

Observation of Large Differences in the Diffraction of Normal- and Para-H₂ from LiF(001)

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Large differences have been observed in the diffraction intensities of normal-hydrogen and pure para-hydrogen scattered from the surface of a LiF(001) single crystal. The observed differences are shown to result from a strong coupling between the quadrupole moment of H₂ and the surface electrostatic field, which, in a zeroth order approximation, is averaged out in the case of para-hydrogen. Analogous effects are expected in scattering of all homonuclear diatomic molecules from ionic solids. [S0031-9007(98)07935-6]

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Historically, experiments in which molecular beams of He or H₂ were scattered from ionic crystal surfaces have served to establish the existence of numerous important physical effects. By showing that He and H₂ scattered from LiF undergo diffraction, Stern and co-workers [1] established the wave nature of atoms and molecules. In 1933, these experiments also led to the discovery of the resonance trapping phenomenon, now known as selective adsorption [2], which today is still the best method for quantitatively determining the atom-surface potential [3]. Experiments on H₂ scattering from LiF(001) were among the first to show that molecules colliding with the surface may change their rotational state as well as diffract (rotationally inelastic diffraction, RID). Today very detailed extensive experimental [4] and theoretical [5–7] results are available for both the rotationally elastic and the rotationally inelastic diffraction of normal-H₂ (a mixture of 75% H₂ in $j = 1$ and 25% in $j = 0$ at low temperature), and many physical aspects of the scattering phenomena appeared to be well understood.

In a recent theoretical paper [8], however, it was first pointed out that the scattering should depend rather strongly on the rotational state of the molecules via the electrostatic interaction of the H₂ molecule with the electric fields at the surfaces on ionic crystals such as LiF(001). Especially the interaction between the H₂ quadrupole moment and the individual surface ions introduces a strong orientational dependence into the short-to-medium range molecule-surface interaction. In contrast, the Pauli or exchange repulsion is not significantly affected, since the charge distribution of the electronic cloud at the outer edges of the molecule is nearly spherical [9] and therefore independent of the orientation. The orientational dependence was predicted to lead to large

differences in the diffraction intensities for ortho- and para-H₂. In a first order picture, nonrotating H₂ ($j = 0$) does not “see” the surface ion charges, while the electrostatic interaction directly affects the diffraction of H₂ in the $j = 1$ state. The importance of the electrostatic interaction has already been realized in studies of physisorption of molecules on ionic surfaces for some time [10,11], but had been completely overlooked in connection with (rotationally elastic) molecular diffraction.

In the present Letter, new high resolution diffraction experiments are reported, in which the diffraction patterns of cold para-H₂ ($j = 0$) are compared with those of cold normal-H₂. Indeed, largely different diffraction probabilities are observed experimentally for scattering of the two hydrogen species from LiF(001), which are explained in terms of the recent theoretical prediction [8]. The experimental data are in good agreement with diffraction calculations which are tailored to the experimental conditions and which include the electrostatic interaction. In contrast, calculations that omit this interaction predict comparable diffraction probabilities for para-H₂ (p -H₂) and normal-H₂ (n -H₂), thus confirming that the experimentally observed differences in the diffraction of p -H₂ and n -H₂ are due to the electrostatic interaction.

The experimental apparatus has been described in detail in Refs. [12,13]. In its fixed angle geometry ($\theta_i + \theta_f = 90.1^\circ$), diffraction patterns (angular distributions) were measured by rotating the crystal around an axis normal to the plane of the incident and scattered beams. Hence, the incident angle θ_i and the final angle θ_f are varied simultaneously. Rotationally cold molecular beams of hydrogen with an energy resolution of $\frac{\Delta E}{E} \sim 8\%$ were generated by free jet expansion from a pressure of about 50 bar through a 10 μm diameter nozzle. By

varying the nozzle temperature from 100 to 330 K, H_2 -beam energies between 21 and 93 meV were obtained. A magnetic mass spectrometer, operating in the ion counting mode, was used to detect the scattered hydrogen molecules with an effective angular resolution of $\Delta\theta = 0.05^\circ$. The surface was prepared by *in situ* cleaving off a small slice from a LiF single crystal with an area of $10 \times 10 \text{ mm}^2$. The $p\text{-H}_2$ was converted from liquid normal- H_2 by an iron oxide and chromium oxide catalyst. The $p\text{-H}_2$ content obtained with this method was previously determined by Jozefowski *et al.* [14] to be about 95%. Because of the large energy difference between the allowed rotational states of $p\text{-H}_2$ ($\Delta E(j = 0 \rightarrow 2) = 44 \text{ meV}$ [15]) and the relatively low source temperatures ($T_N \leq 330 \text{ K}$), only a small fraction ($<4\%$) of the $p\text{-H}_2$ beam is in the $j = 2$ rotational level [16]. Similarly, because of the even larger difference for ortho- H_2 ($o\text{-H}_2$) of $\Delta E(j = 1 \rightarrow 3) = 73 \text{ meV}$ nearly all of the molecules in the $n\text{-H}_2$ beam are in either the $j = 0$ or $j = 1$ states in the ratio of 1:3 determined by the spin degeneracy.

Figure 1 shows two angular distributions for the scattering of normal- and para-hydrogen from the LiF(001) surface measured along the $[110]$ azimuthal directions. The angular distributions are dominated by rotationally elastic, i.e., j -conserving, diffraction peaks which are designated by $(\pm k, l)$, where k is the diffraction peak order in this direction and $l = 0$. As seen from the figure, the first $[I(1, 0)]$ and second order $[I(2, 0)]$ diffraction peak intensities relative to the specular peak $[I(0, 0)]$ are considerably lower for $n\text{-H}_2$ than for $p\text{-H}_2$. The much weaker structures labeled with small letters (*a*, *b*, and *c*) in Fig. 1 have been assigned to rotationally inelastic diffraction involving

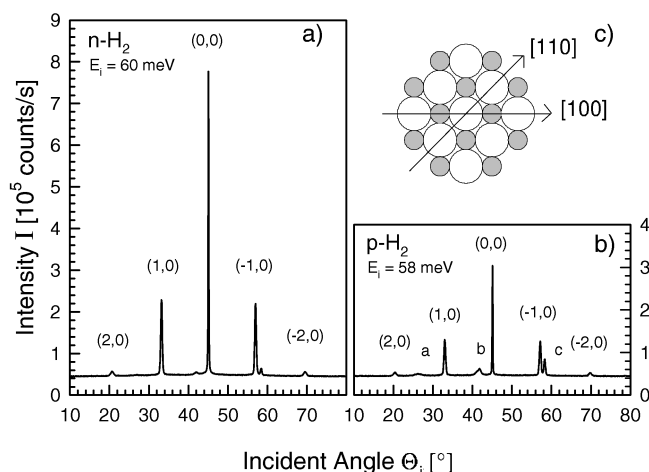


FIG. 1. Two angular distributions of $n\text{-H}_2$ (a) and $p\text{-H}_2$ (b) molecules scattered from LiF(001) along the $[110]$ azimuthal direction measured at the given incident energies E_i and at a surface temperature of $T_s = 300 \text{ K}$; *a*, *b*, and *c* label rotationally inelastic diffraction peaks for the $j = 0 \rightarrow 2$ transition involving the following reciprocal lattice vectors $\mathbf{G} = (G_\perp, G_\parallel)$: *a*— $(0, 0)$, *b*— $(-1, 0)$, and *c*— $(-2, 0)$, respectively. In (c) the structure of the LiF(001) surface is shown; the Li^+ are depicted by grey circles.

the $j = 0 \rightarrow 2$ transition and the reciprocal lattice vectors $\mathbf{G} = (0, 0)$, $(-1, 0)$, and $(-2, 0)$, respectively [17].

In Fig. 2, the integrated intensities of the first and second order peaks relative to the specular peak are plotted as a function of beam energy. To reduce uncertainties due to possibly inaccurate alignment of the crystal, the average of the $(+k, 0)$ and $(-k, 0)$ peak areas is plotted, since the probabilities for scattering in these channels must be equal for the symmetrically corrugated LiF(001) surface. Over the whole range of incident energies, the probabilities for the diffraction into the first and second order diffraction channels are higher for $p\text{-H}_2$ than for $n\text{-H}_2$ [18].

The close coupling (CC) method [5] was used to calculate probabilities for rotationally and diffractively elastic scattering. In its formalism, the time-independent Schrödinger equation is written as a system of coupled second order linear differential equations in the scattering coordinate z , the equations being coupled in a basis of diffraction and rotation functions. In the basis set, $j \leq 4$ and $|k| + |l| \leq 5$ were taken in the calculations for $p\text{-H}_2$, and $j \leq 5$ and $|k| + |l| \leq 5$ in the calculations for $o\text{-H}_2$. In computing a particular diffraction probability, θ_i is taken such that $\theta_i + \theta_f = 90^\circ$, as in the experiments.

The molecule-surface interaction was described by a potential presented in detail elsewhere [8]. Briefly, it contains terms describing the induced dipole-induced dipole interaction, the induced dipole-induced quadrupole interaction, the ionic lattice-induced dipole interaction,

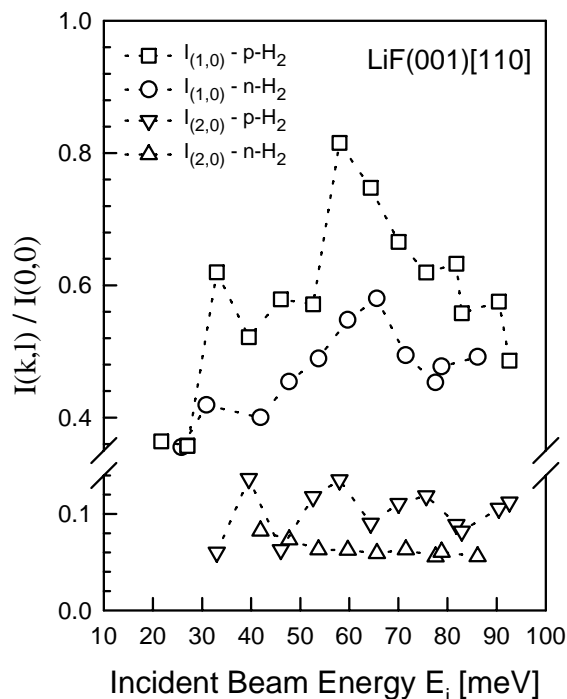


FIG. 2. Ratios of integral intensities of diffraction peaks $I(k, l)$ to the specular peak intensity $I(0, 0)$ for $n\text{-H}_2$ and $p\text{-H}_2$. $I(1, 0)$ corresponds to the first order diffraction peaks along the $[110]$ direction, whereas $I(2, 0)$ denotes the second order diffraction peaks. The experiments were performed at $T_s = 300 \text{ K}$.

and the short range repulsion, which is mostly Pauli or exchange repulsion. The term which is most important to this work is the electrostatic interaction V_{els} which is written as [8,19]

$$V_{\text{els}} = -\Theta \sqrt{\frac{\pi}{30}} \sum_{k,l} \{A_{kl} \exp[iG(kx + ly)] \exp(-\gamma_{kl}z) [\exp(i2\xi)Y_{22}(\theta, \phi) + \exp(-i2\xi)Y_{2-2}(\theta, \phi) - 2i \exp(i\xi)Y_{21}(\theta, \phi) + 2i \exp(-i\xi)Y_{2-1}(\theta, \phi) - \sqrt{6}Y_{20}(\theta, \phi)]\}, \quad (1)$$

where

$$\exp(i\xi) = (k - il) \sqrt{k^2 + l^2}. \quad (2)$$

In Eq. (1), z is the distance to the surface, Θ is the quadrupole moment of H_2 , and $G = \sqrt{2\pi}/a$, where a is the surface lattice parameter ($a = 2.84 \text{ \AA}$). For detailed expressions for the A_{kl} and γ_{kl} coefficients, see Refs. [8,19]. The fact that V_{els} contains products of parallel translational functions and second order spherical harmonics suggests that diffraction may depend on the rotational state j (and m_j).

Differences in the diffraction of $p\text{-H}_2$ ($j = 0$) and $n\text{-H}_2$ (75% $j = 1$, $o\text{-H}_2$) can be understood by considering the effect of orientational averaging on the electrostatic interaction, neglecting changes in the rotational angular momenta j . For $j = 0$ $p\text{-H}_2$, all orientations are equally likely and, hence, the (orientation-dependent) electrostatic interaction averages out to zero. Mathematically, this may be understood from the fact that the matrix element $\langle Y_{00} | V_{\text{els}} | Y_{00} \rangle$ equals zero, because V_{els} is written in terms of second order spherical harmonics (Y_{2m_j}) only [20]. Therefore, in elastic diffraction, $p\text{-H}_2$ does not see the surface electrostatic field, and so its diffraction is not affected. In contrast, for $j = 1$, m_j , $o\text{-H}_2$, the molecule possesses a net orientation depending on m_j , and is affected by the electrostatic interaction leading to diffraction in which j is conserved and m_j may or may not be conserved (changes in only m_j being isoenergetic). Mathematically, this can be attributed to the fact that $\langle Y_{1m'_j} | V_{\text{els}} | Y_{1m_j} \rangle$ differs from zero for all possible m_j and m'_j , since all second order spherical harmonics ($m_j = -2$ to $+2$) occur in the expression for V_{els} .

A similar argument can be derived based on the first order Born approximation, assuming that the molecule-surface interaction can be written in terms of V_{els} and that j is conserved. Under these approximations, only transitions ($j m_j 00 \rightarrow j' m'_j k l$) are allowed for which $\langle j' m'_j k l | V_{\text{els}} | j m_j 00 \rangle$ differs from zero. By the same arguments as used above, this integral can differ from zero for $j = 1$, but not for $j = 0$. Note that, for the integral to differ from zero, $|k| + |l|$ has to be odd, while the largest values of this integral will be obtained for $|k| = 1$ and $|l| = 0$, or vice versa [19]. Therefore V_{els} is expected to have the largest effect on the first order diffraction probabilities which are naturally obtained as the in-plane diffraction probabilities along the $[110]$ direction, as measured in this work.

Figure 3 compares experimental (open symbols) and theoretical results (black symbols) for the scattering of

$p\text{-H}_2$ (a) and $n\text{-H}_2$ (b) in the $[110]$ direction. The calculations reproduce the diffraction probability ratios, which have been experimentally observed to be nearly a factor of 2 larger for $p\text{-H}_2$, within about 15% of this difference between the probability ratios for $n\text{-H}_2$ and $p\text{-H}_2$. In contrast to the calculations that employ the potential including V_{els} , calculations for $n\text{-H}_2$ and $p\text{-H}_2$, respectively, in which the electrostatic interaction V_{els} has been excluded from the molecule-surface potential (triangles in Fig. 3) result in almost equal diffraction probabilities for $n\text{-H}_2$ and $p\text{-H}_2$. This clearly indicates that V_{els} is responsible for the differences between the diffraction of $p\text{-H}_2$ and $n\text{-H}_2$ observed experimentally. The results of analogous calculations and measurements

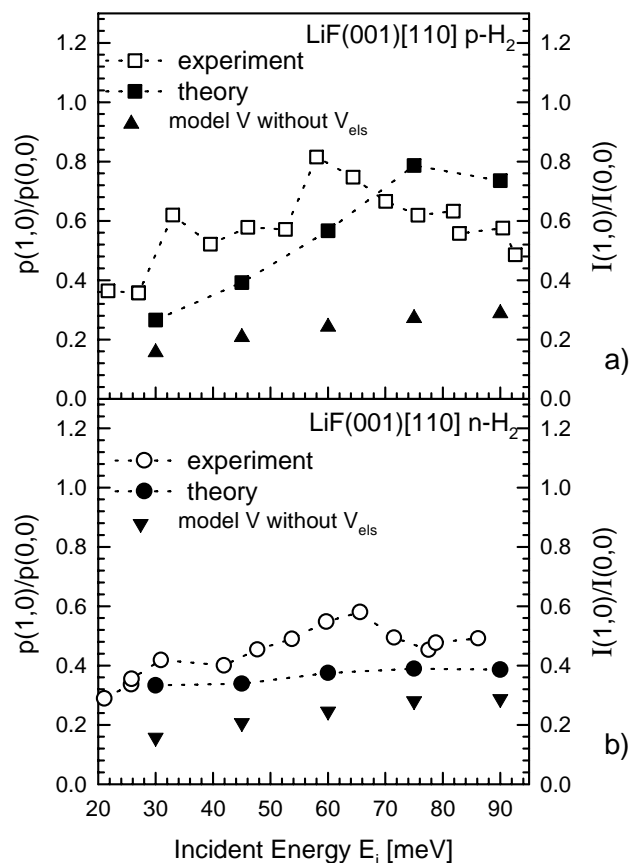


FIG. 3. The ratios of the calculated probabilities of first order diffraction $p(1,0)$ and specular reflection $p(0,0)$ are compared to the ratios of the experimental intensities $I(1,0)$ and $I(0,0)$ for rotationally elastic scattering of $p\text{-H}_2$ (a) and $n\text{-H}_2$ (b) along the $[110]$ direction. The up- and down-pointing triangles represent calculations for $p\text{-H}_2$ and $n\text{-H}_2$, respectively, in which V_{els} was excluded from the model potential.

for the [100] direction, which will be presented in a forthcoming paper [21], are also in good qualitative agreement in that they show significantly different in-plane diffraction probabilities for p -H₂ and n -H₂ only if V_{els} is included into the potential. However, the quantitative agreement between the theory and experiment was not as good as for the [110] direction, which may perhaps be attributed to the fact that in-plane diffraction along the [100] direction is less directly affected by the electrostatic interaction (V_{els} promoting diffraction along this direction only in a higher order perturbative approximation, since $|k| + |l|$ is even). This point and possible reasons for the remaining differences between theory and experiment in Fig. 3 will be addressed in more detail elsewhere [21].

In conclusion, experimental evidence for large differences in the diffraction probabilities of rotationally cold beams of n -H₂ and p -H₂ from the LiF(001) surface is reported. The observed effect is attributed to the electrostatic coupling between the quadrupole moment of H₂ and the ionic lattice. According to first order perturbation theory, the electrostatic interaction strongly affects the diffraction of ($j = 1$) H₂ [the major constituent (75%) of cold n -H₂], while it influences the diffraction of ($j = 0$) H₂ (cold p -H₂) only indirectly. The good agreement between the experimental data and the results of the close-coupling calculations including the electrostatic interaction V_{els} , and the fact that the difference between diffraction of p -H₂ and n -H₂ disappears if V_{els} is omitted from the calculations, unambiguously demonstrates that the electrostatic interaction is responsible for the observed effect.

The investigations presented here open new possibilities to isolate and probe the electrostatic interaction between nonpolar molecules which possess a permanent quadrupole moment and ionic surfaces, such as H₂, F₂, and N₂ interacting with ionic halide, oxide, or other insulator surfaces. In principle, these experiments can provide very direct information on the ionicity of the surface. The effect is expected to be the most pronounced for H₂ due to its large rotational constant, whereas for heavier molecules such as N₂ or F₂, indirect interaction mechanisms may also become important. Because of the better signal to noise ratios, inelastic time-of-flight experiments with D₂ are expected to give even more detailed insight into these very interesting phenomena.

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