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New Predictions on Magnetic Rotational Transitions in Scattering of H_2 by LiF(001)

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New predictions are presented for the scattering of H_2 from LiF(001), based on a potential which includes the interaction between the quadrupole moment of H_2 and the surface ions. Large probabilities are found for transitions in which the magnetic rotational quantum number m_j changes, contradicting the view that rotational scattering of small homoatomic diatomic molecules off inert surfaces obeys a $\Delta m_j = 0$ propensity rule. Scattering of unpolarized H_2 leads to rotationally polarized beams, suggesting a technique for constructing rotationally polarized beams of H_2. [S0031-9007(97)04951-X]

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Experiments on scattering of H_2 from LiF(001) have played an important role in the discovery of new phenomena in molecule-surface scattering. In the early 1930s, Stern and coworkers [1] confirmed the wave nature of molecular particles by showing that H_2 and He were diffracted when scattered from a LiF surface. A closer inspection of their results led Lennard-Jones and Devonshire [2] to the discovery of selective adsorption, which allows a molecule to become trapped in the particle-surface potential well. Experiments on scattering of H_2 from LiF carried out in the mid-1970s by Boato *et al.* [3] were among the first to demonstrate that the molecule may change its rotational state as well as diffract (rotationally inelastic diffraction or RID).

In surface science, the view that rotational scattering of small homoatomic diatomic molecules from inert surfaces obeys a $\Delta m_j = 0$ propensity rule (meaning that the magnetic rotational quantum number is almost conserved) is prevalent. Historically, this view may be traced to experimental studies on RID of H_2 from ionic surfaces [3]. In these, the proposition of the propensity rule was *not* based on direct experimental evidence, but on the observation that early quantal scattering calculations on H_2 + LiF assumed a potential model that either forbade [4,5] or only weakly allowed [6] changes in m_j, and on what we believe was an erroneous interpretation of some of the experimental results (*vide infra*).

The view that a $\Delta m_j = 0$ propensity rule should hold is also implicit in many subsequent calculations on RID of H_2 from LiF [7–9] and other surfaces [10], which all used potential models forbidding changes in m_j. The view has been further reinforced by detailed model studies of m_j changes in scattering of H_2 off of corrugated surfaces [11]. In these studied, only small values ($<1\%$) were obtained for rotational transitions with $\Delta m_j \neq 0$ for physically reasonable choices of the size of the unit cell, and of the corrugation strength of the atom-surface potentials used to model the molecule-surface interaction. Large probabilities for $\Delta m_j \neq 0$ transitions were predicted only for scattering of *large* homoatomic diatomic molecules like Cl_2 [12] (in the model, large probabilities for $\Delta m_j \neq 0$ transitions arise if the molecular bond length is close to the surface lattice constant).

As demonstrated below in scattering calculations for H_2 + LiF(001), large probabilities for $\Delta m_j \neq 0$ transitions can arise in rotational scattering of small homoatomic diatomic molecules from ionic surfaces if the electrostatic interaction V_{els} between the molecule's quadrupole moment and the surface ions is taken into account when modeling the molecule-surface interaction. We also predict that the scattering of initially unpolarized H_2 results in rotationally polarized diffracted beams of H_2. Our results challenge the established view that homoatomic diatomic molecule scattering of inert surface obeys a $\Delta m_j = 0$ propensity rule, and suggest a potentially useful technique for constructing rotationally polarized beams of H_2. The predictions are cast in a form that allows ready testing in experiments by specifying the rotational alignment of H_2 scattered from the initial ($j = 2$, $m_j = 0$) and ($j = 2$) states. Both states can be prepared using the technique of stimulated Raman pumping [13], while the rotational alignment of scattered H_2 can be measured using laser induced fluorescence (LIF) techniques [14].

In our calculations, H_2 is treated as a rigid rotor. The lattice is treated as being static, so phonons are not considered, although, according to Boato *et al.* [3], 75% of the interaction should actually be phonon inelastic. Nevertheless, our conclusions will remain valid as long as rotation-diffraction transitions occur more or less independently from phonon-inelastic transitions, in which case the probabilities for phonon-elastic scattering presented below should simply be multiplied with some constant factor to obtain the probabilities for phonon-elastic scattering in the presence of phonon-inelastic scattering.

The molecule-surface potential [15] is written as a sum of five main contributions,

$$V(x,y,z,\theta,\phi) = V_{\mathrm{rep}} + V_{\mathrm{att}}(6) + V_{\mathrm{att}}(8) + V_{\mathrm{els}} + V_{\mathrm{ind}}\,. \qquad (1)$$

Other contributions have been neglected on the grounds of their being much smaller [16]. Details concerning the repulsive and attractive potentials V_{rep}, $V_{\mathrm{att}}(6)$, $V_{\mathrm{att}}(8)$, and V_{ind} can be found in Ref. [15]. The interaction V_{els}

of the quadrupole moment of H_2 with the ionic lattice is given by [17]:

$$\begin{aligned} V_{\mathrm{els}} = & - \Theta\sqrt{\frac{\pi}{30}} \sum_{n,m} \{A_{nm} \exp[iG(nx + my)] \exp(-\gamma_{nm} z) \\ & \times [\exp(i2\xi) Y_{22}(\theta, \phi) + \exp(-i2\xi) Y_{2-2}(\theta, \phi) \\ & - 2i \exp(i\xi) Y_{21}(\theta, \phi) + 2i \exp(-i\xi) Y_{2-1}(\theta, \phi) - \sqrt{6} Y_{20}(\theta, \phi)]\}, \end{aligned} \tag{2}$$

where

$$\exp(i\xi) = (n - im)\sqrt{(n^2 + m^2)}. \tag{3}$$

In Eq. (2), Θ is the quadrupole moment of H_2, and $G = \sqrt{2\pi/a}$, where a is the lattice parameter ($a = 2.84$ Å for LiF). The summation extends over all integer values n and m except $n = m = 0$. Further details concerning V_{els}, including expressions for A_{nm}, γ_{nm}, can be found in Ref. [15]. Note that the expression for V_{els} is functionally different from the potential form used in the model studies referred to above [11], so that the effect of V_{els} cannot be modeled by taking the summed atom-surface pair potential form [11] and adjusting the corrugations strength parameter. The fact that V_{els} contains all second order spherical harmonics suggests that it can induce changes in both the j and m_j rotational quantum numbers. The presence of products of parallel translational functions and second order spherical harmonics suggests that diffraction depends on j and m_j. Recent calculations showed that taking into account V_{els} leads to predictions of large differences between the diffraction of para-$H_2(j = 0)$ and ortho-$H_2(j = 1)$ [15], which have been verified in subsequent experiments [18].

To obtain probabilities for rotationally and diffractionally (in)elastic scattering of H_2 from LiF(001), a time-dependent quantum mechanical method [the close-coupling wave packet (CCWP) method [19]] was used. The wave function is propagated in time using the Chebychev propagation scheme [20]. A scattering amplitude formalism [21] is used to obtain the S matrix. Grid reduction techniques employed include the use of an optical potential [22] and a projection operator formalism [23]. All calculations are done for a collision energy of 100 meV at normal incidence. All probabilities presented below are converged to within better than 1% with respect to the parameters used.

In Fig. 1, probabilities $P(j = 2, m_j = 0 \rightarrow j'm_j')$ and $P(j = 2 \rightarrow j'm_j')$ for rotationally (in)elastic scattering, obtained by summing over the diffraction channels, are shown. The probabilities for $\Delta m_j \neq 0$ transitions in scattering from the initial ($j = 2$, $m_j = 0$) state are quite large (up to 10%). The total probability that m_j changes is 35%, in clear violation of the hitherto assumed $\Delta m_j = 0$ propensity rule. There is little difference between $P(j = 2, m_j = 0 \rightarrow j' = 0)$ and $P(j = 2 \rightarrow j' = 0)$, because the probabilities $P(j = 2, m_j \rightarrow j' = 0)$ are all of similar size. Scattering from statistical ($j = 2$) H_2 produces a slightly nonstatistical distribution of ($j' = 2$, m_j') states.

It is not possible to measure the populations of (j, m_j) states experimentally, but one can measure the rotational alignment A_j^2, which describes the distribution of the orientation of the rotational angular momentum vector of the molecules, and is proportional to the quadrupole moment of that same distribution. Its maximum value is j dependent and approaches $+2$ in the limit of high j for the definition used [24]. Its minimum value is -1 for all j. For a statistical distribution over m_j of the molecules, $A_j^2 = 0$. If all molecules are rotating with $m_j = 0$, $A_j^2 = -1$, and the molecules are said to rotate in cartwheel-type motion. If all molecules are rotating with $m_j = \pm j$, $A_j^2 = +1$ (for the case $j = 2$ considered here), and the molecules rotate in a "helicopter-type" motion.

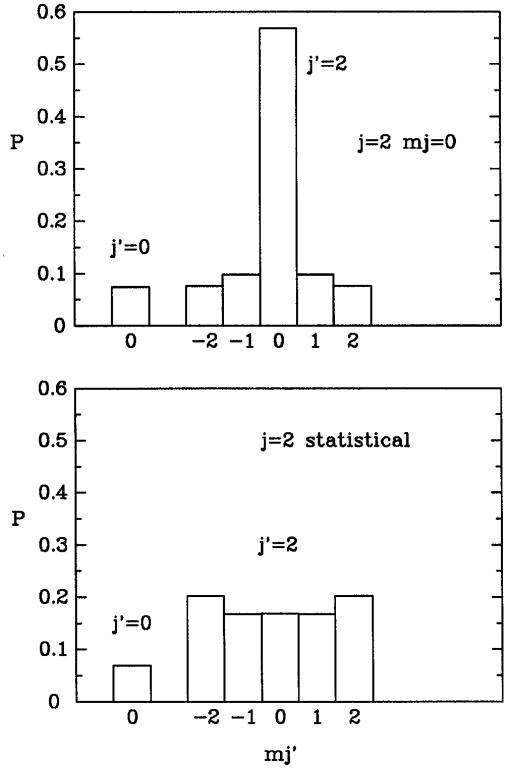

FIG. 1. Probabilities $P(j = 2, m_j = 0 \rightarrow j'm_j')$ and $P(j = 2 \rightarrow j'm_j')$ for rotationally (in)elastic scattering are shown. The upper graph corresponds to scattering of initial ($j = 2$, $m_j = 0$) H_2. The lower graph shows the predictions for scattering of statistical ($j = 2$) H_2.

The total alignment of the scattered molecules with $j' = 2$ in scattering from the initial $(j = 2, m_j = 0)$ state is $A_{j'}^2 = -0.56$. This number is measurable in experiment. By comparing it with the initial alignment $(A_{j'}^2 = -1.0)$, the large magnitude of the $\Delta m_j \neq 0$ transition probabilities predicted here can be confirmed (the maximum value of the alignment is -0.96 in case $P(j = 2, m_j = 0 \rightarrow j' = j, m_j \neq 0) \leq 0.01$ as predicted by the pair potential model studies referred to above [11]. The fact that drastically different results are obtained for $\Delta m_j \neq 0$ transitions when taking into account the electrostatic interaction between the molecule's quadrupole moment and the surface ions clearly suggests that one should consider this interaction when modeling rotational scattering of H_2 off of ionic surfaces. It also suggests that this interaction should be considered when modeling the scattering of slightly larger molecules (like CO and C_2H_2) off of ionic surface, for which experimental results are now emerging [25,26].

Our finding of large probabilities for Δm_j transitions is in disagreement with the $\Delta m_j = 0$ propensity rule suggested by Boato *et al.* [3] for H_2 + LiF(001). We believe their suggestion was based on a misinterpretation of microreversibility. The suggestion was made on the basis of small ratios $P(j = 2 \rightarrow 0)/P(j = 0 \rightarrow 2)$ found experimentally for many diffraction channels. Such a small ratio cannot be attributed to a $\Delta m_j = 0$ propensity rule because such a propensity rule also leads to a smaller value of $P(j = 0 \rightarrow 2)$. Our finding of large probabilities for Δm_j transitions supports the interpretation of Knudsen flow experiments on H_2 + LiF, where some of the results were explained by assuming Δm_j transitions [27].

Figure 2 shows diffraction probabilities, $P(j = 2, m_j = 0 \rightarrow j' = 2, nm)$ and $P(j = 2 \rightarrow j' = 2, nm)$, obtained by summing over the m_j value of the scattered molecules, as a function of the diffraction channel up to and including the third diffraction order (the diffraction order being $|n| + |m|$). From selection rules valid for normal incidence [15], probabilities can be obtained for the symmetry related channels not given here. Rotationally elastic (with respect to j) diffraction from the initial $(j = 2, m_j = 0)$ state is seen to be very different compared to that from $(j = 2)$ H_2, confirming that the diffraction of (j, m_j) H_2 strongly depends on m_j. In particular, $(j = 2)$ H_2 shows relatively more high order diffraction, a trend which is explained below.

In Fig. 3 the alignment is shown as a function of the diffraction channel for scattering of H_2 from the initial $(j = 2)$ state. The alignment is seen to vary strongly over the diffraction channels. Very few molecules with $m_j \neq 0$ are scattered into the specular channel. The most apparent feature about the scattered molecules is the tendency to be more like helicoptering H_2 than cartwheeling H_2 for higher diffraction orders, reaching a maximum alignment of about 0.53 for the diffraction channels (1, 2) and (2, 1).

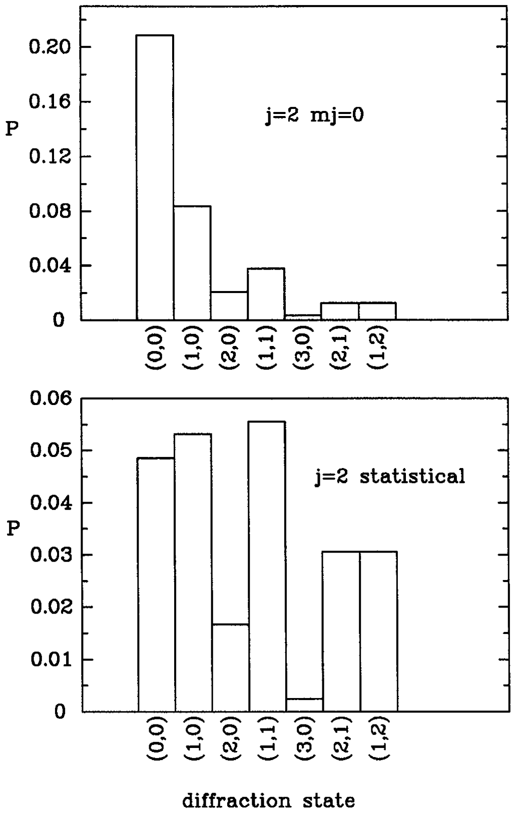

FIG. 2. Probabilities $P(j = 2, m_j = 0 \rightarrow j' = 2, nm)$ and $P(j = 2 \rightarrow j' = 2, nm)$ for diffractionally (in)elastic scattering are shown for diffraction order 0 up to 3. Predictions for scattering of initial $(j = 2, m_j = 0)$ H_2 are plotted in the upper graph. The lower graph gives predictions for scattering of statistical $(j = 2)$ H_2.

The alignment trend in Fig. 3 and the differences in the diffraction of $(j = 2, m_j = 0)$ and $(j = 2)$ H_2 (Fig. 2) can be understood in terms of the "effective" or "rotationally adiabatic" corrugation, which is the corrugation the molecules would see in case it would not be able to change its rotational state [15]. The effective corrugation depends on the value of m_j of the molecule. Helicoptering H_2 sees a highly effective corrugation (because helicoptering H_2 is attracted to the smaller Li^+ ion due to favorable interaction with the excess charge in the H_2 bond, and repelled from the larger F^- ion) and will therefore undergo higher order diffraction, whereas cartwheeling H_2 sees less corrugation, the surface acting more like a mirror, resulting in low order diffraction [15]. Assuming that $\Delta m_j = 0$ during the collision [which is true to the extent that $P(j = 2, m_j \rightarrow j' = 2, m_j) > 50\%$ see Fig. 1 for $m_j = 0$], this behavior leads to a positive alignment in higher order channels and negative alignment in low order diffraction channels for scattering of $(j = 2)$ H_2. This behavior also explains why $(j = 2)$ H_2 (which contains helicoptering H_2) shows more high order diffraction than $(j = 2, m_j = 0)$ H_2 in Fig. 2.

The above effect provides a potentially useful means for constructing rotationally polarized beams of H_2, which

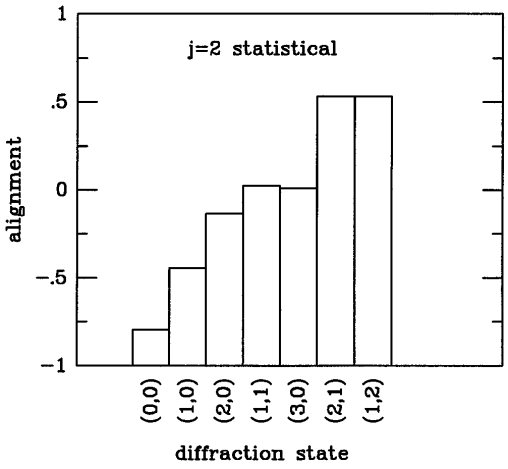

FIG. 3. The alignment $A^2_{j'}$ of the molecules scattered into a particular diffraction channel is shown as a function of the diffraction channel for rotationally and diffractionally (in)elastic scattering of initially statistical ($j' = 2$) H_2.

can be used to study the influence of molecular orientation of H_2 on a variety of inelastic and reactive scattering processes. The construction of rotationally polarized beams in molecule-surface scattering is not new: beams of molecules with negative rotational alignment have been constructed by scattering NO [28] and N_2 [29] from silver. However, in these experiments the polarization of the scattered beam arises from a different physical effect. In scattering of NO and N_2 from Ag, the negative alignment results from transitions with $\Delta m_j \approx 0$ and Δj large. In the scattering of H_2 from LiF(001), the polarization of the beams arises from differences in the diffraction of states with different m_j, so that beams with negative alignment or positive alignment can be constructed by selecting the appropriate diffraction channel.

In summary, predictions are presented for scattering of ($j = 2$, $m_j = 0$) H_2 and ($j = 2$) H_2 from LiF(001). In our calculations, the interaction V_{els} between the quadrupole moment of the molecule and the electrostatic field produced by the crystal ions is taken into account. From its special form one expects transitions to occur that involve changes in the rotational magnetic quantum number and diffraction to be dependent on (j, m_j). Our calculations confirm these expectations, predicting large probabilities for $\Delta m_j \neq 0$ transitions. Our results therefore contradict the hitherto prevalent view that rotational scattering of small homoatomic diatomic molecules off inert surfaces is governed by a $\Delta m_j = 0$ propensity rule. We also predict that scattering of initially unpolarized H_2 should lead to rotationally polarized diffracted beams, suggesting a potentially useful technique for constructing polarized beams of H_2. It should be possible to verify our predictions in experiments on scattering of ($j = 2$, $m_j = 0$) and ($j = 2$) H_2.

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