Matrix Isolation

Infrared Spectra of Indium Hydrides in Solid Hydrogen and of Solid Indane**

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The inherent weakness of the In–H bond might be useful for the design of precursors for chemical vapor deposition (CVD) to make indium-containing semiconductor devices. A few interesting indium hydride complexes have been prepared from InH_3NMe_3 and $LiInH_4$[1–3] but the primary indium hydride, indane (InH_3), has endured a controversial existence. Claims for the early preparation of solid indane by Wiberg et al.[4] could not be reproduced.[5] Mass spectroscopic investigation[6] of the comparative stabilities of AlH_3, GaH_3, and InH_3 also casts doubt on the stability of $(InH_3)_n$. Reviews continue to state that indane has not yet materialized[7] and theoretical calculations suggest that solid indane lacks room-temperature stability.[8] However, bridging In–H–In bonds formed on indium-rich InP semiconductor surfaces are stable at room temperature.[9]

There is spectroscopic evidence for the intermediate InH, InH_2, and InH_3 molecules.[10–14] Recently Mitzel concluded that the next question remaining to be answered concerns the possible isolation of InH_3.[15] In contrast, thalium hydride (TlH) has only been investigated in the gas phase,[10] and there is no experimental evidence to date for TlH_2 and TlH_3.

We recently reported the preparation of dialane using the reaction of laser-ablated aluminum with pure H_2 during condensation at 3.5 K.[16] The reaction first formed AlH, UV photolysis and annealing in solid hydrogen then gave AlH_3 and Al_2H_6. After evaporation of the H_2 matrix host, a solid alane film remained on the CsI window until removed by cleaning at room temperature. This film exhibited broad IR absorptions at 1720 and 720 cm^{-1}, which are almost identical to the 1760 and 680 cm^{-1} bands reported for solid $(AlH_3)_n$ samples containing only bridging Al–H–Al linkages.[16–19] We report herein the first successful preparation of solid $(InH_3)_n$ using this new cryogenic method, and its spectroscopic characterization as being isostructural to solid $(AlH_3)_n$. This work refutes the Wiberg claim[4] for the synthesis of $(InH_3)_n$.

The laser-ablation experiment in conjunction with pure hydrogen as a matrix at 3.5 K has been described elsewhere.[16,17,20] Clearly the ablation laser energy must be limited or the heat load from material and radiation directed to the cold window will prevent the deposition of solid hydrogen.

Indium (99.99 %) was melted into a steel cup and the soild indium sample was rotated to minimize local heating of the target. A series of infrared spectra were recorded after matrix sample preparation to form indium-hydride intermediate species in a solid-hydrogen matrix at 3.5 K, and after various subsequent treatments (Figure 1). Analogous experiments with D_2 give the spectra shown in Figure 2.

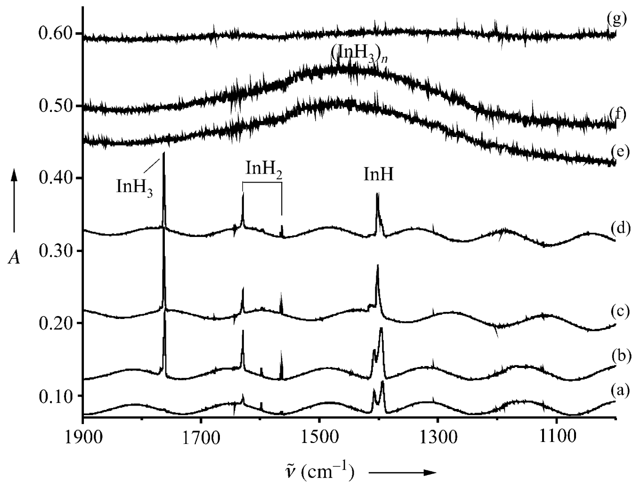

Figure 1. Infrared spectra in the 1900–1000 cm^{-1} region for laser-ablated indium codeposited with normal isotopic hydrogen at 3.5 K. a) Pure H_2 and In deposited, b) after 193 nm irradiation for 3 min, c) after 193 nm irradiation for 58 min (total), d) after annealing to 6.2 K, e) after annealing to 8 K and removing the H_2 matrix host, f) spectrum recorded at 70–100 K, and g) spectrum recorded at 180–200 K.

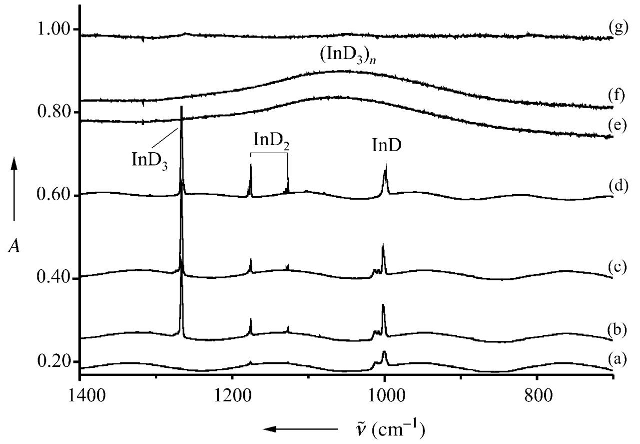

Figure 2. Infrared spectra in the 1400–700 cm^{-1} region for laser-ablated indium codeposited with deuterium at 3.5 K. a) Pure D_2 and In deposited, b) after 193 nm irradiation for 20 min, c) after 193 nm irradiation for 40 min (total), d) after annealing to 9.0 K, e) spectrum recorded at 30–60 K after removal of the D_2 matrix host, f) spectrum recorded at 110–130 K, and g) spectrum recorded at 200–220 K.

Infrared spectra after 193 nm irradiation, Figure 1 b and Figure 2 b, show the pronounced growth of new strong bands at 1393.4 and 997.7 cm^{-1},respectively, which are between the gas phase (1424.8 and 1023.5 cm^{-1})[10–12] and solid argon

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[**] This work was supported by the National Science Foundation (CHE00-78836).

DOI: 10.1002/ange.200353216

(1387.4 and 995.9 cm^{-1})[13] fundamentals for InH and InD, respectively. The weaker 1628.9/1563.3 cm^{-1} and 1175.4/1126.3 cm^{-1} band pairs are assigned to InH_2 and InD_2, respectively, as these bands are 13–15 cm^{-1} higher the corresponding bands documented in argon matrix.[13] Continued irradiation at 193 nm, Figure 1 c and Figure 2 c, maximizes the intensity of new absorptions at 1760.9 and 1266.2 cm^{-1} (Table 1) which are assigned to InH_3 and InD_3 in solid H_2 and solid D_2, respectively, as they appear at slightly higher wavenumbers than the 1754.5 and 1261.2 cm^{-1} argon-matrix bands[13].

Table 1: Infrared absorptions [cm^{-1}] observed for indium and thallium hydrides in solid hydrogen or deuterium at 3.5 K.

In, H_2	In, D_2	Tl, H_2	Tl, D_2	Hydride
1760.9	1266.2	1748.4	1254.6	MH_3
1628.9	1175.4	1520.0	1098.8	MH_2
1563.3	1126.3	1390.2	1007.5	MH_2
1407.7	1011.6			MH site
1393.4	997.7	1311	940	MH
979.6	709.9	909.7	652.9	M_2H_2
1460.0[a]	1060.0[a]	–[b]	–[b]	$(MH_3)_n$

[a] Broad bands appeared after warming above 7(10) K to remove H_2(D_2) and disappeared above 200–210 K. [b] Not observed for Tl.

Annealing the H_2 sample to 6.2 K increases the InH_2 absorptions and sharpens the InH band with little effect on the InH_3 absorption (Figure 3). Further annealing to higher temperatures was carried out to search for the possible formation of In_2H_6: A neon "overcoat" enabled the solid H_2 to be annealed above 7 K. The InH_3 monomer decreases and the weak absorptions at 1820, 1803, 1297, and 1059 cm^{-1} increase on annealing in the 7–8 K range. These absorptions, labeled DI for diindane, increase together on annealing to 7.2 K (Figure 3 d) and are joined by others in the lower region at 718, 535 and 526 cm^{-1} (not shown) These absorptions are destroyed by 193 nm radiation, and regenerated in part by further annealing to 7.0 K (not shown). Similar behavior was found for deuterium: Weak new bands were observed at 1297, 1291, 943, and 767 cm^{-1} on annealing to 9–12 K.

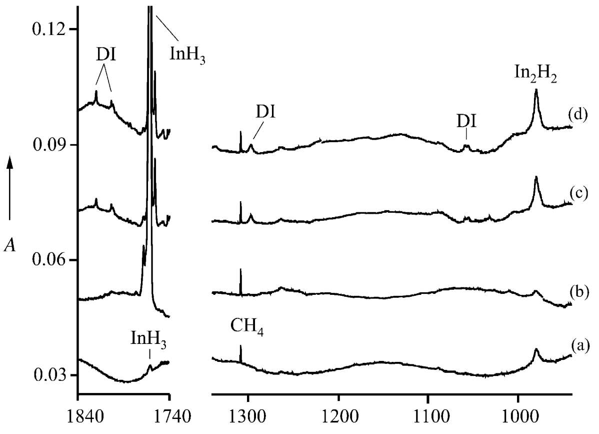

Figure 3. Infrared spectra in the 1840–1740 and 1340–940 cm^{-1} regions for laser-ablated indium co-deposited with hydrogen at 3.5 K. a) Pure H_2 and In deposited, b) after 193 nm irradiation for 15 min, c) after annealing to 6.2 K, and d) after annealing to 7.2 K.

The spectrum after removing the H_2 matrix host shows that the sharp InH_3 product absorptions are replaced by a broad (300 cm^{-1} full-width at half-maximum) band centered at 1460 ± 20 cm^{-1} (Figure 1 e). Similar behavior is observed for In and D_2: the strong InD_3 band at 1266.2 cm^{-1} is replaced by a broad (200 cm^{-1} full-width at half-maximum) band centered at 1060 ± 20 cm^{-1} (Figure 2 e). Spectra were recorded for both samples continuously as they warmed to room temperature. The broad 1460 cm^{-1} band in H_2 experiments is observed in spectra recorded at 30–60 K and up to 160 K, is decreased in the 160–180 K range, and is absent above 180 K (Figure 1 g). The broad 1060 cm^{-1} band in spectra with D_2 at 30–60 K (Figure 2 e) remains in the spectra recorded up to 180–200 K and is absent above 200 K (Figure 2 g). Indium metal is deposited on the window at room temperature.

Electronically excited indium hydride is formed very efficiently in these experiments by activation with 193 nm excitation[21] of In in an endothermic (46 kcal mol^{-1})[10] Equation (1). This electronically excited InH* reacts straightaway with the hydrogen matrix cage to form InH_3 [Eq. (2)].

$$In + H_2 \xrightarrow{193\,nm} InH^* + H \tag{1}$$

$$InH^* + H_2 \rightarrow InH_3 \tag{2}$$

The In_2H_2 (In_2D_2) product is detected at 979.6 (709.9) cm^{-1}, which is slightly higher than the recently reported argon-matrix counterparts,[22] as expected. Annealing to 6.5 K (Figure 3 c) triples the intensity of the 979.6 cm^{-1} In_2H_2 band and sharpens the InH absorption. Further annealing to 7.2 K increases In_2H_2 at the expense of InH and decreases InH_2 and InH_3, while the above seven bands increase in intensity. Higher polymers of InH with In–H–In linkages should absorb near In_2H_2 (or to lower wavenumber). Hence, the broad 1460 and 1060 cm^{-1} bands can be assigned to absorptions of solid $(InH_3)_n$ and $(InD_3)_n$ (Figure 1 and 2).

The positions of the broad bands in the In/H_2 and In/D_2 spectra define a H/D ratio 1460/1060 = 1.377 appropriate for an In–H stretching vibration ($InH_{1,2,3}$ intermediates exhibit H/D ratios ranging from 1.386 to 1.394). Solid alane exhibits a broad band $(AlH_3)_n$/$(InH_3)_n$ ratio (1720/1460 = 1.18), which is comparable to the Al/In frequency ratios in solid hydrogen for the MH (1.16), MH_2 (1.12, 1.15), and MH_3 (1.07) molecules (M = metal), and for the calculated parallel ring-stretching mode (b_{3u}) frequency ratio for M_2H_6 molecules (1483/1280 = 1.16). This result demonstrates that the broad bands in $(AlH_3)_n$ and $(InH_3)_n$ are due to fundamental Al–H–Al and In–H–In stretching vibrational modes, respectively, and implies that network solid $(AlH_3)_n$ and $(InH_3)_n$ have similar structures although a different coordination environment of In cannot be excluded on this basis.

Solid gallane has an oligomer structure with both terminal and bridging Ga–H bonds.[23] The chemistry of Al, Ga, and In is influenced by a d-orbital contraction for Ga, which makes Ga atoms smaller and more electronegative. In contrast Al and In are more electropositive, and better Lewis acids, and stabilize the sixfold coordination network[18] with M–H–M bridge bonds in solid $(AlH_3)_n$ and in solid $(InH_3)_n$.

We also find evidence for In_2H_6 molecules: This dimer is produced during the later stages of the annealing at 6–8 K before the solid film is formed, which suggests a small barrier to dimerization. Although the amount of In_2H_2 also increases on annealing by dimerization reaction ($2\,InH \rightarrow In_2H_2$), the further addition of $2\,H_2$ to form In_2H_6 probably requires substantial activation energy. The indane dimerization reaction ($2\,InH_3 \rightarrow In_2H_6$) is calculated to be exothermic by only 1 kcal mol^{-1}.[8] The new 1820, 1803, 1297, 1059, 718, 535, and 526 cm^{-1} absorptions are appropriate for dibridged In_2H_6 based on comparisons with recent MP2 calculations[8] (Table 2) and the spectrum of Al_2H_6 in solid hydrogen.[16,17] The two terminal In-H_2 modes at 1820 and 1803 cm^{-1} are higher than for InH_3, as calculated and observed, and as found for the aluminum analogs. The two In-H-In bridging modes at 1297 and 1059 cm^{-1} are 35 cm^{-1} above and 30 cm^{-1} below the calculated values, and of course below the observed values for Al_2H_6.

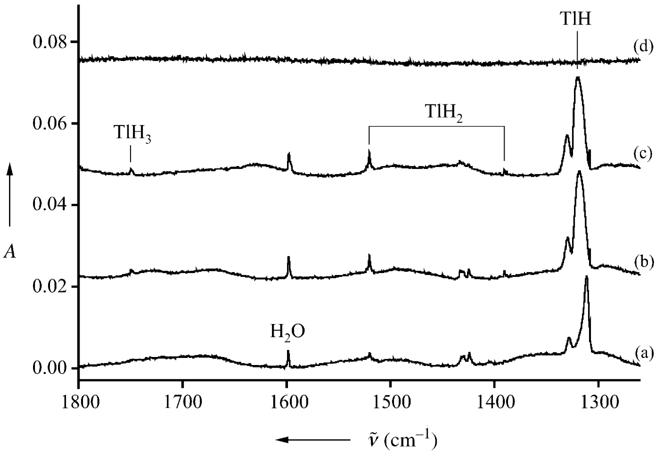

Figure 4. Infrared spectra in the 1800–1260 cm^{-1} region for laser-ablated thallium codeposited with hydrogen at 3.5 K. a) Pure H_2 and Tl deposited, b) after 193 nm irradiation for 5 min, c) after $\lambda > 240$ nm irradiation for 10 min, and d) after annealing to 8 K.

Table 2: Calculated and observed infrared active vibrational modes for dibridged In_2H_6 (D_{2h}).

Symmetry	Calcd[a] [cm^{-1}]	Intensity[a]	Observed[b] [cm^{-1}]	Intensity[b]	Observed[c] [cm^{-1}]	H/D ratio
b_{3u}	1841	(139)	1820	(0.004)	1297	1.403
	1262	(1372)	1297	(0.011)	943	1.375
	607	(834)	535	(0.034)	–	–
b_{2u}	1089	(420)	1059	(0.005)	767	1.381
	588	(259)	526	(0.008)	–	–
b_{1u}	1837	(522)	1803	(0.002)	1291	1.397
	753	(261)	718	(0.005)	–	–
	202	(10)				

[a] Ref. [8]: intensities (km mol^{-1}). [b] This work, observed in hydrogen matrix on annealing to 6–8 K: Intensities (integrated absorbance). [c] This work, observed for In_2D_6 in deuterium matrix on warming to 9–12 K.

Similar experiments with laser-ablated thallium and hydrogen (deuterium) give weak bands at 1311 (940) cm^{-1}, which increased on ultraviolet irradiation and are slightly lower than gas-phase TlH (TlD) fundamentals[10] of 1345.3 (963.7) cm^{-1} and are due to diatomic thallium hydride molecules in solid H_2 (D_2). Weak absorptions are observed at 1520.0 (1098.8) and at 1390.2 (1007.5) cm^{-1} for the TlH_2 (TlD_2) dihydrides and at 1748.4 (1254.6) cm^{-1} for the TlH_3 (TlD_3) trihydrides (see Table 1). Our TlH_3 frequency is in excellent agreement with the MP2 prediction.[8] Thallium hydride spectra are illustrated in Figure 4. In addition we observe weak absorptions for the Tl_2H_2 (Tl_2D_2) dimers at 909.7 (652.9) cm^{-1}, in spite of the fact that Tl_2H_2 was not predicted to be stable.[8] Our TlH_3 band absorbance is much less intense than that observed for InH_3, which in turn is expected to be much less than that observed for GaH_3 and AlH_3.[16,17,24,25] Evaporation of the H_2 (D_2) matrix gave no evidence of broad absorption bands in the 1500–700 cm^{-1} region that might be due to solid thallium hydride. Our failure to observe $(TlH_3)_n$ at low temperature is due to the inherent instability of the Tl^{III} hydride, which is also manifested in a low yield of TlH_3.[8,25] Finally, this result casts doubt on the claimed synthesis of $(TlH_3)_n$.[26,27]

Received: October 31, 2003 [Z53216]

Keywords: hydrides · indium · IR spectroscopy · matrix isolation · thallium

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