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LETTERS

Infrared Spectra of H_2 Molecules Near H Atoms Trapped in Solid H_2

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Laser-ablation irradiation of normal hydrogen during condensation at 3.8 K produces new IR absorptions in p-H_2 and o-H_2 cage molecules at 4151.8 and 4143.4 cm^{-1} that are redshifted 1.0 and 3.3 cm^{-1}, respectively, from induced IR absorptions for each nuclear spin isomer in solid n-H_2. Assignment to perturbed p-H_2 and o-H_2 molecules, respectively, are confirmed by experiments with p-H_2-enriched samples. Deuterium experiments give rise to analogous bands for o-D_2 and p-D_2 at 2985.2 and 2982.4 cm^{-1}, respectively, that are redshifted 1.6 and 2.2 cm^{-1} from the absorptions induced for each nuclear spin isomer in solid n-D_2. However, investigations with solid HD give a single, sharp new line at 3621.7 cm^{-1}, redshifted by 3.0 cm^{-1} from the sharp induced solid HD absorption. Comparable intensity half-lives recently observed for H atom electron spin resonance signals in solid H_2 suggest trapped H atoms as the origin of substantial induced IR intensity in adjacent H_2 molecules in the solid. The H atom−H_2 molecule interaction is stronger for o-H_2 than for p-H_2 owing to anisotopic charge distribution for o-H_2 that is lacking in p-H_2.

Introduction

Solid molecular hydrogens (SMH) are important media for investigating numerous chemical and physical phenomena. Hydrogen atoms have been observed in solid H_2 and are found to diffuse at temperatures below 4 K; however, the mechanism is not completely understood nor do all reports agree.[1−7] The Moscow group prefers physical diffusion, and the Nogoya workers claim that chemical diffusion through the tunneling reaction $H + H_2 \rightarrow H + H_2$ is the dominant mechanism.[2−6] These investigations employ electron spin resonance (ESR) to monitor the diffusion and reaction of H atoms but use different methods to prepare solid samples. Nevertheless the diffusion and recombination of H atoms in solid hydrogen is much faster than for D atoms in solid deuterium.[1−6] Very recent investigations into the pressure effect on the recombination rate are offered in support of chemical rather than physical diffusion.[8] Hydrogen atoms produced by γ radiolysis are found to occupy substitutional sites in the solid hydrogen lattice with little perturbation based on ESR, electron spin−echo, and electron nuclear double resonance (ENDOR) investigations.[9−12]

Knight has generated and trapped H atoms in solid hydrogen (normal and para) by X irradiation and by pulsed laser ablation of numerous metals in the presence of condensing H_2 gas.[13] The observed ESR absorption for H atoms yielded magnetic parameters in very close agreement with the 1420-MHz gas-phase value and a H_2 matrix hyperfine value (1422 MHz) between argon and neon matrix values.[14] One major difference was observed between solid H_2 (normal or para) and neon matrices: The H atom absorption intensity in neon did not change over a 37-h period at 4.2 K, but in either form of solid H_2, the signal prepared by X irradiation decreased to approximately half its original value at 2.5 ± 0.3 K within 130 ± 20 min. By use of laser ablation (Co and Mg), the intensity “half-life” at 2.5 ± 0.3 K was about 3 h. The ESR absorption line width in n-H_2 was approximately 0.7 G compared to about 0.06 G in p-H_2.[13]

All of the previous work[1−7,13,14] on the H atom−solid H_2 interaction has been from the H-atom perspective based on ESR

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absorption of the H atom. Here we investigate this system from the H_2-molecule perspective for the first time and report substantial H-atom-induced IR intensity and small redshifts for the H−H fundamental vibration in $(H)(H_2)_n$ species in the solid.

IR spectroscopy has been employed to probe the effects of radiation on SMH, and new absorptions have been assigned to perturbations by charge centers.[15−17] Recently, we have shown that the major new IR absorption is due to the hydride anion cluster $(H^-)(H_2)_{12}$ $[(D^-)(D_2)_{12}]$ in the SMH microcrystal with coordination number 12 through the use of laser-ablated metals as a radiation source to produce H [D] atoms and electrons to form H^- $[D^-]$ anions.[18] These experiments also reveal strong, sharp new metal independent lines that are redshifted only slightly from the induced SMH IR absorptions,[19] which decrease with time at 3.8 K with similar half-lives as observed for H atoms in recent ESR experiments.[13] Hence, the new IR bands appear to arise from perturbation on H_2 $[D_2]$ cage molecules by the trapped H [D] atoms. Our calculations showed that the H_2 ligands in the $(H^-)(H_2)_{12}$ cluster are fixed and directed like the spokes of a wheel;[18] however, the much weaker interaction in $(H)(H_2)_n$ allows cage complexes free rotation in the H_2 ligand as manifested by the observation of both para ($J = 0$) and ortho ($J = 1$) IR absorptions.

Experimental Section

Our basic laser-ablated metal and solid hydrogen experiment has been described previously.[20−22] Briefly laser-ablated metal atoms, cations, electrons, and photons in the vacuum ultraviolet through IR ranges are co-deposited with 2−3 mmol of normal hydrogen (also D_2 and HD) onto a 3.8 ± 0.2-K window for transmission IR spectroscopic examination. The samples are subjected to time delay periods in the dark, to further irradiation from a filtered medium-pressure mercury arc lamp or an ArF laser, and to annealing cycles until the solid evaporates, and more IR spectra are recorded at each stage in the experiment. Additional experiments were done using $J = 0$ enriched nuclear spin isomer mixtures made by condensing the gases on $Fe(OH)_3$ catalyst in a copper tube immersed in the cold gas over liquid helium. Hydrogen samples subjected to tesla coil discharge in a quartz tube during condensation at 3.8 K were also investigated.

Results and Discussion

New absorptions in the H−H [D−D] stretching region will be reported for solid normal hydrogen [deuterium] samples subjected to irradiation or discharge to form H [D] atoms during deposition at 3.8 K. In an investigation of the reaction of over 30 different laser-ablated metals with pure hydrogen, we discovered several metal-independent IR absorptions. These absorptions are thus associated with common species involving H atoms from dissociation of H_2 via laser-ablation plume irradiation and laser-ablated electrons. The strong, broad absorptions at 3972 [2870] cm^{-1} have recently been identified as $(H^-)(H_2)_{12}$ $[D^-)(D_2)_{12}]$ cluster anions,[18] and new strong, sharp 4143.4 [2982.4] cm^{-1} bands will be presented here.

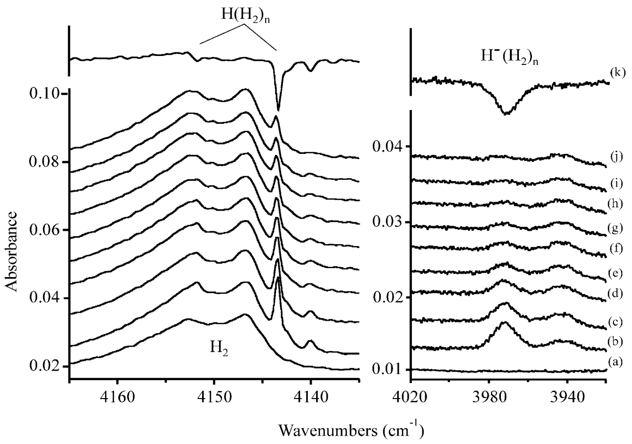

Figure 1. IR spectra in the 4165−4135- and 4020−3920-cm^{-1} regions for laser-ablated In co-deposited with normal hydrogen at 3.8 K. (a) Spectrum of pure hydrogen, (b) spectrum after In and H_2 co-deposited for 30 min, (c) after 20 min delay + 8 min scan time, (d−j) spectra after 20 min delays and 8 min scans, and (k) difference of spectrum (j) − spectrum (b).

Figure 1 compares spectra for hydrogen samples at 3.8 K. The reference scan a illustrates the spectrum of a pure normal hydrogen sample containing 25% p-H_2 and 75% o-H_2 molecules,[23] which are responsible for the two broad induced absorptions at 4152.8 and 4146.7 cm^{-1}, respectively. These measurements are in agreement with IR spectra recorded earlier (4153.0 and 4146.6 cm^{-1})[19] for much thicker H_2 samples at 1.9 K and recent spectra of p-H_2 with 2500 ppm o-H_2 (4152.8 and 4146.6 cm^{-1})[24] and are assigned to p-H_2 ($J = 0$) and o-H_2 ($J = 1$) molecules, respectively.[19] Scan b shows the spectrum recorded for laser-ablated In co-deposited with H_2 at 3.8 K for 30 min, and scans c−j were taken at 28-min intervals (20-min delay + 8-min scan time for 256 scans at 0.5-cm^{-1} resolution) with the sample held at 3.8 K. A strong, sharp new 4143.4-cm^{-1} band and a weaker, sharp 4151.8-cm^{-1} peak are observed on the side of the induced solid hydrogen absorptions in scan b. The full-width at half-maximum of the 4143.4-cm^{-1} signal is 0.3 cm^{-1} when recorded at 0.125-cm^{-1} resolution. It is significant that the sharp new 4151.8 and 4143.4 cm^{-1} bands decrease with elapsed time at 3.8 K. In addition, the broad o-H_2 absorption decreased and the p-H_2 absorption increased a few percent and a weak new 4140.0-cm^{-1} absorption decreased. The intensity half-life of the strong 4143.4-cm^{-1} absorption is 140 ± 20 min. Meanwhile IR bands due to InH and InH_3 increased during this period, and bands for InH_2 reached maximum absorbance in about 40 min and then decreased.[25] The top trace (Figure 1k) gives the difference of spectrum j minus spectrum b and shows the cumulative effect of the 224-min delay at 3.8 K. Finally, we note that the weak 4140.0-cm^{-1} absorption intensity tracks directly with water impurity, and it is due to o-H_2 induced by interaction with H_2O.[26]

Experiments were performed with Ca using low laser energy, and the spectrum of the deposited sample is compared with a n-H_2 spectrum in parts a and b of Figure 2. The new sharp peaks at 4151.8 and 4143.4 cm^{-1} are approximately 1:10 ± 1 relative intensity. The intensity half-life of the new peaks was 75 ± 10 min at 3.8 K. Samples enriched in p-H_2 were treated in a similar manner. The major peaks in 60:40 para/ortho hydrogen reversed (Figure 2c); as expected,[19] the product peaks shifted to 4151.4 and 4143.8 cm^{-1} with relative intensity 1.0:4.0 ± 0.4 (Figure 2d), and revealed an intensity half-life of 110 ± 10 min. The dominant solid hydrogen absorption appeared at 4152.9 cm^{-1} in 80% p-H_2 with a weaker band at 4146.6 cm^{-1}, and the product absorptions at 4150.9 and 4144.5 with In ablation are 1.0:1.3 ± 0.1 relative intensity (parts e and f of Figure 2). The intensity half-life of the new peaks was 75 ± 10 min at 3.8 K. With 90% p-H_2 and Al ablation, the new peaks shifted to 4150.2 and 4145.2 cm^{-1} with 1.0:0.30 ± 0.03 relative intensity (Figure 2h). Experiments are in progress to make this measurement in almost pure parahydrogen.

Complementary experiments were performed with normal hydrogen flowing through a quartz tube and subjected to tesla

TABLE 1: Induced IR Absorptions (cm^{-1}) for Normal Solid Molecular Hydrogens[a] and for Molecular Hydrogens Interacting with Trapped H or D Atoms at 3.8 K

	H_2			HD			D_2		
rot	n-H_2	$(H)(H_2)_n$	$\Delta\nu$	HD	$(H \text{ or } D)(HD)_n$	$\Delta\nu$	n-D_2	$(D)(D_2)_n$	$\Delta\nu$
$J = 0$	4152.8	4151.8	1.0	3624.7	3621.7	3.0	2986.8	2985.2	1.6
$J = 1$	4146.7	4143.4	3.3				2984.6 sh	2982.4	2.2

[a] Induced by interaction with $o-H_2$ or $p-D_2$. See ref 19.

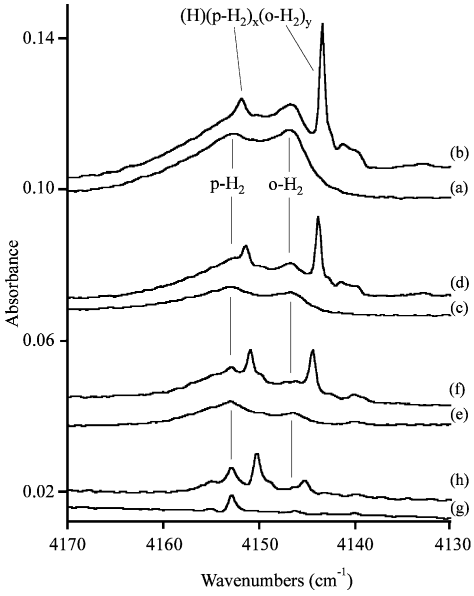

Figure 2. IR spectra in the 4170−4130-cm^{-1} region for laser-ablated metal co-deposited with different para-enriched hydrogen samples at 3.8 K. (a) Normal hydrogen sample, (b) normal hydrogen sample with Ca laser-ablation, (c) para-enriched hydrogen (para/ortho approximately 60:40), (d) 50:40-enriched hydrogen sample with laser-ablation, (e) para-enriched hydrogen (para/ortho approximately 80:20), (f) 80:20-enriched hydrogen sample with In laser-ablation, (g) para-enriched hydrogen (para/ortho approximately 90:10), and (h) 90:10-enriched sample with Al ablation.

coil discharge. A similar spectrum was observed in the 3900−4200-cm^{-1} region. The sharp 4151.8 and 4143.4 cm^{-1} features decreased together with time at 3.8 K with a 80 ± 10 min half-life. In addition, HO_2 was observed at 3416.4, 1392.7, and 1100.5 cm^{-1} in solid hydrogen,[27] and these absorptions increased about 25% while the above signals decreased by half on standing for 1 h at 3.8 K.

Analogous experiments were done with deuterium. Representative spectra are shown in Figure 3. The spectrum of pure normal deuterium reveals the major peak at 2986.8 cm^{-1} with a shoulder at 2984.6 cm^{-1} (Figure 3a). These absorptions were also observed at 2986.8 and 2984.6 cm^{-1} for a thicker sample at 1.9 K and assigned to $Q_1(0)$ and $Q_1(1)$ transitions of o-D_2 ($J = 0$) and p-D_2 ($J = 1$), respectively.[19] Sharp new absorptions appeared at 2685.2 and 2982.4 cm^{-1} upon passing deuterium through a tesla coil discharge (Figure 3b) and upon laser-ablation of U with irradiation of D_2 during condensation at 3.8 K (Figure 3c). These peaks decreased together on annealing stepwise to 10 K (other experiments) and on filtered mercury-arc irradiation (parts d−h of Figure 3). The final trace (i) illustrates the cumulative effect of irradiation from the difference of spectrum (h) minus spectrum (c).

The same spectrum was observed in the 3000−2970-cm^{-1} region for a laser-ablated In and D_2 sample, which was maintained at 3.8 K for successive IR spectra. The absorbance−time profile shows only a 10% decrease in the 168-min period of the observation. If the same loss rate were maintained, an

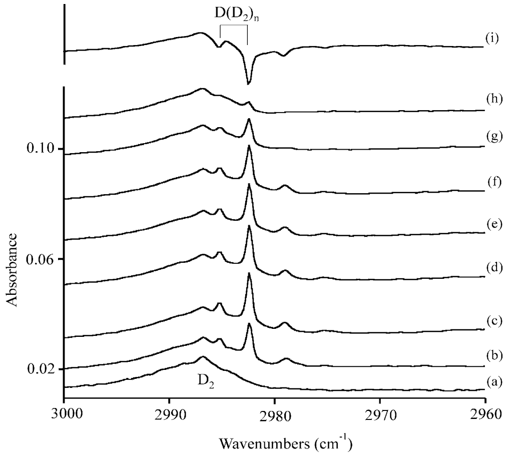

Figure 3. IR spectra in the 3000−2960-cm^{-1} region for samples of normal deuterium at 3.8 K. (a) Spectrum of pure deuterium, (b) spectrum of pure deuterium passed through tesla coil discharge, (c) spectrum of pure D_2 co-deposited with radiation from laser-ablated U, (d) after irradiation at $\lambda > 530$ nm, (e) after irradiation at $\lambda > 470$ nm, (f) after irradiation at $\lambda > 380$ nm, (g) after irradiation at $\lambda > 290$ nm, (h) after irradiation at $\lambda > 240$ nm, and (i) difference of spectrum (h) − spectrum (c).

intensity half-life near 1400 ± 100 min would be determined. This compares favorably to the approximately 10^5-s (1 700-min) value reported by the Moscow group for the ESR absorption of D atoms in solid D_2 at 4.2 K.[6] Even after warming stepwise to 8.0 K over the next 4 h, the 2982.4 cm^{-1} band intensity decreased only 20% further.

Similar experiments were done with HD (97.9%). A single sharp absorption was observed for the H−D fundamental at 3624.7 cm^{-1} in HD, Figure 4 a, which is induced by interaction with o-H_2 ($^3/_4$ of 2.0%) impurity and is in agreement with the 3624.95-cm^{-1} measurement on a larger sample at 1.9 K.[19] On co-deposition with laser-ablated metals, a new strong, sharp 3621.7-cm^{-1} absorption was observed (Figure 4b). The sharp 3621.7 cm^{-1} feature decreased from 0.017 to 0.010 in 168 min at 3.8 K, which extrapolates to a half-life near 280 ± 20 min. A final $\lambda > 240$ nm irradiation almost destroyed the sharp feature (Figure 4g). The absorption band frequencies observed here are summarized in Table 1.

The sharp new IR absorptions are believed to be due to H−H [D−D or H−D] vibrations perturbed in frequency and intensity by interacting with H [D] atoms trapped in the SMH lattice. Previous investigations have concluded that H [D] atoms are trapped in substitutional sites in the SMH lattice;[9−12] hence, we appear to be dealing with large cage complexes $(H)(H_2)_n$ $[(D)(D_2)_n]$. We do not know what effect charged species trapped in the solid may have on this interaction.

First, the absorbance-time profiles of the sharp new 4151.8 and 4143.4 cm^{-1} IR absorptions reveal comparable intensity half-lives as recent ESR matrix spectra of H atoms in similar solid H_2 experiments,[13] where the concentration of H atoms is expected to be comparable. The intensity half-life measurements vary somewhat depending on sample preparation and temperature, but the ESR experiments of Knight involve condensation

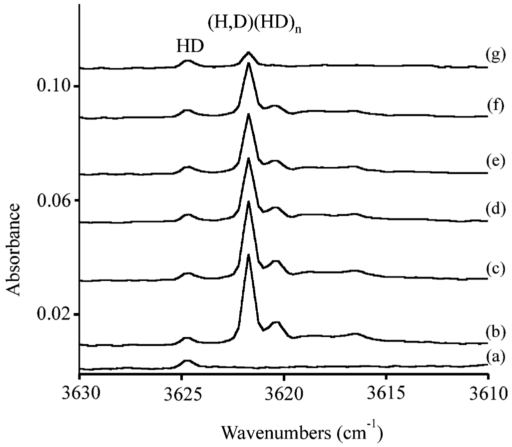

Figure 4. IR spectra in the 3630−3610 cm^{-1} region for laser-ablated U co-deposited with pure HD at 3.8 K. (a) Spectrum of pure HD, (b) spectrum after U and HD co-deposited at 3.8 K, (c) after 20 min delay + 8 min scan time, (d) spectrum completed after 84 min, (e) spectrum completed after 140 min, (f) spectrum completed after 196 min, and (g) after $\lambda > 240$ nm irradiation all at 3.8 K.

of H_2 gas much like our matrix IR experiments.[28] Furthermore, the intensity half-life of our 2982.4 cm^{-1} signal in solid D_2 at 3.8 K is near that found for the ESR absorption of D atoms prepared by radio frequency discharge and trapped in solid D_2 at 4.2 K.[6] This is sufficient agreement to suggest the ESR-active H atom as the source of the induced IR activity for adjacent H_2 molecules in the cage whose vibrations we observe by IR absorption.

Second, the two new IR absorptions at 4151.8 and 4143.4 cm^{-1} for H_2 are related to the solid H_2 absorptions at 4152.8 and 4146.7 cm^{-1} owing to induced activity in para ($J = 0$) and ortho ($J = 1$) H_2 nuclear spin isomers, respectively. The relative intensities of the new bands are approximately 1:10 ± 1, which is clearly different from the 1:3 para/ortho ratio for normal hydrogen.[23] It appears that the $J = 1$ H_2 molecule gains more IR intensity than the $J = 0$ H_2 molecule from the H atom perturbation owing to anisotropy in the $J = 1$ state charge distribution. The induced IR activity for interacting p-H_2 and o-H_2 molecules in the solid is a complicated matter, and the basic intermolecular interaction is affected by the surrounding H_2 molecules[23] and the guest H atom−H_2 host interaction.[29] Pure solid p-H_2 has no IR absorption and the 4153.0-cm^{-1} signal is taken as a measure of o-H_2 impurity inducing activity in p-H_2 molecules.[19,24,30] Para-enriched samples (Figure 2) show increases in the former new product absorption at the expense of the latter new product band and confirm their dependence on p-H_2 and o-H_2 molecules, respectively. These spectra also reveal continuous shifts in both sharp product absorptions and demonstrate a cooperative interaction among the perturbed H_2 ligands in the first solvation shell where interaction with the H atom is the strongest.

Third, sharp new IR bands are also observed in solid D_2 redshifted by similar amounts from SMH absorptions, but these bands decay much more slowly with time. The sharp 2985.2- and 2982.4-cm^{-1} product bands are 1.6 and 2.2 cm^{-1} below the solid D_2 absorptions, respectively, whereas the new product bands in solid H_2 are down by 1.0 and 3.3 cm^{-1}. The major absorption in solid D_2 at 2986.8 cm^{-1} is due to ortho ($J = 0$) D_2 perturbed by interaction with para ($J = 1$) D_2 molecules as pure o-D_2 is expected to be IR silent.[19] The 1.0:5.0 ± 0.5 relative intensity of the 2985.2- and 2982.4-cm^{-1} product bands does not match the 2:1 abundance ratio of the o-D_2 ($J = 0$) and p-D_2 ($J = 1$) nuclear spin isomers,[19,23] which suggests that D induces more IR intensity in the rotating ($J = 1$) than in the nonrotating ($J = 0$) D_2 molecule analogous to the effect for hydrogen.

Fourth, one sharp new product absorption is observed at 3621.7 cm^{-1}, shifted 3.0 cm^{-1} below the sharp induced solid HD fundamental. The 3621.7-cm^{-1} band has an apparent intensity half-life between the shorter solid H_2 and longer solid D_2 determinations. All HD molecules are in the $J = 0$ rotational state,[19,23] and we observed a single HD species perturbed by interaction with H or D atoms in solid HD.

The interaction between the H atom guest and the H_2 molecule host in solid hydrogen is clearly very weak, but this interaction is stronger with the $J = 1$ isomer than with the $J = 0$ isomer. Our conclusion is based on the strong new bands observed for both p-H_2 and o-H_2 molecules redshifted 1.0 and 3.3 cm^{-1}, respectively, from the values for these molecules as induced in solid normal H_2 and the greater relative intensity for the $J = 1$ isomer. This probably arises from the anisotropic charge distribution for the $J = 1$ isomer that is absent in the $J = 0$ isomer.[23,31] The same experimental effect is found for the D atom interaction with D_2, which produces new bands for $J = 0$ and $J = 1$ states redshifted by 1.6 and 2.2 cm^{-1}, respectively, and the 1:5 relative band intensities suggest even more intensity increase for the $J = 1$ D_2 isomer. We expect that the $J = 1$ isomers seek out the H [D] atoms on condensation of the solid samples and locate initially in the nearest neighbor position more than a random distribution. Our results are consistent with recent observations for H_2−HF and D_2−HF complexes in the gas phase and in helium nanodroplets, which find the $J = 1$ complexes to be more stable in all cases.[32,33] Frequency redshifts for HF in these complexes in helium increase for H_2−HF (7.8 cm^{-1} for $J = 0$ to 11.5 cm^{-1} for $J = 1$) and for D_2−HF (12.1 cm^{-1} for $J = 0$ to 13.8 cm^{-1} for $J = 1$) with HD−HF intermediate (9.7 cm^{-1}) and these redshifts parallel the calculated dissociation energies.[33]

Recent ENDOR spectra suggest that almost all of the nearest-neighbor o-H_2 molecules are converted to p-H_2 and that o-H_2 molecules in the second and third nearest sites are pushed out by 4% of the lattice parameter.[11] The initial H atom ESR absorption line widths in n-H_2 are an order of magnitude broader than in p-H_2,[3−5,13] but they decrease with time at 4.2 K, which demonstrates a decreasing interaction between H atoms and o-H_2 molecules in solid n-H_2 that is rationalized in part by ortho > para conversion.[3] Our IR spectra show a small decrease in o-H_2 and increase in p-H_2 itself at 3.8 K (Figure 1), which is consistent with ortho > para conversion, but the diffusion of both o-H_2 and H atoms maintains close enough proximity to induce considerable IR intensity and redshift both p-H_2 and o-H_2 molecules. If the intensity increase is substantially more for o-H_2 than for p-H_2 complexes, the observed 1:10 ratio for the new $(H)(H_2)_n$ bands is consistent with depletion of o-H_2 in the nearest-neighbor positions. Although the IR bands for SMH and $(H^-)(H_2)_n$ anion clusters are broad,[18] the new $(H)(H_2)_n$ IR bands are very sharp.

It appears that both physical and chemical diffusion of H atoms is occurring in these matrix isolation experiments. The rapid initial decay of these IR absorptions at 3.8 K followed by a continued steady decrease at 3.8 K suggests that physical diffusion and bimolecular recombination is dominant at first when the atom concentration is highest and that chemical diffusion is more important at later states in the experiment when the atom concentration is lower. Finally, the growth observed for HO_2 and InH absorptions at 3.8 K in appropriate experiments is a direct chemical consequence of H atom diffusion and reaction.[25,27]

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