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Novel Pressure-Induced Interactions in Silane-Hydrogen

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We report novel molecular compound formation from silane-hydrogen mixtures with intermolecular interactions unprecedented for hydrogen-rich solids. A complex H_2 vibron spectrum with anticorrelated pressure-frequency dependencies and a striking H-D exchange below 10 GPa reveal strong and unusual attractive interactions between SiH_4 and H_2 and molecular bond destabilization at remarkably low pressure. The unique features of the observed $SiH_4(H_2)_2$ compound suggest a new range of accessible pressure-driven intermolecular interactions for hydrogen-bearing simple molecular systems and a new approach to perturb the hydrogen covalent bond.

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The strength of the H_2 covalent bond in a variety of thermodynamic conditions and chemical environments is of great interest. Compression may yield substantial weakening of the intramolecular potential, despite relatively small perturbations in vibrational frequency, and eventual dissociation [1]. Under appropriate conditions of pressure, temperature, and chemical environment, hydrogen-rich solids are predicted to exhibit novel quantum dynamics and electronic properties [2,3]. Owing to the low mass of the proton and symmetry constraints on the wave function, solid molecular hydrogen is observed to show a suite of intriguing dynamics starting at low to modest pressures [4,5]. Specifically, H_2 intramolecular vibrational excitations (vibrons) provide key information on covalent interactions and effective intermolecular potentials [6]. In bulk H_2 the vibrons span a range of frequencies with wave vector due to coupling between neighboring molecules, which increases dramatically with pressure, as manifested by a divergence in the Raman and infrared (IR) vibron frequencies [5,7]. According to the model of Ref. [6], the width of the vibron exciton band is $8\epsilon'$, where ϵ' is the vibrational coupling parameter, and the difference between the IR and Raman frequencies is $\sim 6\epsilon'$. This increased vibron coupling gives rise to a number of intriguing pressure-dependent phenomena such as the bound-to-unbound transition of the D_2 bivibron [8], vibron localization-delocalization [9], and mode anharmonicity [10].

Much effort has been devoted to the study of H_2-containing simple molecular mixtures. H_2 may be contained in rare-gas matrices, and in the absence of vibrational coupling, the frequency of the hydrogen vibron increases monotonically with pressure [11]. H_2 crystallizes with molecules like Ar, CH_4, and Xe into stoichiometric van der Waals compounds [12–14], where the rotational and vibrational dynamics of H_2 within these materials are well described by small perturbations to pure hydrogen [15]. Over the range of conditions studied, these compounds remain as insulating molecular solids with H_2 vibron frequencies contained within the excitation band for pure H_2. Here we report pressure-induced novel compound formation in the molecular silane-hydrogen system. This material exhibits intermolecular interactions unique compared to all previously reported molecular compounds, with a vibron excitation band completely outside that of pure solid hydrogen and H_2 bond weakening at remarkably low pressure. Additional observations have implications for controversial pressure-induced changes in electronic properties reported for pure SiH_4.

The phase behavior of $SiH_4 + H_2$ mixtures was determined through a series of loadings over a range of compositions. The phase relations at the *P*-*T* conditions studied can be described by a simple eutectic phase diagram [Fig. 1(a)]. Up to ~5 GPa, all compositions resulted in a homogeneous, completely miscible single phase fluid with a single hydrogen vibron at 4200 cm^{-1}, ν_1 symmetric stretching band of SiH_4 at 2250 cm^{-1}, ν_2 bending mode of SiH_4 at 1000 cm^{-1}, as well as H_2 rotons at 360, 605, 835, and 1055 cm^{-1} [Fig. 1(b)]. With increasing pressure, two phases appeared, marking the phase boundaries of solid H_2 + fluid $H_2 + SiH_4$ and solid SiH_4 + fluid $H_2 + SiH_4$ depending on the bulk composition of the sample.

Upon further pressure increase, the $SiH_4 + H_2$ fluid phase solidified into a new crystalline compound near 7 GPa. This phase transformation was evidenced by changes in the Raman spectrum that are unprecedented for H_2 containing systems. The spectrum of the $SiH_4 + H_2$ compound revealed extremely rich behavior with at least seven resolvable Raman active H_2 vibrons which were significantly softened relative to bulk H_2 at the same conditions [Fig. 1(b)]. At 7 GPa, the lowest frequency vibron occurred nearly 75 cm^{-1} below that of solid H_2 (~20 cm^{-1} below free H_2). Compared with the fluid phase, the silane ν_1 stretching band from the compound decreased by more than a factor of 3 in breadth and displayed a noticeable increase in intensity. Additionally, the ν_3 and ν_4 modes of SiH_4 appeared at 2280 and 935 cm^{-1} and another mode appeared at 2165 cm^{-1} which we tentatively attribute to the $2\nu_2$ overtone. Although all of the Raman bands representing silane fundamental modes displayed some asymmetry, no direct splitting of these bands was observed,

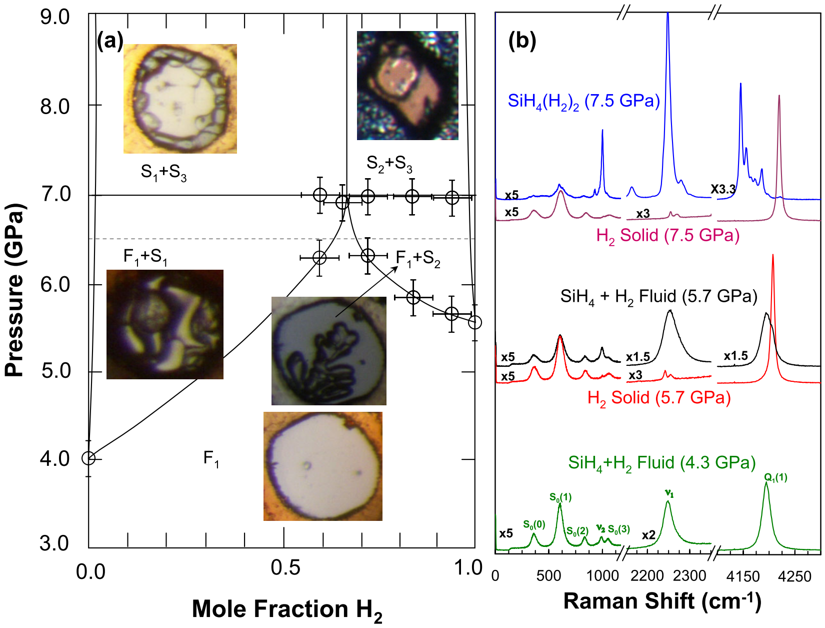

FIG. 1 (color online). (a) Proposed P-x phase diagram for $SiH_4 + H_2$. Fluid 1 (F_1) = $SiH_4 + H_2$, solid 1 (S_1) = solid silane, solid 2 (S_2) = solid H_2, solid 3 (S_3) = $SiH_4(H_2)_2$. The dotted horizontal line shows the reported phase transition from silane III to silane IV [17]. Photomicrographs for each region of the phase diagram are included. We cannot rule out additional stability fields in certain regions of the phase diagram. (b) Representative Raman spectra for an H_2-rich sample during compression.

suggesting that the silane molecules within the new structure are orientationally disordered and lie on sites of relatively high symmetry. Spectral and volumetric measurements show the coexistence with solid hydrogen above ~70 mole % H_2 and with solid silane below ~70 mole % H_2 suggesting a stoichiometry near $2H_2$:$1SiH_4$.

The frequencies of several of the Raman H_2 vibrons were anticorrelated with pressure, indicating increased attractive interactions and the onset of covalent H_2 bond destabilization at the appearance of the new phase, a characteristic previously unobserved in such materials (Fig. 2). Three of the Raman vibrons began to decrease in frequency immediately on compression above 7 GPa, with the others turning over at higher pressure. Compared with the vibron frequency turnover pressure in solid H_2 (30 GPa [5]), it is remarkable the Raman bands of the $SiH_4 + H_2$ compound decrease in frequency starting at only 7 GPa. The H_2 vibrons of $CH_4(H_2)_2$ and $Ar(H_2)_2$ monotonically increase with pressure to the highest pressures studied (36 and 220 GPa) [12,13,16], while the turnover pressures of the Raman vibrons of the newly discovered Xe-H_2 compound [14] are similar to pure solid H_2. We are unaware of any other hydrogen-bearing compound that exhibits these characteristics.

Because IR vibrational spectra are essential for identifying possible covalent bond weakening (e.g., Ref. [5]), IR absorption spectra were also measured. Using synchrotron IR radiation, four resolvable $Q_1(J)$ H_2 vibrons were observed (a weak fifth band was observed above 26 GPa). The frequency of these bands closely followed four of the Raman bands. The concurrence of the IR and Raman vibron frequencies is indicative of a noncentrosymmetric unit cell. As with the Raman vibrons, the IR vibrons decrease in frequency with increasing pressure (Fig. 2). In solid H_2 the difference between the IR and Raman frequencies diverge with increasing pressure due to vibrational coupling, and molecular H_2 bond weakening is not observed until pressures above 145 GPa [7]. Vibron frequencies for previously reported H_2 van der Waals compounds and H_2 dissolved in rare-gas matrices increase monotonically with pressure, and for the compounds they

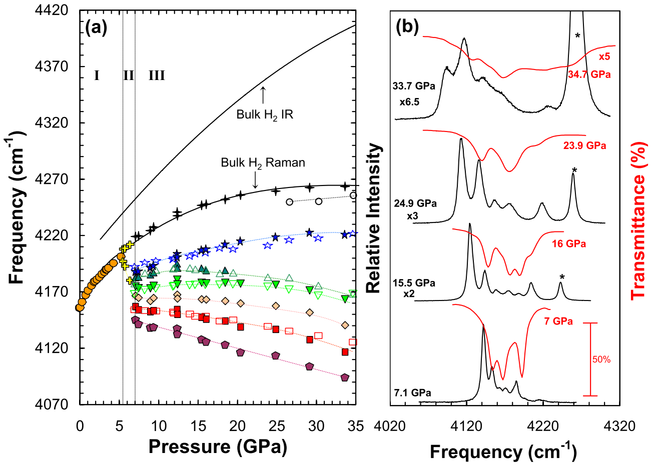

FIG. 2 (color online). (a) Frequency of Raman (filled symbols) and IR (open symbols) H_2 vibrons as a function of pressure. Regions I, II, and III indicate fluid, mixed fluid-solid, and solid phases (298 K). Dashed lines are drawn through the data to guide the eye. Solid lines represent Raman and IR data [5] for bulk H_2. Note the vibron "band" for $SiH_4 + H_2$ falls completely outside the "band" for bulk H_2. (b) Raman and transmission IR spectra for $SiH_4(H_2)_2$ as a function of pressure. Asterisks denote contributions from solid H_2, and another weak band is present as indicated by measurements on SiH_4-rich samples and D_2/HD measurements. Spectra are scaled by indicated values due to the decrease in intensity of Raman scattered light and IR transmission with increasing pressure.

lie within the H_2 vibron exciton band. The IR vibron frequency of $Ar(H_2)_2$ increases with pressure above 200 GPa [16]. The observed trend of decreasing frequency with increasing pressure for both the IR and Raman bands (completely outside the bandwidth of bulk H_2) of the $SiH_4 + H_2$ compound indicates interactions notably different from other molecular compounds and low pressure weakening of the H_2 bond.

With increasing pressure, the opacity of the new compound increased, and samples eventually turned completely black at ~35 GPa. This darkening was accompanied by a progressive decrease in the intensity of scattered Raman light, and above ~35 GPa Raman and IR transmission signals were no longer detectable. This is consistent with observations for pure silane in this pressure range where a progressive sample darkening was observed with increasing pressure, leading to metallization at 60 GPa [17,18]. The darkening of the $SiH_4 + H_2$ compound concurs with electronic structure changes approaching a metallic state. Indeed, preliminary IR reflectivity measurements indicate a progressive increase in reflectivity with pressure; however, at least part of this change arises from the formation of tungsten hydride near the gasket boundary as shown by diffraction measurements above ~30 GPa. Pressure-induced interactions between silane, hydrogen, and the gasket material thus reveal additional complexity and may have implications for discrepancies among experimental and theoretical silane metallization and superconducting pressures [17–19]. Further studies are required to elucidate contributions from bulk silane and to determine the role of H_2. Up to 35 GPa, SiH_4 remained molecular, and we observed no evidence for decomposition or formation of silicon.

Synchrotron powder x-ray diffraction was measured to obtain additional information about the above behavior. The patterns measured over this pressure range can be indexed to a cubic Bravais lattice, and the lack of mixed indices indicates that the structure is face-centered cubic [Fig. 3(a)]. The diffraction and spectroscopic data are consistent with the space group $F\bar{4}3m$. The unit cell volume at formation is 1.3% smaller than the sum of the volumes of four silane molecules and eight H_2 molecules based on the equations of state (EOS) of the pure components [20,21] [Fig. 3(b)]. Spectroscopic and volumetric measurements based on photomicrographs [e.g., Fig. 1(a)] place the composition near 70% H_2; the compound stoichiometry of $SiH_4(H_2)_2$ is thus fully consistent with these data and the EOS. With increasing pressure, the 1.3% volume reduction at formation from the end-member assemblage increased markedly to 5% at 35 GPa, indicating strong attractive interaction of the component molecules. This volume collapse approaches the hypothetical density of the equivalent amount of molecular hydrogen trapped in high-pressure silicon [22] [Fig. 3(b)].

A key proxy for the H_2 covalent bond strength is the intramolecular vibrational stretching frequency, and its correlation with pressure, measured by Raman and IR spectroscopic techniques. As discussed above, the H_2 vibron frequency monotonically increases with pressure in the absence of vibrational coupling (e.g., H_2 in D_2), and for H_2 dissolved in rare-gas matrices [11]. At room temperature, $Ar(H_2)_2$ and $CH_4(H_2)_2$ contain a single H_2 vibron at higher frequency compared to bulk H_2, which stiffens with pressure. The H_2 vibron is driven to substantially lower frequency ($-500\ \mathrm{cm}^{-1}$) when hydrogen is trapped as an impurity in semiconducting thin films like silicon [23]. First-principles calculations for H_2 trapped in GaAs reveal redistribution of charge density from the bonding to antibonding orbitals compared with the free hydrogen molecule, leading to significant elongation of the H_2 bond and a Raman vibron frequency near $3900\ \mathrm{cm}^{-1}$ [24]. The softening of the H_2 vibrons in $SiH_4(H_2)_2$ with pressure evident in the observed Raman and IR spectra demonstrate the presence of strong interactions that go beyond the standard vibrational coupling or dispersion model, and point to a redistribution of charge density associated with bond destabilization.

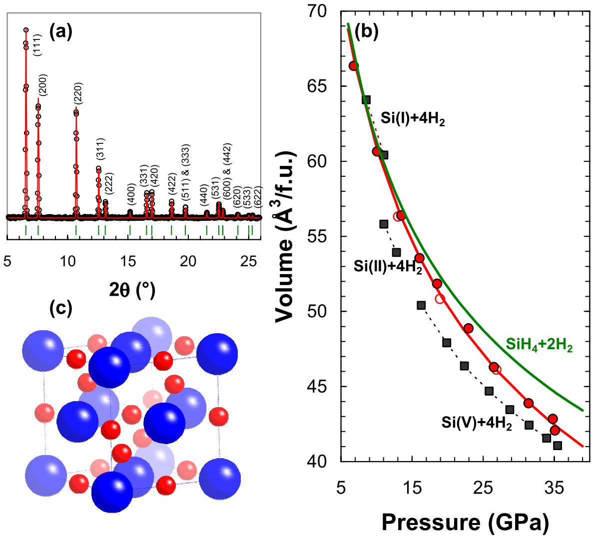

FIG. 3 (color online). (a) Synchrotron x-ray ($\lambda = 0.4246$ Å) diffraction pattern of $SiH_4(H_2)_2$ obtained at 6.8 GPa (300 K) (points) and fit to data using the Le Bail intensity extraction method with $a = 6.426(2)$ Å. At this pressure the valence electron density of hydrogen within the solid corresponds to that of bulk H_2 compressed to ~9 GPa. The tick marks indicate allowed reflections for the $F\bar{4}3m$ structure. (b) Experimental EOS (volume per formula unit) for $SiH_4(H_2)_2$. Filled circles and open circles are data obtained upon compression and decompression, respectively. The labeled curves represent the volumes obtained for the assemblage of four SiH_4 and eight H_2 using volumes of bulk silane [20] and hydrogen [21] and the assemblage of four H_2 and crystalline Si(V) [22]. The data were fit to a second order Birch-Murnaghan EOS with $V_0 = 410(12)$ Å^3, $K_0 = 6.8(7)$ GPa with K_0' fixed at 4. (c) Proposed structure with large and small spheres as SiH_4 and H_2, respectively.

Measurements with isotopic substitution led to surprising findings. In experiments performed on $SiH_4 + D_2$ mixtures to confirm vibrational mode assignments, we

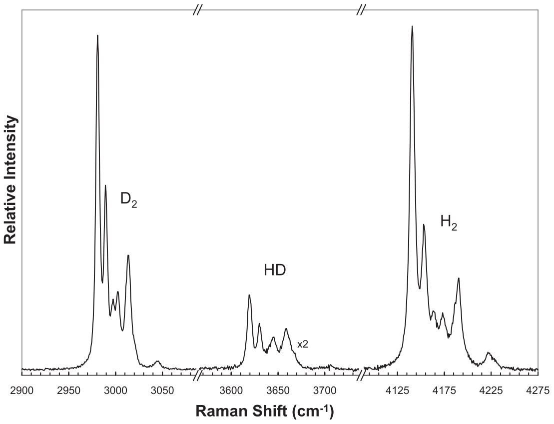

FIG. 4. Raman spectra at ~8 GPa for $SiH_4(X)_2$ where X is D_2, HD, or H_2. The D_2 and HD spectra were obtained from the same measurement ~24 h after the formation of $SiH_4(D_2)_2$. The H_2 spectrum is shown for comparison.

observed a remarkable exchange of D and H atoms to create H-D and Si-D stretching modes in the compound (Fig. 4). H-D exchange is known to occur in when deuterium impinges onto the surface of hydrogenated silicon inside a plasma reactor [25]. Metal gasket catalyzed fluid-phase H-D exchange has been observed in equimolar H_2/D_2 mixtures near 4 GPa [26]. No H-D exchange was reported for matrix isolated SiH_4 in solid D_2 at ambient pressure [27]. In contrast to these observations, the exchange observed here occurs in the compressed solid. Our observations reveal strikingly high proton mobility, perhaps related to the pressure-induced quantum sublattice melting predicted for related low-Z materials [2,28]. This phenomenon confirms the presence of enhanced interactions and the low pressure destabilization of the H_2 bond, and should be examined further theoretically.

The behavior observed for the $SiH_4 + H_2$ system contrasts with previously reported molecular systems containing H_2. At the highest pressure obtained in this study (35 GPa), the frequency of the softest Raman vibron band was 4090 cm^{-1}. A pressure nearly 4 times greater than this is required to achieve this frequency in bulk H_2. The frequency reduction in both IR and Raman bands indicates molecular bond weakening and dissociation at significantly reduced pressures. Additionally, the combination of a group 14 hydride containing "precompressed" hydrogen [2] with a second hydrogen-rich sublattice represents an alternative path for the pressure-induced dissociation of molecular hydrogen to be investigated experimentally and theoretically. The unique features observed in this system suggest a range of previously inaccessible intermolecular interactions in H_2-bearing molecular systems and a potential new class of dense low-Z materials.

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