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## Direct Observation of H<sub>2</sub> Binding to a Metal Oxide Surface

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Inelastic neutron scattering is used to probe the dynamical response of H<sub>2</sub> films adsorbed on MgO(100) as a function of film thickness. Concomitant diffraction measurements and a reduced-dimensionality quantum dynamical model provide insight into the molecule-surface interaction potential. At monolayer thickness, the rotational motion is strongly influenced by the surface, so that the molecules behave like quasipolar rotors. These findings have a direct impact on understanding how molecular hydrogen binds to the surface of materials used in catalytic and storage applications.

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When H<sub>2</sub> molecules adsorb on a surface, H<sub>2</sub>-surface interactions mix together the rovibrational quantum states of a gas-phase H<sub>2</sub> molecule and thus shift the energy levels of the adsorbed molecules away from those of gas-phase H<sub>2</sub> [1]. Experimental probes of these shifts, when paired with quantum dynamical models of the adsorbate's perturbed rovibrational states, provide direct insight into the functional form of the H<sub>2</sub>-substrate interaction. A detailed understanding of these interactions plays a central role in efforts to elucidate the mechanistic aspects of heterogeneous catalysis, can facilitate the rational design of catalytically active nanoscale materials, and will aid in the development of new materials for fast-cycling, high-capacity hydrogen storage technologies. In this Letter, we show that inelastic neutron scattering (INS) spectroscopy techniques provide detailed information about H<sub>2</sub> interactions with the prototypical metal oxide surface MgO(100).

INS techniques are unrivalled in sensitivity and precision for probing the rovibrational dynamics of condensed-phase H<sub>2</sub> molecules [2]. They present several advantages over infrared spectroscopic and helium atom scattering methods for interrogating the dynamics of H<sub>2</sub> adsorbates: Neutron scattering does not depend on the weak transition dipole moment induced in H<sub>2</sub> adsorbates by the underlying surface (i.e., no optical selection rules), neutrons can penetrate deeply through bulk matter to provide information about adsorbate dynamics in the multilayer adsorption regime, and, unlike infrared or helium atom scattering techniques (see, for example, Refs. [3,4]), INS spectroscopy can directly probe the para → ortho ( $j = 0 \rightarrow 1$ ) transition of H<sub>2</sub> adsorbates.

Here we report INS studies of monolayer and multilayer H<sub>2</sub> films adsorbed on nearly defect-free MgO(100) surfaces and interpret these studies with the aid of a reduced-dimensionality quantum dynamical model for the H<sub>2</sub> adsorbates. Our studies show that, for this system, the  $j = 0 \rightarrow 1$  rotational transition previously observed in INS studies of both bulk H<sub>2</sub> and H<sub>2</sub> adsorbed on carbon-based

materials is shifted to substantially lower energy due to interactions between the H<sub>2</sub> adsorbates and the MgO(100) surface. Our findings suggest that these interactions substantially hinder the adsorbates' end-over-end rotational motion and that the hindering potential is strong enough that the first-layer H<sub>2</sub> molecules acquire partial two-dimensional (2D) character.

We have recently developed a process [5] for synthesizing large quantities of highly pure, nearly defect-free MgO nanocubes (with edge length approximately 200 nm) that have essentially only the MgO(100) surface exposed. Before employing them in our adsorption studies, the nanocubes are heated to  $T = 950^\circ\text{C}$  for more than 48 hours *in vacuo* ( $p \approx 10^{-7}$  torr) to homogenize their surfaces and then, within an Ar-filled dry box, transferred to a thin-walled Al neutron scattering cell. An automated adsorption apparatus [6] is then used to record a set of high-resolution volumetric adsorption isotherms for H<sub>2</sub> and D<sub>2</sub> on the nanocubes at temperatures between 7 and 15 K. Figure 1(a) shows a typical adsorption isotherm for H<sub>2</sub> on MgO at  $T = 10$  K and clearly demonstrates that film growth takes place in a layer-by-layer fashion (where six adsorption steps are readily visible). These thermodynamic features are consistent with the earlier findings of Vilches and co-workers [7].

We probe the rotational dynamics of H<sub>2</sub> adsorbates on these MgO nanocubes using TOSCA at ISIS, an inverted geometry crystal analyzer spectrometer that covers a broad energy transfer range (1–500 meV) with good energy resolution ( $\Delta E/E \approx 2\%$ ). Figure 1(b) shows the neutron energy loss spectra for H<sub>2</sub> films on MgO(100) as a function of thickness; these INS difference spectra were obtained by subtracting the signal of the bare MgO nanocubes from the H<sub>2</sub> + MgO sample signal.

The spectra evolve as follows with increasing coverage  $\Theta$  [8]. For the lowest coverage film, a single narrow feature appears at an energy transfer of 11.25 meV [9]. This feature is located substantially below the  $j = 0 \rightarrow 1$  transition energy of 14.7 meV for a free-rotor H<sub>2</sub> molecule in

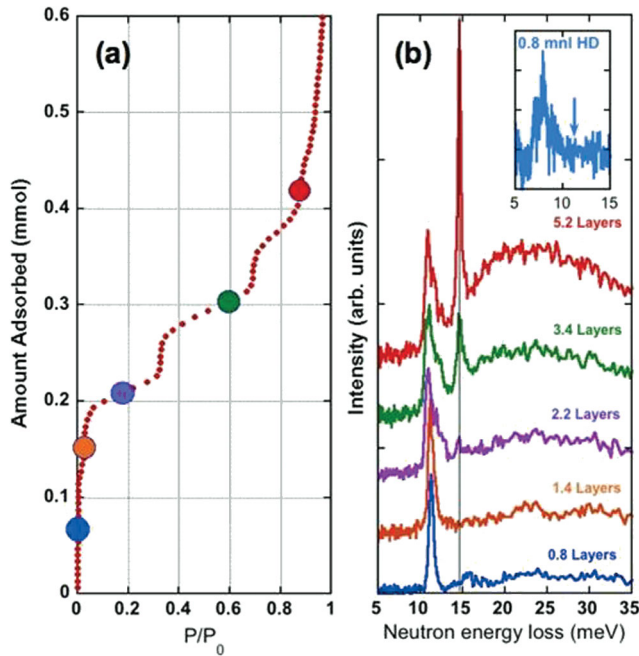


FIG. 1 (color). (a) Adsorption isotherms for  $\text{H}_2$  on  $\text{MgO}(100)$  at  $T = 10$  K. (b) Neutron energy loss spectra at  $T \approx 12$  K. Spectra recorded at color-coded point in (a). The hairline located at 14.7 meV in (b) locates  $j = 0 \rightarrow 1$  transition energy in bulk solid  $\text{H}_2$ . The inset shows a spectrum for 0.8 layer of HD; the arrow marks the 11.25 meV feature of 0.8-layer  $\text{H}_2$  film.

3D space ( $14.7 \text{ meV} = 2B_{\text{HH}} = \hbar^2/I_{\text{HH}}$ , where  $I_{\text{HH}}$  is the  $\text{H}_2$  moment of inertia) and well above the 7.35 meV  $j = 0 \rightarrow 1$  transition energy for planar free-rotor  $\text{H}_2$  molecules ( $7.35 \text{ meV} = B_{\text{HH}}$ ). To confirm that this feature is associated with the adsorbates'  $j = 0 \rightarrow 1$  transition, we also recorded the INS spectrum of a 0.8-layer film of HD on  $\text{MgO}(100)$ . As the inset in Fig. 1(b) shows, the corresponding transition in the HD film occurs at 7.9 meV, which is between the  $j = 0 \rightarrow 1$  HD transition energies of 5.55 (2D) and 11.1 meV (3D). Molecular free-rotor energies scale with rotational constant  $B$ , and  $B_{\text{HD}}/B_{\text{HH}} = 0.75$ ; applying this scaling factor to the 11.25 meV transition for  $\text{H}_2$  gives a predicted transition energy of 8.4 meV for HD in reasonably good agreement with the observed transition energy. (Excitations associated with molecular vibration against the  $\text{MgO}$  surface would scale inversely with the square root of the adsorbate mass; in this case, the 11.25 meV feature for  $\text{H}_2$  would shift to 9.7 meV for HD.)

As  $\Theta$  increases, the feature at 11.25 meV redshifts and broadens on its higher energy transfer side. For  $\Theta > 2$ , the now-broadened peak at 11.25 meV has developed a noticeable high-energy shoulder. At  $\Theta = 3$ , a second inelastic feature emerges from the background at an energy transfer of 14.7 meV, which matches the transition energy for the  $j = 0 \rightarrow 1$  transition in both gas-phase  $\text{H}_2$  molecules and the low temperature bulk  $\text{H}_2$  solid. With further increases in  $\Theta$ , the intensity of the feature at 14.7 meV grows steadily, and a broad multiphonon hump, peaked at roughly

22 meV, appears. However, throughout this entire coverage regime, neither our thermodynamic studies nor our structural studies (described next) indicate that bulk solid  $\text{H}_2$  forms in the sample cell.

To help us analyze the INS data, we performed a detailed neutron diffraction investigation of the evolution of the films' structure with increasing coverage (see Ref. [10]). These diffraction studies used  $\text{D}_2$  as the adsorbate because deuterium has a large coherent neutron scattering cross section (whereas hydrogen has a large incoherent scattering cross section). The left panel in Fig. 2 shows the diffraction profiles for two  $\text{D}_2$  films at different coverages; as before, these profiles are difference traces. The upper diffraction profile in Fig. 2(a) corresponds to the lowest coverage (0.8 layer) INS spectrum shown in Fig. 1(b); the lower profile [Fig. 2(b)] approximately corresponds to the most dense monolayer film (1.4 layers) shown in Fig. 1(b). The diffraction patterns recorded in the monolayer regime exhibit the classic sawtooth profile [11] expected from a powder-averaged "2D solid," while patterns recorded for thicker films (not shown) are consistent with the formation of multilayer solids [12].

Our diffraction measurements reveal that, for the coverage range  $0.20 < \Theta < 0.80$ ,  $\text{D}_2$  films form a commensurate solid that grows islandlike in a  $c(2 \times 2)$  structure [Fig. 2(c)] until it covers the  $\text{MgO}$  surface; in such a structure, all of the  $\text{D}_2$  molecules reside above identical

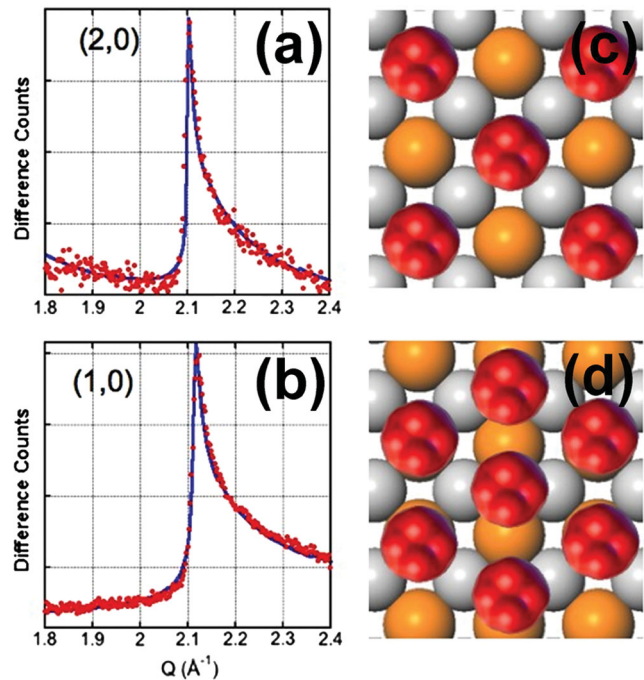


FIG. 2 (color). Neutron diffraction difference profiles for (a) 0.8-layer and (b) 1.2-layer  $\text{D}_2$  films on  $\text{MgO}(100)$ . Solid lines represent line fits using powder-averaged 2D Lorentzian line shapes for a  $c(2 \times 2)$  and a hexagonal structure schematically shown in (c) and (d). Quasiplanar rotation is pictured using orblike  $\text{H}_2$  molecules. Note uniform occupation of atop  $\text{Mg}^{2+}$  sites in (c) and displacement from the atop site in (d).

surface sites. For coverages in the range  $0.80 < \Theta < 1.05$ , a uniaxial compression of the  $c(2 \times 2)$  structure takes place. It appears that this process involves the formation of a sequence of commensurate solids that can be indexed as  $p(2 \times 4)$  and  $p(2 \times 6)$ ; however, we are still in the process of analyzing the data self-consistently by combining diffraction data recorded at fixed temperature as a function of coverage with that recorded at fixed coverage as a function of temperature. At monolayer completion, a hexagonally close-packed solid with a lattice constant of  $\approx 3.3 \text{ \AA}$  forms [see Fig. 2(d)]. This translates to a density of  $\approx 0.106 \text{ \AA}^2/\text{molecule}$ , a value consistent with the findings of Ma *et al.* ( $0.104 \text{ \AA}^2/\text{molecule}$ ) [7,13].

While our diffraction data are generally consistent with a brief communication by Degenhardt, Lauter, and Haensel [14], we are unable to use their intermediate coverage structural parameters to self-consistently fit our diffraction data. The enhanced quality of our MgO substrates and the higher resolution and intensity of the diffractometers used in the present work (OSIRIS at ISIS and D20 at Grenoble's Institut Laue Langevin) yield diffraction profiles and structural parameters that are better resolved and statistically superior to these earlier measurements.

The 11.25 meV feature seen in the bottom INS spectrum of Fig. 1(b) measures the energy difference between the lowest para and ortho states for first-layer  $\text{H}_2$  molecules adsorbed onto MgO(100). To understand how the  $\text{H}_2$ -MgO(100) interaction controls this difference, we construct a quantum dynamical model for isolated  $\text{H}_2$  adsorbate molecules bound to the MgO surface by an empirical potential energy function  $V = V_{\text{el}} + V_{\text{ind}} + V_{\text{disp}} + V_{\text{rep}}$ . Here  $V_{\text{el}}$  is the electrostatic interaction between the  $\text{H}_2$  quadrupole moment and the MgO(100) near-surface electric field;  $V_{\text{ind}}$  is the induction energy arising from interaction of the  $\text{H}_2$  anisotropic dipole polarizability tensor with this field;  $V_{\text{disp}}$  is a sum of anisotropic  $\text{H}_2$ - $\text{O}^{2-}$  dispersion interactions, estimated using the Slater-Kirkwood formula [15], the  $\text{H}_2$  anisotropic dipole polarizability tensor, and the  $\text{O}^{2-}$  in-crystal isotropic dipole polarizability of 11.34 a.u. [16]; and  $V_{\text{rep}}$  is a sum of repulsive atom-atom interactions taken from an earlier theoretical study of  $\text{CH}_4$  adsorbates on MgO(100) [17]. (Because the  $\text{Mg}^{2+}$  in-crystal polarizability is small [16], we neglect  $\text{H}_2$ - $\text{Mg}^{2+}$  dispersion interactions.) The atomic partial charges of the Mg and O ions in the top surface layer, which determine the MgO near-surface electric field [18], are treated as adjustable parameters. Other similar approaches include studies by Novaco and Wroblewski, who examined the rotational states of  $\text{H}_2$  levels on graphite, and by Silvera and Nielsen [19], who used a two-parameter potential [20] to describe  $\text{H}_2$  rotors adsorbed on alumina.

We approximate the  $\text{H}_2$  adsorbate wave function  $\Psi$  as the product of an anisotropic 3D harmonic oscillator function describing the adsorbate's center-of-mass motion and a rotational function describing the hindered rotational motion of the adsorbate, that is, a linear combination of

free-rotor states. For a given value of the surface-layer Mg ionic charge  $q$  (measured in units of  $q_e$ ), we variationally optimize  $\Psi$  for para- and ortho- $\text{H}_2$  adsorbates above  $\text{Mg}^{2+}$  ions [21] and take the difference  $\Delta_{\text{po}}$  between the adsorbate binding energies as an estimate of the para-ortho splitting probed in our INS experiments. The computed binding energy of a single para- $\text{H}_2$  adsorbate molecule  $E_p$  is closely related to the isosteric heat of adsorption  $Q_{\text{st}}$  for  $\text{H}_2$  monolayers on MgO(100), although  $E_p$  neglects lateral  $\text{H}_2$ - $\text{H}_2$  interactions. The para- $\text{H}_2$  rotational wave function correlates with the free rotor's  $(j, m) = (0, 0)$  state, while the ortho- $\text{H}_2$  wave function correlates with the  $(j, m) = (1, \pm 1)$  free-rotor state.

Figure 3 shows how  $E_p$  and  $\Delta_{\text{po}}$  depend on the surface-layer ionic charge  $q$ . For large  $q$  values, the adsorbates bind strongly to the MgO(100) surface and are almost completely horizontal; the para-ortho splitting  $\Delta_{\text{po}}$  is only slightly greater than the 7.35 meV splitting for  $\text{H}_2$  rotors in 2D. As  $q$  decreases, though,  $V_{\text{el}}$  and  $V_{\text{ind}}$  weaken,  $E_p$  decreases, and  $\Delta_{\text{po}}$  rises, indicating a gradual transition from "helicopter-style" rotation of nearly planar  $\text{H}_2$  molecules to a rotational motion which is intermediate between two and three dimensions in character. This is in accord with the fact that  $V_{\text{el}}$  dominates the anisotropy of the  $\text{H}_2$ -MgO interaction. The strong dependence of  $E_p$  on  $q$  suggests that precise measurements of the isosteric heat of adsorption  $Q_{\text{st}}$  for this system would provide additional information about the underlying  $\text{H}_2$ -MgO(100) interaction.

At  $q = 1$ , the computed  $\Delta_{\text{po}}$  values are comparable in magnitude to the experimentally observed para-ortho splitting of 11.25 meV. Such a departure from fully ionic character of the MgO surface was observed [22] in studies that employed a similar empirical molecule-surface interaction to compute the adsorption energy for  $\text{NH}_3$  molecules on MgO(100); these workers found that the computed  $\text{NH}_3$ -MgO adsorption energy agreed well with experiment for  $q \approx 1$ . Recent density functional studies of  $\text{CH}_4$  adsorbates on MgO [23] suggest that quantum chemical calculations could shed further light on the value of  $q$ .

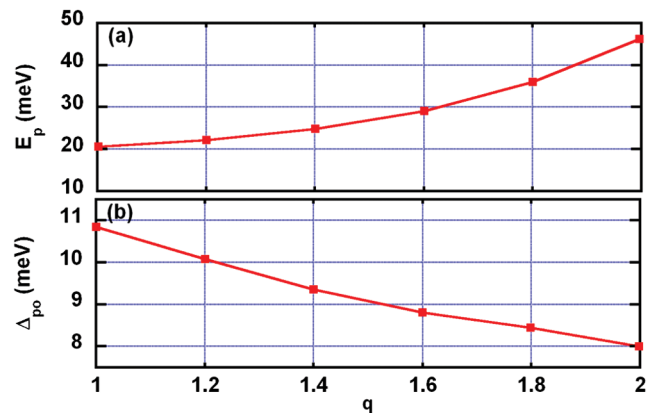


FIG. 3 (color). Variations of (a)  $E_p$  and (b)  $\Delta_{\text{po}}$  with the surface-layer Mg atomic charge  $q$ .

We note, however, that the  $q$  value obtained from periodic slab models of the bare MgO(100) surface is fairly sensitive to the size of the orbital basis set used in the calculations [24], indicating that careful basis set convergence studies are needed to obtain reliable  $q$  values from quantum chemical studies.

We have used a combination of thermodynamic measurements, neutron diffraction studies, INS techniques, and computational methods to investigate the binding of H<sub>2</sub> and D<sub>2</sub> to the MgO(100) surface. Our INS results indicate, and our computational studies substantiate, that the 11.25 meV energy transfer feature observed for first-layer H<sub>2</sub> adsorbates is associated with the hindered, quasiplanar rotational motion of H<sub>2</sub> molecules adsorbed atop Mg<sup>2+</sup> cations on the MgO(100) surface. Measurements using HD verify that we have correctly associated the inelastic feature with the adsorbates' rotational motion.

At coverages  $\Theta$  above those that complete the  $c(2 \times 2)$  adsorption phase, this feature broadens asymmetrically, acquiring a shoulder on its high-energy side; we interpret this as evidence that some of the adsorbate molecules have been displaced slightly from the atop-Mg<sup>2+</sup> site (a conclusion consistent with our diffraction data). At even higher surface coverages ( $\Theta > 2$ ), another feature appears in the INS spectrum at 14.7 meV, very close to the transition energy for the  $j = 0 \rightarrow 1$  transition of individual H<sub>2</sub> molecules in the bulk solid. This feature intensifies with increasing coverage, although the low-energy feature near 11.25 meV remains visible in the INS spectra of films as thick as five layers. These observations are consistent with a picture in which molecules in the third layer and above experience nearly isotropic local potentials dominated by H<sub>2</sub>-H<sub>2</sub> interactions rather than H<sub>2</sub>-MgO interactions. (Recall that the electrostatic component of  $V$ , which makes up the dominant portion of the H<sub>2</sub> orientational potential, decays exponentially as  $z$  increases.) Such a picture is reminiscent of the dynamics of CH<sub>4</sub> adsorbates on MgO(100) in a similar coverage regime [25]. Our future efforts will be aimed at obtaining a quantitative model for the H<sub>2</sub>-MgO interaction that can be used to understand H<sub>2</sub> adsorbate dynamics in both monolayer and multilayer films.

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