The PASADENA Effect at a Solid Surface: High-Sensitivity Nuclear Magnetic Resonance of Hydrogen Chemisorption

Paul J. Carson,[†] C. Russell Bowers,[‡] and
Daniel P. Weitekamp*

Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, California 91125

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The use of parahydrogen as a high-sensitivity spin label for nuclear magnetic resonance (NMR) was first proposed[1] and then demonstrated[2] to provide orders-of-magnitude signal enhancement in species which are formed from the molecular addition of hydrogen. The phenomenon known as the PASADENA effect (parahydrogen and synthesis allow dramatically enhanced nuclear alignment) derives from the fact that deviation of the parahydrogen mole fraction in a sample of H_2 from its statistical high-temperature limit of 1/4 is associated with an inherent form of spin order. Upon molecular addition of the two protons from a single H_2 molecule into coupled, magnetically inequivalent environments, this order is manifested as large nonequilibrium spin population differences across allowed NMR transitions.

Since its prediction and initial demonstration, the PASADENA effect has been applied to several systems involving homogeneous catalysis.[3−6] It has been used to detect hydrogenation intermediates, as well as to study reaction mechanisms and kinetics. Here we describe the first extension of the PASADENA method to the *solid state*.[7,8]

Reversible H_2 adsorption on ZnO was performed in an NMR probe[9] using both normal and para-enriched H_2. Figure 1a shows the spectrum observed when a burst of n-H_2 was delivered to the sample. The 1 kHz-wide line is attributed to gas-phase o-H_2 (gas-phase p-H_2 is not NMR active). The broad weak resonance is due to species present before the H_2 burst.

Figure 1b shows the same experiment repeated with para-enriched H_2. A prominent antiphase pattern is seen that is interpreted as the PASADENA NMR of hydrogen chemisorbed on ZnO. Signal from the same adsorption sites is not detected in the n-H_2 spectrum, nor is it seen in previous NMR studies of H_2 on ZnO.[10,11] To obtain the pure PASADENA signal, a fit to the gas-phase peak in Figure 1a was weighted by a factor of 2/3 and then subtracted from Figure 1b, since the ortho mole fraction was 3/4 in n-H_2 and 1/2 in the para-enriched H_2. A fit to the broad background resonance in Figure 1a was also subtracted. The resulting pure PASADENA spectrum is shown in Figure 1c.

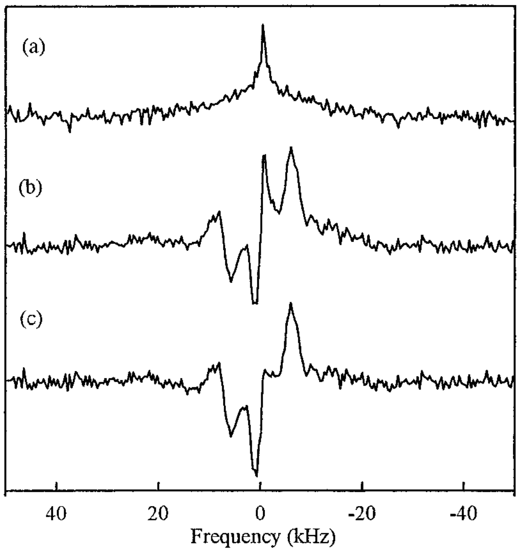
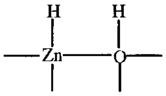


Figure 1. (a) ^1H NMR spectrum immediately after a nominal 50 ms burst of n-H_2 delivered to polycrystalline ZnO. (b) Spectrum taken under the same conditions as in (a) but using para-enriched H_2 instead of n-H_2. Strong PASADENA enhancement is seen for sites not detected in the n-H_2 experiment. (c) Pure PASADENA spectrum obtained by taking the ortho-weighted difference of (a) and (b), as described in the text.

The zinc oxide substrate used in these studies is an important component in methanol synthesis catalysts, as well as olefin hydrogenation catalysts. Adsorption, kinetic, and infrared studies have all contributed to the construction of possible models for the active sites and intermediates.[12−14] Isotope studies[15] have shown that the two protons remain in close proximity to each other once adsorbed, a requirement for PASADENA enhancement.

Two main types[16] of hydrogen adsorption are known to occur on ZnO at room temperature. Type 1 is fast and reversible and is accompanied by O−H and Zn−H absorption bands in the IR spectrum,[17] suggesting the formation of the surface species



Type 2 is initially fast but then slows and is irreversible and is not accompanied by O−H or Zn−H bands in the IR spectrum.

Experiments in which ZnO is exposed to continuous p-H_2 showed that the enhancement disappears over a period of tens of

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[*] To whom correspondence should be addressed.

[†] Present address: Dept. of Chem., Univ. of Calif., Santa Barbara, CA.

[‡] Present address: Dept. of Chem., Univ. of Florida, Gainesville, FL.

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(9) Experiments were performed on powdered ZnO (99.8% purity, 3.5 m^2/g mean surface area, 0.31 μm mean particle size, Strem Chemicals, Inc., Newburyport, MA) at room temperature, under moderate vacuum. A 0.3 g sample (and glass wool plug) in a glass tube was connected to a p-H_2 delivery line (standing pressure 160 kPa) and to vacuum. The sample was first heated under vacuum to 673−723 K for > 4 h. Parahydrogen was prepared by passing H_2 gas through activated Apachi nickel silica gel (Houdry, Div. of Air Products and Chemicals, Inc., Philadelphia, PA) at 77 K, resulting in a calculated para mole fraction of ∼0.5. NMR was performed at 4.7 T (198 MHz ^1H) with a six-turn solenoid (length 1.7 cm, i.d. 0.7 cm, $Q \approx 300$). For each spectrum, evacuation (typically several minutes) was followed by a burst of p-H_2 and then reevacuation. Burst lengths reported refer to the nominal "valve-open" time. A resonant rf pulse (1.8 μs, 45° flip angle) was delivered at the end of the burst, followed by detection of precessing magnetization (128 points at 10 μs/point after 20 μs delay). The transients (all single shots) were zero-filled to 256 points before Fourier transformation without apodization.

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seconds, suggesting that sites observed fill up over this period. This is qualitatively consistent with kinetic data for Type-1 adsorption. The enhanced spin order decayed by ordinary spin-lattice relaxation, as expected. The experiment in which a short burst of p-H_2 gives PASADENA signal was consistently repeatable with several seconds of evacuation between shots. This indicates a reversible binding site also consistent with Type-1 adsorption. Difference spectroscopy based on the different kinetics of Type-1 and Type-2 adsorption may be able to distinguish the two types.

Larger signal amplitude is observed with burst lengths of 100 and 200 ms (not shown), indicating that the amount of dissociatively adsorbed hydrogen increased with exposure time. This growth is accompanied by a change in the shape of the enhanced spectrum, suggesting that different adsorption sites are occupied at different rates. Alternatively, spin diffusion may transfer order to spectroscopically distinct protons near the binding site.

A quantitative analysis was made of the spectrum obtained with a 50 ms burst length. The product state is taken to be a fixed magnetically isolated two-spin system formed by dissociative chemisorption. Structural and chemical information about the binding site is embodied in the truncated, rotating-frame spin Hamiltonian for this system, which dictates the complex line shape: $\mathscr{H} = \omega_{1z}I_{1z} + \omega_{2z}I_{2z} + D(3I_{1z}I_{2z} - \mathbf{I}_1\cdot\mathbf{I}_2)$ (in units of radians/s). The chemical shifts ω_{1z} and ω_{2z} represent the Zeeman interaction for the two spins. The dipolar coupling parameter is given by $D = \pi\nu_D(1 - 3\cos^2\theta)$ and $\nu_D = \gamma_n^2\hbar/2\pi r^3$, where γ_n is the gyromagnetic ratio, r is the internuclear distance, and angle θ subtends the internuclear vector and applied magnetic field direction. The scalar coupling between the spins is assumed to be negligible.

For a powder-averaged pair of protons (i.e., averaged over all orientations) bound to a fixed solid surface, a total of 12 parameters related to the chemical environment and geometry contribute to the spectral shape: the internuclear distance, three chemical shift principal values for each spin, and five Euler angles describing the relative tensor orientations. These parameters determine both the energy levels and the initial populations of the adsorbed protons.

Population inversion upon reaction across two of the four enhanced dipole-allowed transitions results in the characteristic antiphase appearance of PASADENA spectra. This antiphase character leads to unavoidable partial cancellation between spectra from different crystallite orientations. The data reported here confirm our earlier numerical prediction[18] that despite considerable destructive interference, large PASADENA enhancement is possible in powdered systems.

Using the powder-averaging method of Alderman et al.,[19] PASADENA spectra have been simulated by integrating the theoretical PASADENA line shape for an oriented, isolated two-spin system over all possible crystallite orientations. A random search of Hamiltonian parameter space, totaling 2×10^6 simulations, showed distinct clustering of the interproton distance around 1.8 or 2.5 Å among the best matches to the spectrum shown in Figure 1c. One such simulation is shown in Figure 2. Because of the wide variety[12-14] of proposed models of the active sites on ZnO, neither interproton distance is easily excluded. A study using 2D nutation NMR to spectroscopically isolate the contribution of dipolar order formed upon reaction of p-H_2 with the surface,[20] gives a single clustering of the interproton distance[21] in a random search around 2.3 Å.

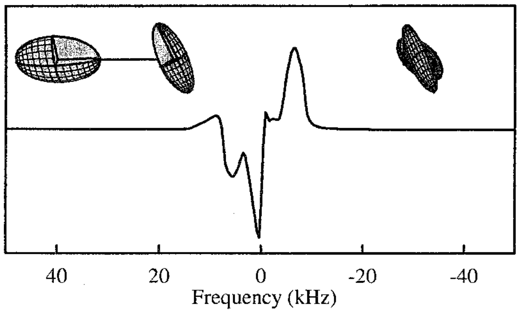

Figure 2. Simulated PASADENA line shape in a powdered system with an interproton distance of 2.6 Å (dipolar coupling parameter $\nu_D = 6$ kHz, flip angle 45°). The principal components of the chemical shift tensors (shown from two orthogonal viewpoints) are $\sigma_1 = \{5.0, 0.8, -3.8\}$ and $\sigma_2 = \{2.5, 1.0, -5.4\}$ (in kHz), with Euler angles $\Omega_1 = \{0, 71, 37\}$ and $\Omega_2 = \{116, 71, 21\}$ (in degrees). The spectrum has been convoluted with a 1 kHz-wide Lorentzian line.

For the simulations that were near matches to the spectrum shown in Figure 1c, the average isotropic shift of the two protons ranged roughly from 5 to 15 ppm, relative to H_2 gas, for the cluster around 1.8 Å interproton distance, and from −15 to 25 ppm for the cluster around 2.5 Å. The isotropic shift difference for the two clusters ranged from roughly 0 to 20 ppm for both clusters. Because of this large range of tensor parameters that gave reasonable matches to the spectrum, and because of the lack of data in the literature for surface bound OZnH and ZnOH shifts, the tensor parameters are not considered reliable in this instance. Also, even if the two protons formed a zinc dihydride, either with dissociative bonding or in an η_2 complex with restricted rotation, the requirments could still, in principle, be met for PASADENA enhancement.

The enhancement factor of the measured surface-PASADENA signal, defined as the integrated magnitude relative to the expected signal from equilibrium polarization, is estimated from the simulations to be in the neighborhood of 400−1000, corresponding to a sensitivity on the order of 5×10^{12} spins/cm^2. This represents roughly 1−10% of the Type 1 chemisorption sites.[22]

The NMR spectra of chemisorbed H_2 show a strong dipolar coupling which is not detected without PASADENA enhancement. This indicates the selectivity of the method for molecular binding and its potential for structural and mechanistic studies at the solid-fluid interface. Application of the converse effect,[23] in which the NMR of surface species is detected by measuring the ortho/para branching fractions of desorbed H_2, is potentially capable of giving the greater sensitivity needed to examine a *single* crystal surface.

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