*Inorg. Chem.* **2004**, *43*, 3035–3037

Inorganic Chemistry

Communication

# The Observation of the First Vibrational Overtone of Dihydrogen in the Luminescence of Zeolites at Low Temperatures

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Received January 8, 2004

Dehydrated zeolites NaA, NaY, and barium-exchanged NaY luminesce when irradiated with the 1064 nm laser light of an FT-Raman instrument. When hydrogen is adsorbed in the zeolite, the luminescence is altered in several ways. Most remarkable is the appearance of "absorptions" in the positions of the first vibrational overtones of $H_2$ and HD. Although these features are in the expected positions with reasonable band profiles for overtone absorptions, the large extinction of the luminescent intensity requires a more efficient mechanism than simple reabsorption of emitted photons. In addition to the appearance of holes in the luminescence spectrum, other luminescent features are substantially quenched by the presence of hydrogen or, in one case, augmented.

The infrared spectrum of dihydrogen has been investigated in zeolite hosts for a number of years.[1] We undertook a comparison of the Raman spectrum of dihydrogen adsorbed in zeolites with its infrared spectrum. The motive for such a comparison evolved from studies of dihydrogen complexes of alkali halides in argon and neon matrices.[2,3] Particularly in argon matrices, hydrogen exhibits a preference for interaction with the anion of alkali halide ion pairs.[2] The perturbed fundamental vibration of hydrogen varied only by about 4 $cm^{-1}$ in a series of complexes, MCl, where M = Li, K, Rb, and Cs. Upon reading that the spectrum of dihydrogen in alkali metal-exchanged zeolite X also exhibited very little variation,[4] we wondered whether the infrared spectrum was actually reporting on dihydrogen that was interacting with anion sites in the framework of the zeolite. The Raman spectrum could be trusted to give a report on all adsorbed dihydrogen regardless of the geometry of coordination, and we sought corroboration of the infrared spectrum in the Raman. The Raman results will be reported elsewhere. We report here luminescence observations that are quite unprecedented.

Dried zeolites NaY, BaY, or NaA occasionally luminesce in the Stokes region of the Raman spectrum when subjected to illumination at 9395 $cm^{-1}$ from the Nd:YAG laser of a Perkin-Elmer 2000 Fourier transform spectrometer.[5] It is clear that there are at least four distinct luminescence spectra that can be produced by different treatments. The details of the luminescences will be described below. For the moment, it is important to realize that the luminescence is altered by the presence of hydrogen in several key ways.

What is most remarkable about the luminescence is the appearance of a dip in the luminescent intensity at the position which corresponds to the first vibrational overtone of dihydrogen.[6] (See Figure 1.) For NaA at 77 K, the dip

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(5) Zeolite samples were observed in two different fashions. In one configuration, samples were contained in valved, quartz esr tubes which were heated while being evacuated to 20 $\mu$m pressure. The tubes were then filled at 77 K on a vacuum line and observed while cooled to liquid nitrogen temperatures. Alternatively, pressed pellets of the zeolites were heated in vacuo in a vessel that was then transferred to an inert atmosphere box where they were quickly loaded in a holder which could be attached to an Air Products, model CS-202 refrigerator equipped with an exchange-gas inlet at the sample. The sample holder included a CsI window that had been sealed to the holder by several methods. The seals were never completely successful, and hydrogen leaked into the vacuum system when it was reversibly bound to the zeolite. Still observations were possible from 16 to 45 K. Raman measurements were performed in both configurations by collecting 180° backscattered radiation. The esr tubes were used exclusively for Raman measurements. The samples were immersed in liquid nitrogen in an unsilvered Dewar designed for esr spectroscopy. Infrared measurements were made of the pellets in the Air Products apparatus by reflection. The infrared beam of the spectrometer was deflected approximately 80° on to the sample by a front silvered plane mirror. Scattered radiation was collected by a large front silvered parabolic mirror which was focused on the detector. The specular reflectance from the holder was not totally absent from what reached the detector. Luminescence was also noted in FT Raman spectra reported by Ferwerda, R.; van der Maas, J. H. *Spectrochim. Acta* **1995**, *A51*, 2147.

10.1021/ic049957j CCC: $27.50 © 2004 American Chemical Society
Published on Web 04/14/2004

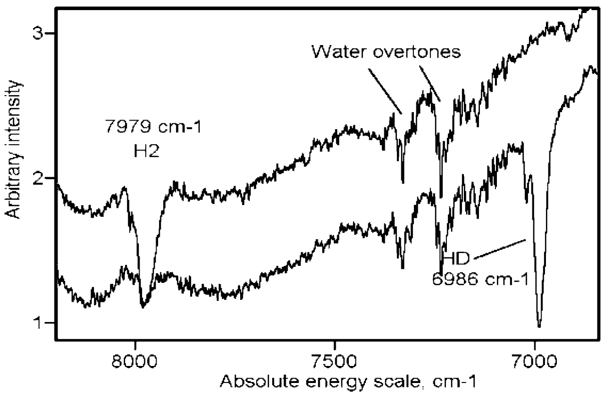

**Figure 1.** Raman spectrum of $H_2$ and HD in barium-exchanged zeolite NaY[8] at 17 K showing loss of luminescent intensity at positions of water and hydrogen vibrational overtones.

matches the shape and position of what has been seen in the reflectance spectrum taken under similar conditions.[6] In the presence of HD, the dip is seen in the appropriate position for its first overtone. Using $D_2$, the position of the first overtone is outside the viewing range of the optics. The position of the second overtone of $D_2$ is observable, but we observe no dip in that region. With $H_2$, the size of the dip is weakly dependent on the amount adsorbed over the range of applied pressures from 15 cm of Hg to 76 cm of Hg at 77 K; the trend line does not extrapolate to zero intensity at zero pressure. At the lowest pressures, there is roughly 0.5 $H_2$ molecule for every sodium ion. At higher pressures, the amount of hydrogen exceeds the number of sodium ions and there is concomitant growth of a shoulder to higher wavenumber that is seen both in the dip and in the Raman spectrum of $D_2$.

The dips in the luminescence spectra closely resemble what is seen in fluorescence hole burning experiments, but there is one key difference. In photochemical hole burning experiments, the widths of the holes are characteristic of the emission spectra of the fluorescent states. The broad profile of fluorescence spectra is understood as an envelope of fluorescences, the energies of which are modulated by the particulars of the site, a phenomenon referred to as inhomogeneous broadening.[7] As reported above, the dip in the luminescence spectrum of NaA has the same width and position as the overtone absorption in the reflectance spectrum.[6] The widths of the dips seen in the luminescence spectra of NaY and barium-exchanged NaY are more narrow than the width seen in NaA.

Although the positions and widths of the dips are as expected for vibrational transitions, we do not believe the dips are caused by the simple reabsorption of photons emitted by the sample. We have found that the absorbance of the fundamental H−H stretching vibration is small; for NaY we have typically seen optical densities of less than 0.01 in reflectance. By contrast, the optical densities of the dips in the luminescence spectrum are typically more than 10 times more intense for similar loadings. We can infer from a figure showing the fundamental and overtone of $H_2$ in NaCaA that the fundamental is approximately 100 times more intense.[9] In an earlier report, they claim the fundamental of $D_2$ is 35 times as intense as the overtone.[10] Rather than there being simply a reabsorption of an emitted photon, there must be coupling between the excited vibrational levels of hydrogen and the luminescent state whereby energy is transferred to the vibrational manifold of hydrogen and then relaxed nonradiatively. Fluorescence resonance energy transfer has been described for a number of systems.[11] The mechanism involves dipole coupling and will only be prominent when the transition dipole for the acceptor is large. It is unlikely this can be the case for hydrogen. In order for the hydrogen to efficiently relax the excited state, the hydrogen wave functions must be mixed with the electronic states of the emitter such that there can be a simultaneous electronic relaxation as the hydrogen is excited to its second excited vibronic level. The selection rules for such a process will depend on the symmetry properties of the product functions. This is no different from vibronic coupling in high symmetry Werner-type transition metal complexes.[12] The absence of a dip corresponding to the second overtone of $D_2$ may be a reflection of the different symmetry properties of that of a $\nu = 3 \leftarrow 0$ transition. That the line widths of the dips are so similar to the widths of vibrational transitions suggests that there is very inefficient state-to-state energy transfer among excited states that are almost in resonance with the first overtone of hydrogen and those which are in resonance. Further evidence for such coupling between the hydrogen wave functions and those of the electronic excited states comes also from the alteration of luminescence intensity as a function of $H_2$ binding across the entire luminescence spectrum that we monitor, vide infra.

This is the first instance in our awareness where a discrete vibrational transition has resulted in loss of luminescence of an optical transition only at the wavelengths of the vibrational transition. Conceivably, the phenomenon is not commonly observed simply because very few luminescence measurements are made deep in the near-infrared with species whose overtones are so high in energy. Indeed, we have observed smaller dips in the region of the O−H stretching overtone region of water in several samples that reasonably have picked up some water after having been dried. (See, for example, Figure 1.) We are undertaking experiments that will substantiate this latter finding under controlled conditions.

While the dips in the luminescence may be correctly described, the source of the luminescence itself is not so easily understood. Luminescence in zeolites has been re-

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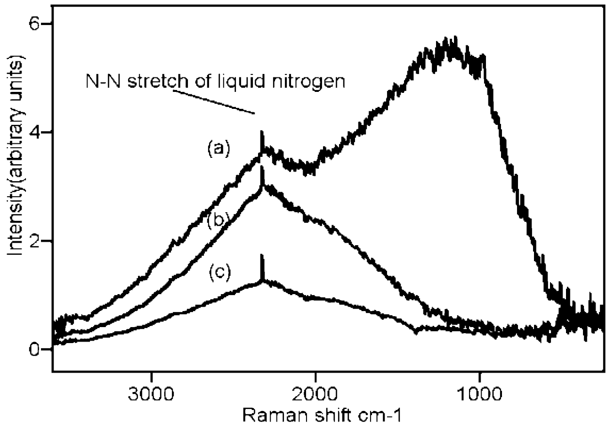

**Figure 2.** Luminescence seen in NaY as observed by Raman spectroscopy at 77 K: (a) zeolite NaY having been heated under vacuum to 770 K; (b) same sample as in part a after having been annealed at 620 K for 8 h; (c) same sample as in part a with 1 atm of hydrogen, taken prior to annealing. Note that the feature at 1145 $cm^{-1}$ can be completely quenched by hydrogen.

ported by several, and the causes have been attributed to iron impurities[13] and organic impurities.[14] We have attempted to show that these sources are responsible for the luminescent behavior of our samples but have only partly succeeded. We have identified at least four different types of luminescence. To establish iron as a luminescent center, we have synthesized NaA with various amounts of iron present.[15] There is no correlation between the luminescent intensity in the infrared region and the amount of iron present.

(a) Organic impurities do cause a luminescence after the sample has been heated. Acetone, ethanol, and toluene which have been pyrolyzed in a vacuum all give a broad emission that is most intense at the position of the laser excitation and becomes less intense at longer wavelength in an approximately exponential fashion. Intensity of this sort is eliminated after heating in an oxygen atmosphere at 625 K or higher temperatures.

(b) The luminescences that are shown in Figure 2 are not associated with any obvious impurity.[16] The luminescence centered at 1070 $cm^{-1}$ (8320 $cm^{-1}$, unshifted) can be achieved in NaY by heating to 820 K. It is not affected by oxygen treatments but can be eliminated simply by heating at relatively mild temperatures (620 K) in a vacuum.

(c) The luminescence at 2320 $cm^{-1}$ (7080 $cm^{-1}$, unshifted) may behave in a similar fashion. We have not determined the conditions that will reproducibly give the same large emissions of this sort that are shown in the figure.

(d) Finally, another luminescence involves $BaSO_4$, which we have occasionally used to assist in sample alignment. The presence of $BaSO_4$ appears to be associated with luminescence in BaY and in NaA.

With the exception of the luminescence associated with $BaSO_4$, the intensities of the luminescences are altered by the presence of hydrogen, irrespective of its mass. The luminescence associated with pyrolyzed organic impurities becomes more intense upon hydrogen adsorption whereas the other two luminescences are quenched by the presence of hydrogen, as shown in Figure 2. Since deuterium and hydrogen behave similarly, we believe that the quenching mechanism involves a shift in the energy levels, making the laser more or less efficient in populating the luminescent excited state. Interactions between a donor such as dihydrogen and an acceptor will result in a destabilization of the empty energy levels of the acceptor.[17] Electronic excitations from a populated level to this destabilized acceptor level will blue shift as a result of the donor−acceptor interaction. For luminescence to be quenched, the blue shift must be large enough to bring the onset of the excitation spectrum to higher energy than the 9395 $cm^{-1}$ laser light.

It seems clear from these experiments that adsorbed hydrogen is proximal to the luminescent centers in dehydrated zeolites so that it can relax luminescent excited states that are in resonance with the vibrational energy levels of hydrogen and so that the actual transition energies of the luminescent centers are altered to the extent that the laser is no longer effective in exciting the luminescence. We will attempt to characterize the excitation spectrum of these samples to determine if luminescence can be switched back on with higher energy excitations. Preliminary studies with dinitrogen show that the luminescence shown in Figure 2 can also be quenched in an analogous fashion by adsorbed dinitrogen although no dips have been seen in the region of the overtones of nitrogen. We are attempting to determine whether the binding sites that give rise to luminescence perturb the vibrational spectrum of hydrogen in a unique way as compared to what is seen in nonluminescent samples.

**Acknowledgment.** We wish to thank the donors of the Petroleum Research Fund for the partial support of this research. In addition, we acknowledge the support of the Louisiana Quality Education Support Fund for the purchase of the FT Raman spectrometer. We wish to acknowledge Mr. Tam Cao, Ms. Donitia Neiner, Professor John Wiley, and the Department of Chemistry at UNO for their contributions.

IC049957J

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