Transmission Infrared Spectroscopy of Ammonia Borane

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Transmission infrared spectroscopy can potentially offer unique advantages in studying the mechanisms of hydrogen loss from complex hydrides that are being considered for use as hydrogen storage materials. An apparatus that permits infrared spectra to be obtained over a temperature range of 85 to 1200 K and under either an ambient pressure of selected gases or under vacuum has been designed and its performance characterized. While the method is capable of producing high quality spectra at room temperature and below, several difficulties arise as the sample temperature is increased to the point where hydrogen loss occurs. These challenges include reaction with the host matrix, reaction with residual water or oxygen in the system, and loss of transparency of the sample. The performance of the method is illustrated with spectra obtained for ammonia borane, NH₃BH₃.

Introduction

Complex hydrides containing hydrogen covalently bonded to other light atoms are attractive candidates as hydrogen storage materials because they contain more hydrogen per unit volume than liquid hydrogen or high-pressure hydrogen gas¹. Of the elements of lower atomic weight than carbon, only boron forms an extensive array of compounds with hydrogen. For this reason, many of the complex hydrides considered for hydrogen storage applications contain boron. The covalent bonds to hydrogen are associated with intense and characteristic vibrational peaks, as observable with Raman or infrared (IR) spectroscopy. For complex hydrides to be useful for hydrogen storage, the mechanism by which hydrogen is released from these compounds must be understood. It is especially important to identify and characterize any intermediate species that form in the course of hydrogen release. Furthermore, reversibility is a key requirement for a practical hydrogen storage material and the ability of intermediates to react with H₂(g) to reform the starting materials is of great importance. As vibrational spectra have a high degree of chemical specificity, it should be possible to distinguish the various chemical species that form as a complex hydride releases or gains hydrogen. Other material characterization techniques generally lack such sensitivity to chemical speciation or even to the presence of hydrogen. Although Raman and IR spectroscopies are similar in providing vibrational spectra, IR has some potential advantages. For example, H₂(g) is invisible to IR radiation whereas H₂(g) is Raman active so that the rehydrating process under high pressures of H₂(g) can be studied with IR spectroscopy without interference by features from the gas. For the potential advantages of transmission IR spectroscopy to be fully realized, several potential experimental challenges must be addressed. These challenges are illustrated here with transmission IR spectra obtained on ammonia borane, NH₃BH₃.

Ammonia borane, H₃N·BH₃ (AB), is a colorless stable solid (m.p. 104 °C) that is relatively nonhazardous and has low toxicity. It has a high hydrogen weight percentage of 19.6 % and as such is one of the leading complex hydrides being considered for hydrogen storage applications². Consequently, a variety of studies have been performed on the mechanism of hydrogen release from AB. For example, Palumbo et al.³ have recently used thermogravimetry and differential thermal analysis coupled with mass spectrometric analysis of volatile species to characterize the thermal decomposition at sub-ambient pressure. A similar study was recently performed by Frueh et al.⁴. In both cases, amino borane (BH₂NH₂) and borazine (B₃N₃H₆) were observed as gas phase products with mass spectrometry. Miranda and Cedar⁵ have used density functional theory to suggest two routes for AB dehydrogenation. The first route involves formation of polyaminoborane, [BH₂NH₂]ₓ, and polyiminoborane, [BHNNH]ₓ, whereas the second route starts with the formation of the cyclic compounds/polymer borazine, cycloborazalene, (H₂BHNH)₃, and polyborazalene, [B₃N₃H₄]ₓ. Each of the intermediate species will have a unique vibrational spectrum. For many of these species appropriate reference spectra are available.

There have been previous relevant IR studies of ammonia borane⁶,⁷ and of amino borane in the gas⁸ and solid⁹ phases, or trapped in inert matrices¹⁰–¹². The loss of hydrogen to form amino borane-like structures with a B≡N double bond should be apparent in the IR spectra. In earlier IR matrix isolation studies of the thermal decomposition of AB¹⁰, it was possible to isolate the amino borane molecule (H₂N·BH₂) and to observe all 11 of its IR active fundamentals. Based on observed B¹⁰ and N¹⁵ isotopic shifts and normal mode calculations, new assignments for some of the fundamentals reported in an earlier gas phase study⁸ were proposed. The results¹⁰ indicate that the B≡N stretch of amino borane occurs at 1334 cm⁻¹. However, labeling the fundamental that occurs at this frequency as the B≡N stretch is an oversimplification as three fundamentals of modes of A₁ symmetry for this C₂ᵥ molecule occur at 1120, 1334, and 1620 cm⁻¹ due to the BH₂ bend, the B≡N stretch, and the NH₂ bend and the actual normal modes contain significant contributions from each of these internal coordi-
nates. The mixed nature of these modes explains the fact that the 1334 cm\(^{-1}\) band shifts by a smaller amount than expected for a B=N diatomic molecule. From the normal mode analysis, Carpenter and Ault\(^{10}\) find that the potential energy distribution for the 1334 cm\(^{-1}\) band shows roughly 35% B=N stretch character, 40% BH\(_2\) bend character, and 25% NH\(_2\) bend character. The previous vibrational studies of AB and related compounds provide a good starting point for the interpretation of the results obtained in studies such as ours.

**Experimental**

The apparatus consists of an evacuable infrared cell equipped with differentially pumped KBr windows and a sample holder that permits spectra to be obtained over the temperature range of 85 to 1100 K. A detailed description is given elsewhere\(^ {13}\).

The IR spectra were collected with a Mattson Cygnus 25 Fourier transform infrared (FTIR) spectrometer using Winfirst software. The IR cell was evacuated to a pressure of 9 \times 10^{-2} torr during data acquisition. The FTIR was purged with air that was nominally free of CO\(_2\) and H\(_2\)O, although inadequate purging occasionally resulted in IR bands due to these two gases. A transmittance spectrum consists of the ratio of a sample spectrum to a reference spectrum. Experiments consisted of taking spectra of the AB sample, resistively heating it to the desired temperature under a flow of argon (to minimize sample evaporation), allowing it to cool back to room temperature, removing the argon flow, evacuating the cell, and finally acquiring another sample spectrum. The reference spectra were obtained in different ways for different samples.

Two methods of sample preparation were used here. In the first method, the AB powder (Sigma Aldrich, 97% pure) was mixed with a powder of an IR transparent salt such as KBr (Fluka, IR grade) or CaF\(_2\) (Alfa Aesar, 99%). A range of ratios of AB:salt were used, spanning from 1:5 to 1:25. One rectangle of the sample mixture and one rectangle of the salt only (as a background) were spread onto a steel block and then a high transparency tungsten mesh and another steel block were stacked over it. This assembly was then compressed with a hydraulic press, crushing the powder into the tungsten grid, thereby forming two reasonably transparent windows. This is done with 10-15 tons of force. The grid is then screwed into the sample holder, the holder is loaded into the IR cell and the cell is evacuated. A sketch of the sample holder is shown in Figure 1(a). The system has a linear translator that allows the sample holder to be moved into position to take a spectrum of first the background (pure KBr or vacuum) and then the sample (AB with KBr or CaF\(_2\)). For CaF\(_2\), vacuum was used for the background spectrum as pure CaF\(_2\) would not stick to the mesh.

In the second method, AB was dissolved in tetrahydrofuran solvent, applied to a 13 mm x 1 mm KBr disk and then dried. The disk was then tied onto a blank tungsten mesh using tantalum wires and heated and cooled in the same way as for the pressed powder samples. However, since the thermal contact between the disks and the mesh is not as good as with the pressed powder samples, the accuracy of the temperature measurements is reduced. A photograph of a mounted AB-coated KBr disk is shown in Figure 1(b). Vacuum was used for the reference spectrum for the transmittance spectra of the AB-coated KBr
disks.

Results and Discussion

Although our focus is on the utility of IR spectroscopy for the study of hydrogen storage materials, we have also characterized the samples with Raman spectroscopy. Solid ammonia borane has a tetragonal structure and Hess et al.,\textsuperscript{14} have used factor group analysis to show that in this phase the vibrational spectrum can be understood based on the symmetry of the free molecule. Because the isolated AB molecule has C\textsubscript{3v} symmetry, all of the modes that are Raman active are also IR active. Of the twelve fundamentals, only the torsional mode of A\textsubscript{2} symmetry is inactive. The Raman spectrum of our ammonia borane powder is shown in Figure 2. As there have been many previous Raman studies of ammonia borane\textsuperscript{7,14–17}, our spectra serve to establish both the purity of the sample and the extent to which our sample yields the same results as others have obtained. All of the expected fundamentals are observed and are within 5 cm\textsuperscript{−1} of previously reported values. In the highest wavenumber region, two fundamentals in both the NH and BH stretch region are expected. Thus the peaks at 3257 and 3317 cm\textsuperscript{−1} are assigned to symmetric (A\textsubscript{1}) and asymmetric (E) NH\textsubscript{3} stretch vibrations. In the BH stretch region, the sharp peak at 2284 is assigned to the symmetric (A\textsubscript{1}) BH\textsubscript{3} stretch. The broader peak at 2376 cm\textsuperscript{−1} has an unresolved shoulder at 2328 cm\textsuperscript{−1}. This was also observed by Hess et al.\textsuperscript{14} and this peak, rather than the one 2376 cm\textsuperscript{−1}, was assigned to the asymmetric (E) BH\textsubscript{3} stretch vibration, as the 2328 cm\textsuperscript{−1} peak was depolarized. Peaks observed here that are not fundamentals of \textsuperscript{11}BH\textsubscript{3}NH\textsubscript{3} were also reported by others. Thus, the peak at 798 cm\textsuperscript{−1} is due to the B-N stretch of \textsuperscript{10}BH\textsubscript{3}NH\textsubscript{3}. The peak at 3176 cm\textsuperscript{−1} is likely due to an overtone of the NH\textsubscript{3} asymmetric bend, the fundamental of which is seen at 1599 cm\textsuperscript{−1}. The unlabeled peak at 1450 cm\textsuperscript{−1} is likely an overtone of the fundamental at 729 cm\textsuperscript{−1}. In previous studies, Raman spectra extended only to 3400 cm\textsuperscript{−1}, so whether or not the peak that we observe at 3474 cm\textsuperscript{−1} was seen in the earlier studies cannot be determined. It can plausibly be assigned to a combination of the modes with fundamentals at 1181 and 2328 cm\textsuperscript{−1}. If we accept the assertion by Hess et al.\textsuperscript{14} that the 2376 cm\textsuperscript{−1} peak is not the asymmetric BH\textsubscript{3} stretch fundamental, then an alternative assignment is to the overtone of the asymmetric BH\textsubscript{3} deformation, the fundamental of which we observe at 1181 cm\textsuperscript{−1} and Hess et al.\textsuperscript{14} observed at 1189 cm\textsuperscript{−1}. With all of the major peaks assigned to ammonia borane, the Raman spectra indicate that the sample is pure and provide a good basis for interpreting the IR spectra.

A set of transmission IR spectra as a function of annealing temperature of ammonia borane mixed with KBr at an AB:KBr ratio of 1:25 are shown in Figure 3. The initial spectrum taken at 300 K prior to annealing shows most of the AB vibrations identified with Raman spectroscopy, although the peaks are shifted somewhat and are considerably broader. This broadening is related to the degree of scattering by the sample and varies from one sample preparation to the next. Individual peaks are not resolved in the NH and BH stretch regions, although broad absorptions centered at about 3300 and 2300 cm\textsuperscript{−1} are observed. The relative intensities are also different from those seen with Raman spectroscopy. For example, the symmetric and asymmetric NH\textsubscript{3} deformation peaks at 1376 and 1604 cm\textsuperscript{−1} in the IR spectra of Figure 3 have the opposite relative intensity of the corresponding peaks at 1371 and 1599 cm\textsuperscript{−1} in the Raman spectra in Figure 2.

Annealing to a temperature of only 433 K results in profound changes in the spectrum with the appearance of new and sharper peaks, the most prominent of which are at 1126, 2225, and 2295 cm\textsuperscript{−1}. As these are essentially at the same position as observed by Harvey and McQuaker\textsuperscript{18} for KBH\textsubscript{4}, it is evident that AB has reacted with the KBr host to form KBH\textsubscript{4}. The 433 K anneal also produces a broad feature at a slightly higher frequency than the 1376 cm\textsuperscript{−1} peak seen in the 300 K spectrum. This peak grows in intensity and shifts slightly lower in frequency with further annealing. This feature is associated with the formation of hexagon boron nitride (h-BN), which is characterized by an intense and broad peak at approximately this position\textsuperscript{19,20}. Unfortunately, since the NH\textsubscript{3} symmetric deformation mode of AB occurs at nearly the same value, the temperature at which h-BN begins to form is not clear. Nevertheless, the
peak shape undergoes changes with annealing temperature indicative of a reaction path involving intermediate species. The KBH$_4$ peaks gradually decrease in intensity as the annealing temperature is raised. However, the structure in the BH stretch region is distorted by the presence of CO$_2$(g) peaks from incomplete purging of the optical path. The 913 and 993 K spectra show two sharp peaks at 1959 and 2029 cm$^{-1}$, that are exact matches to the peaks attributed to the asymmetric OBO stretches of $^{11}$BO$_2$ and $^{10}$BO$_2$ by Hisatsune and Suarez. In their case, the BO$_2$ was obtained either by oxidizing KBH$_4$ or by dehydrating KB(OH)$_4$. The intensity ratio of the 1959 to 2029 cm$^{-1}$ peaks reflects the natural abundance ratio of $^{11}$B:$^{10}$B of 4:1. The sharpness of these peaks indicates the formation of isolated BO$_2$ molecules that are trapped in the KBr host.

The results of Figure 3 illustrate the various obstacles that must be overcome before transmission IR can be effectively used to characterize the dehydrogenation mechanism of hydrogen storage materials such as ammonia borane. The most severe problem is reaction with the host material. This problem is exacerbated by using mixed pressed powders as the two materials thereby have a high degree of contact. Two approaches can be used to overcome these difficulties. One is to use a less reactive host material, such as CaF$_2$, which has the additional advantage of a higher melting point than KBr. However, it was more difficult to obtain transparent samples with CaF$_2$ and the peaks obtained were even broader and less distinct than with KBr. The second approach is to use a thin film of the material on a transparent window of the host. We have tried this method by preparing a solution of 0.9 mg of AB dissolved in 0.7 ml of THF and applying it to a KBr disk. Spectra obtained with these two methods are compared with a spectrum obtained with a KBr host in Figure 4. In the spectrum obtained with CaF$_2$, the AB peaks are so weak that the spectrum is essentially flat in the NH stretch region. Given the poor quality of the initial spectrum at room temperature, there is little hope that subsequent spectra obtained after annealing would yield useful information. With the AB film on the KBr disk, different problems arise. The CH stretch at 2919 cm$^{-1}$ reveals the presence of a hydrocarbon contaminant, indicating that the THF had not been completely removed. The remaining peaks are likely a combination of those due to AB and to residual THF. For example, the prominent peak at 1241 cm$^{-1}$ is well removed from any peak seen with Raman spectroscopy for AB itself. Nevertheless, sharper peaks are seen in the BH and NH stretch regions indicating that this method has some promise provided complete removal of the solvent can be achieved. Future work will therefore focus on using thin films of sample deposited onto IR-transparent disks. Given that reaction with KBr powder was observed, it is possible that reaction would also occur at the interface between a KBr disk and the deposited AB film. If this problem occurs, a CaF$_2$ disk could be used instead. The poor quality of the spectra obtained with CaF$_2$ powder is largely due to light scattering associated with the low transparency of the sample. This should not be a problem with disks made of CaF$_2$, which have the same high transparency as those made from KBr.

Conclusions

Vibrational spectroscopy has great potential for identifying the intermediates that form during hydrogen release from complex hydrides used as hydrogen storage materials. The method we have described allows spectral changes to be monitored as a function of annealing temperature without exposing the sample to ambient conditions. This is in contrast to the attenuated total reflectance FTIR method employed by Frueh et al. The IR spectra clearly reveal the formation of the expected end product of AB decomposition, hexagonal boron nitride. However, this study has revealed several experimental obstacles that still must be overcome. First and most important is the potential for reaction with the host material. The IR results presented here show that AB reacts with KBr at temperatures as low as 433 K to form KBH$_4$. Second, any oxygen or water contamination must be thoroughly removed to prevent formation...
of oxidation products, such as the BO$_2$ molecule. Third, the asymmetric stretch of gas phase CO$_2$ can obscure the BH stretch vibrations and therefore the optical path must be thoroughly purged. Fortunately, none of these obstacles are insurmountable and once appropriate measures are taken, transmission IR could be a powerful tool for characterizing the chemical reactions associated with the use of complex hydrides for hydrogen storage.

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