_{3-x}Fe_5O_{12}$ the anisotropy of the host crystals at 77 °K was taken as that of $Y_3ScFe_4O_{12}$ ($K_1 = -0.7\times10^4$ erg/cm^3) and $Y_3Fe_5O_{12}$ ($K_1 = -2.2\times10^4$ erg/cm^3), respectively. Implicit here is the assumption that the anisotropy of Fe^{3+} (d^5) is independent of the rare-earth present. Yttrium, of course, does not contribute to K_1. For the $Pr_xGd_{3-x}Fe_5O_{12}$ compositions the contribution of the Fe^{3+} ions was again taken from the YIG value and the contribution per Gd ion was deduced from the value obtained for $Gd_3Fe_5O_{12}$ at 77 °K (-3.7×10^4 erg/cm^3). Here it is assumed, as will be partially justified later, that the anisotropy per Gd ion does not vary with composition. For the sample containing $Sc_{0.5}Fe_{4.5}$, the average