Inelastic Neutron Scattering, Infrared, and Raman Spectroscopic Studies of Mg_2FeH_6 and Mg_2FeD_6

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The combination of the three types of vibrational spectroscopy, infrared, Raman, and inelastic neutron scattering, has enabled all of the internal, and most of the external, modes of Mg_2FeH_6 and Mg_2FeD_6 to be observed and assigned, as well as some of the modes of Mg_2FeD_5H. As an aid to the assignment, a reliable, empirical force field has been developed. The spectra also show evidence for a dynamic distortion of the hexahydrido complex, an effect that is not observed for the deuterated species.

Introduction

Metal hydride complexes are of considerable interest for hydrogen storage applications.[1] One criterion for an ideal material would be a very high hydrogen density. Mg_2FeH_6 was first synthesized in 1984[2] and has a 2:1 hydrogen-to-metal (H:M) ratio and a high hydrogen concentration. The structure was characterized by neutron and X-ray powder diffraction and Mössbauer, infrared, and Raman spectroscopies and showed the presence of discrete FeH_6^{4-} complexes of octahedral symmetry.[2] Metal hydride complexes that do not contain other ligands, e.g. phosphines or CO, are comparatively rare and also serve as model systems for hydrogen-in-metal materials and for homogeneous and heterogeneous catalytic processes. Vibrational spectroscopy is frequently used to investigate such systems; thus, a detailed knowledge of the vibrational spectrum is essential for identification of such species. In this paper we report inelastic neutron scattering (INS), infrared, and Raman spectra of Mg_2FeH_6 and Mg_2FeD_6. The combination of all three forms of vibrational spectroscopy enable an unambiguous assignment of the modes to be made and a reliable force field to be obtained.

Experimental Section

Mg_2FeH_6 and Mg_2FeD_6 were synthesized by direct reaction of the elements at elevated temperature and pressure as previously reported.[3] By X-ray powder diffraction unreacted iron was detected in both samples, and so the presence of magnesium-containing impurities (not detected by X-rays) cannot be excluded. However, the vibrational spectra showed no evidence for any such impurities and the presence of unreacted metal would not affect the results. The compounds are air stable but moisture sensitive so for transport from Switzerland to the U.K. they were sealed in glass ampules.

The inelastic neutron scattering experiments were performed using the high-resolution broadband spectrometer, TFXA, at the ISIS pulsed spallation neutron source at the Rutherford Appleton Laboratory, Chilton, U.K.[4] This is an inverted geometry time-of-flight spectrometer where a pulsed, polychromatic beam of neutrons illuminates the sample at 12 m from the source. The backscattered neutrons are Bragg reflected by a pyrolytic graphite analyzer and those with a final energy of ∼32 cm^{-1} are passed to the He^3 detector bank. Energy transfer and spectral intensity is then calculated using standard programs to convert to the intermediate scattering function $S(Q,\omega)$, where Q is the momentum transfer ($Å^{-1}$) and ω (cm^{-1}) the energy transfer. TFXA offers high resolution, ∼2% of the energy transfer between 16 and 4000 cm^{-1}. The samples were transferred from the ampules to sealed aluminum cans in an argon filled drybox, loaded into a closed cycle cryostat, and cooled to ∼20 K, and the spectra were recorded.

The compounds are an intense, dark green, and attempts to record Raman spectra using far-red 752 nm and near-infrared 1064 nm excitation were unsuccessful, presumably due to absorption of the laser beam. Room-temperature Raman spectra were successfully recorded using a Renishaw 2000 dispersive Raman microscope spectrometer with 514.5 nm excitation from an argon ion laser. The instrument has been described in detail elsewhere.[5] The key to success was the use of low power, 4 mW, at the sample to avoid sample decomposition. The spectra were recorded from the samples in the glass ampules. By using the microscope to focus through the glass it was possible to obtain spectra without interference from the container. Slight sample fluorescence resulted in a sloping baseline that has been removed from the spectra presented here.

Mid-infrared, 4000−400 cm^{-1}, spectra were recorded at room temperature from KBr discs with a Digilab FTS-60 Fourier transform infrared (FTIR) spectrometer equipped with a room-temperature

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deuterated triglycine sulfate (DTGS) detector using 256 scans at 4 cm^{-1} resolution with triangular apodization. No further data processing was carried out.

Inelastic Neutron Scattering Spectroscopy. The intensity of the *i*th INS band at an energy transfer of ω_i is given by[6]

$$S(Q,\omega_i) \propto \sigma Q^2 U_i^2 \exp(-Q^2 U_\mathrm{T}^2) \qquad (1)$$

where σ is the neutron total scattering cross section, U_i^2 is the mean-squared displacement of the atoms in the mode, and U_T^2 is the total mean-squared displacement:

$$U_\mathrm{T} = \sum_i U_i \qquad (2)$$

The total scattering cross sections of hydrogen, deuterium, magnesium, and iron are 82.0, 7.64, 3.71, and 11.62 barns (1 barn = 1 × 10^{-28} m^2), respectively,[7] and since the intensity is dependent on the amplitude of vibration, which is larger for light atoms, the spectra will be dominated by motions that involve displacement of hydrogen or deuterium.

Equation 1 is noteworthy in that the intensity of a mode is determined only by the cross section, the momentum transfer, and the amplitude of vibration; hence, it is purely dynamic. The electronic contributions (dipole moment and polarizability) that make the intensities of infrared and Raman spectra so complex to calculate are absent. This has two implications: First, there are no selection rules and all modes are allowed. Second, from a conventional Wilson−Decius−Cross[8] normal coordinate analysis it is possible to calculate *both* the energies (from the eigenvalues) and intensities (from the eigenvectors) for INS spectra of molecular species. The requirement to fit the INS intensities is a stringent test of any force field.

The program CLIMAX[9,10] has been developed to carry out the normal coordinate analysis using both energy and intensity information as constraints. The input to the program consist of the atomic positions,[2] the experimental frequencies, the internal coordinates (six Fe−H stretches and 12 H−Fe−H bends), and the symmetry coordinates. INS spectra differ from infrared and Raman spectra in that overtones and combination bands are allowed transitions in the harmonic approximation. Combination bands (phonon wings) between internal modes and external (lattice) modes maybe particularly strong. CLIMAX can optionally calculate the spectrum with the inclusion of phonon wings, first overtones, and binary combinations.

Infrared and Raman bands are observed at zero wavevector (Brillouin zone center), and since acoustic modes have zero frequency at the Brillouin zone center they are unobservable by these methods. In contrast, INS spectroscopy is sensitive to modes at all wavevectors across the Brillouin zone and acoustic modes may be observed. The INS is the amplitude-of-motion and cross section weighted vibrational density of states. To first approximation, this is given by the projection of the dispersion curves onto the frequency axis. This has the result that undispersed modes, of which internal vibrations are typical, give sharp lines, whereas dispersed features give broader, structured features.

Results

At room temperature Mg_2FeH_6 crystallizes in the cubic space group $Fm\bar{3}m \equiv O_h^5$ (number 225) with four molecules in the unit cell.[2] There is one formula unit in the Bravais cell, and the ions all lie on special sites: the Mg^{2+} ions on tetrahedral T_d sites and the FeH_6^{4-} ions on octahedral O_h sites. Using the correlation method[11] the vibrations can be classified as shown in Table 1. It should be emphasized that INS spectroscopy is not subject to the same selection rules that Raman and infrared spectroscopies and that all the modes are allowed in INS spectroscopy. Figures 1 and 2 show the infrared, Raman, and INS spectra of Mg_2FeH_6 and Mg_2FeD_6, respectively. Similarities and differences are apparent between all three spectra and emphasize the need to have all three types of spectra for a complete analysis.

Table 1. Classification of Vibrations of Mg_2FeH_6 and Mg_2FeD_6

vibration	representations[a]
Fe−H/D stretches	A_{1g} (R) + E_g (R) + T_{1u} (IR)
Fe−H/D bends	T_{2g} (R) + T_{1u} (IR) + T_{2u} (ia)
libration	T_{1g} (ia)
translations	T_{2g} (R) + T_{1u} (IR)
acoustic	T_{1u} (ia)

[a] Activity shown in parentheses: R = Raman active; IR = infrared active; ia = inactive in both Raman and infrared. Note *all* vibrations are allowed in the INS spectrum.

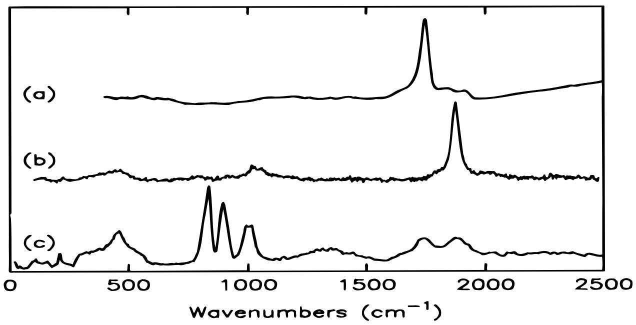

Figure 1. (a) Infrared, (b) Raman, and (c) INS spectra of Mg_2FeH_6.

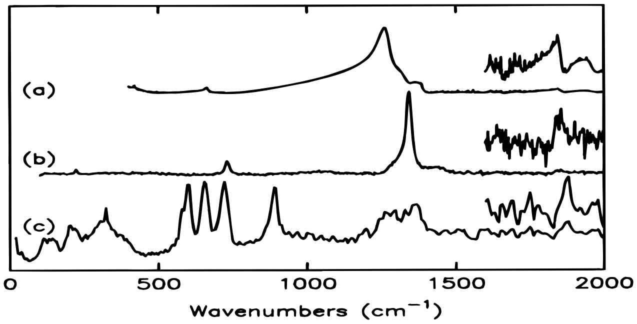

Figure 2. (a) Infrared, (b) Raman, and (c) INS spectra of Mg_2FeD_6. The insets show the region 1600−2000 cm^{-1} and are ordinate expanded ×10 for (a) and (b) and ×3 for (c).

The assignment of the stretching modes is more complicated than might be expected. The band at 1873 cm^{-1} in the Raman and INS spectra is the A_{1g} mode; the band at 1740 cm^{-1} in the infrared and INS spectra is the T_{1u} mode. In the Raman spectrum, the E_g mode is usually much weaker than the A_{1g} mode,[12] so the failure to observe it is not surprising; however, it should have significant INS intensity but only two bands are observed. The same behavior is apparent for the deuterated species: 1342 cm^{-1} (A_{1g}), 1262 cm^{-1} (T_{1u}).

The solution is provided by the use of CLIMAX. The ratio of the calculated intensities of the A_{1g}, E_g, and T_{1u} modes is approximately 1:2:3, and for the INS feature at 1878 cm^{-1} to be of similar intensity to that at 1740 cm^{-1}, the A_{1g} and E_g modes must be accidentally degenerate. The same situation also applies to the deuterated species.

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Table 2. Force Constants of Mg_2FeH_6 and Mg_2FeD_6 in O_h Symmetry

force constant[a]	value	description
k_1	1.933	Fe−H stretch
k_{trans}	0.188	axial Fe−H/Fe−H stretch interaction
k_{cis}	0.000	adjacent Fe−H/Fe−H stretch interaction
k_2	0.453	H−Fe−H bend
k_{opp}	−0.070	H−Fe−H bend interaction with no common H atom (opposite sides of octahedron)
k_{adj}	0.010	H−Fe−H bend interaction with a common H atom (same side of octahedron)

[a] Diagonal force constants have units of mdyne/Å^{-1}, and interaction force constants have units of mdyne/Å^{-2}.

The assignment of the bending modes is straightforward. The split band at 1019/1057 cm^{-1} in the Raman and INS spectra is the T_{2g} mode. The band at 899 cm^{-1} in the INS spectrum is the T_{1u} mode and should be present in the infrared spectrum; however, no band is observed even in concentrated samples. The band at 836 cm^{-1} in the INS spectrum is the T_{2u} mode. For the deuterated species, the corresponding assignments are 719 cm^{-1} (T_{2g}), 655 cm^{-1} (T_{1u}), and 599 cm^{-1} (T_{2u}).

As all of the internal vibrations have been accounted for, it follows that the features below 600 cm^{-1} are the external modes, and since they exhibit significant INS intensity, it is likely that they relate to the metal hydride ion. Using the force constants given in Table 2 and with the inclusion of phonon wings and binary overtones and combinations of the internal modes, the excellent fit to the INS spectrum of the FeH_6^{4-} ion shown in Figure 3 is obtained. This also demonstrates that the strong, broad feature at 1340 cm^{-1} is the phonon wing of the bending modes.

When the same force constants are used for the deuterated species, the fit is again excellent, Figure 4a,b, except that it does not account for the strong feature at 888 cm^{-1}. Comparison with the spectrum of the hydrogenous compound, suggests an assignment to an Fe−H bending mode. Further support is the presence of a weak feature at 1848 cm^{-1}, see the insets in Figure 2, which can be assigned to the corresponding Fe−H stretching mode. The low level of hydrogen impurity (0.5%) present in the D_2 used for the synthesis would result in the formation of 3% Mg_2FeD_5H; this is observable because of the greater sensitivity of INS to hydrogen over deuterium. This species would have C_{4v} symmetry and a calculation using the same force constants gave the spectrum shown in Figure 4c. Summation of Figure 4 parts b and c gave Figure 4d, and comparison with Figure 4a leaves no doubt that the analysis is substantially correct.

The following external modes in the region below 600 cm^{-1} are expected to occur (in order of energy): librational > translational > acoustic. Thus the natural assignment is that the strong, broad mode in the INS spectrum at 460 cm^{-1} that exhibits a deuterated counterpart at 324 cm^{-1} ($=460/\sqrt{2}$) is the librational mode. A small rotation of the FeH_6^{4-} ion would result in a large amplitude motion of all six hydrogen atoms, accounting for its high intensity, and since it is the hydrogen atoms that move, deuteration would be expected to give the full isotope shift. The only difficulty with this assignment is that the mode is seen in the Raman spectrum of Mg_2FeH_6 (although not of Mg_2FeD_6) where it is formally forbidden. This is discussed later.

In contrast to the libration, since a translation involves displacement of the ion from its lattice position, any isotope shift would be expected to be small: $(62/68)^{1/2} = 0.95$. Hence the weak band near 220 cm^{-1} in the Raman and INS spectra that shows virtually no isotope shift is assigned to the T_{2g} translation.

In the absence of lower frequency Raman and infrared data, the assignment of the last two features in the INS spectrum is unclear. Some of the intensity below 200 cm^{-1} is due to the acoustic mode, and dispersion in this mode could give rise to a feature with the observed shape. However, the remaining translational mode would also be expected in this region and may account for some of the intensity.

The only remaining bands are the shoulders on the Fe−H stretching modes in the infrared and Raman spectra. The weak shoulders can be assigned as overtones and combinations of the bending modes whose intensity is enhanced by Fermi resonance with the stretching mode. Fermi resonance is caused by interaction of the anharmonic terms in the potential energy; this may result in a shift in energy and intensity "borrowing" by the less intense feature.[13] In principle the modes are also present at the same energies in the INS spectrum since the transition energy is given by the vibrational potential for all three forms of vibrational spectroscopy. The intensity increase observed with infrared and Raman spectroscopies does not occur since this is an electronic effect.

Discussion

The only other metal hydride complexes for which vibrational data are available are Na_2PdH_2,[14] Mg_2NiH_4,[15] and K_2ReH_9,[16] and only for the Pd complex are the data complete. Direct comparison is complicated by the different structures adopted: linear ($D_{\infty h}$), tetrahedral (T_d), and face-capped trigonal prism (D_{3h}), respectively. The stretching (1600−2000 cm^{-1}) and bending modes (800−1000 cm^{-1}) of the complexes all occur in the same regions as those of the Fe complex, and the diagonal stretch and bend force constants for the PdH_2^{2-} ion (1.98 and 0.431 mdyne/Å)[14] are similar to those of FeH_6^{4-}.

The assignment of both of the A_{1g} and E_g modes to the 1847 (H)/1342 (D) cm^{-1} bands is unusual, since for MX_6 (X = halogen, O) the bands are separated with $A_{1g} > E_g$.[12] The evidence from the INS spectrum for the correctness of the assignment is compelling, since all other assignments for the E_g mode gave markedly inferior fits. The difference between the hexahydrido and the hexahalo and hexaoxo complexes must lie in the mass difference between hydrogen and the other elements. In the present case, there is a factor of 50 difference; for no other complex is the ratio so large. This effectively decouples the Fe−H vibrations from each other, and in the limit of no coupling, all three stretching modes are coincident. The form of the A_{1g} and E_g modes is similar in that the modes do not involve motion of the iron atom and adjacent Fe−H bonds behave as independent oscillators. Since the splitting between the A_{1g} and E_g modes is determined by the degree of coupling between the individual Fe−H vibrations, in its absence, the modes are accidentally degenerate. In contrast, the T_{1u} mode involves movement by the iron atom providing an efficient means of coupling between opposing oscillators.

The complex shape of the librational mode of the FeH_6^{4-} ion at 460 cm^{-1} in the INS spectrum is clear evidence of dispersion in this mode. (Its deuterated counterpart at 324 cm^{-1} has the same shape, although this is less apparent because the

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Table 3. Observed Bands (cm^{-1}) and Assignments for Mg_2FeH_6 and Mg_2FeD_6 in O_h Symmetry and Mg_2FeD_5H in C_{4v} Symmetry

IR		Raman		INS		
H	D	H	D	H	D	assgnt[a]
		2010 w	1437 w			2 δ(Fe−H/D) (T_{2g})
1912 w	1370 w					δ(Fe−H/D) (T_{2g}) + δ(Fe−H/D) (T_{1u}) FR
		1873 vs	1342 vs	1878 m	1363 m	ν(Fe−H/D) (A_{1g})
				1878 m	1363 m	ν(Fe−H/D) (E_g)
	1841 w		1848 w		1874 w	ν(Fe−H)[b] (A)
1843						δ(Fe−H/D) (T_{2g}) + δ(Fe−H/D) (T_{2u}) FR
1746 vs	1260 vs	1789 vw	1309 vw	1740 m	1277 m	ν(Fe−H/D) (T_{1u})
		1019/1057 m	730 m	990/1016 m	719 s	δ(Fe−H/D) (T_{2g})
	661 w			899 s	655 s	δ(Fe−H/D) (T_{1u})
					891 s	δ(Fe−H)[b] (E)
				836 s	599 s	δ(Fe−H/D) (T_{2u})
		430 br		460 br	324 br	libration (T_{1g})
		223 w	223 w	209 w	206/218 w	translation (T_{2g})
				157 w	150 w	translation or acoustic mode
				103 w	116 w	translation or acoustic mode

[a] ν = stretch, δ = bend, s = strong, m = medium, w = weak, br = broad, v = very, FR = Fermi resonance enhanced. [b] Mg_2FeD_5H mode.

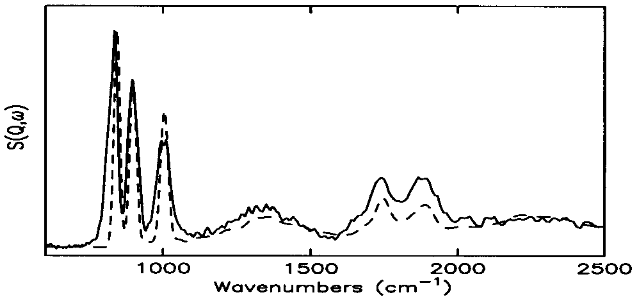

Figure 3. Comparison of observed spectrum (solid line) and CLIMAX fit to Mg_2FeH_6 (dashed line).

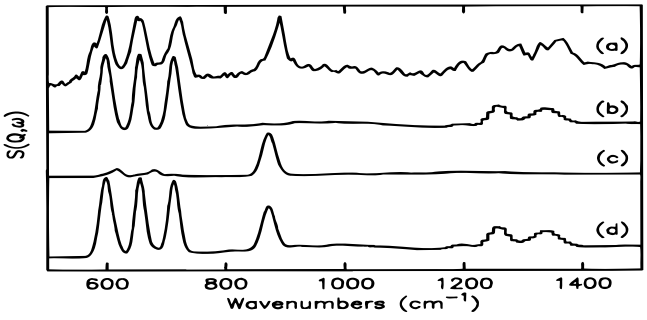

Figure 4. Comparison of (a) spectrum of Mg_2FeD_6, (b) CLIMAX fit to Mg_2FeD_6, (c) CLIMAX fit to Mg_2FeD_5H, and (d) sum of (b) and (c).

mode overlaps the translational and acoustic modes). The dispersion implies that there is some interaction between adjacent molecules.

The analysis presented has assigned all of the bands in the spectra on the basis of O_h symmetry for the parent molecules. For the perdeuterated complex the assignment is completely consistent with the spectra. For the hexahydrido complex there are some difficulties. These are the splitting of the T_{2g} bending mode at ~1000 cm^{-1} in both the Raman and INS spectra, the presence of the formally forbidden T_{1g} librational mode in the Raman spectrum, and the asymmetry of the T_{2u} mode in the INS spectrum suggestive of a small splitting. The presence of the splitting in both the room-temperature Raman spectrum and the 20 K INS spectrum suggests that a phase change is not responsible for the effect. The line shape of the INS bands could be accounted for by weak dispersion in the modes, although this would not account for the splitting in the Raman spectrum.

An alternative possibility is that the molecule undergoes a small axial distortion to D_{4h} symmetry. If the distorted axis was randomly oriented in the crystal, then the average symmetry would be O_h, as observed crystallographically, but the local symmetry as probed by vibrational spectroscopy would be D_{4h}. In order to account for the Mössbauer[2] results, which indicated a symmetric structure, the distortion would have to be dynamic on a time scale which was fast compared to the ^{57}Fe Mössbauer time scale of a few nanoseconds.

Under D_{4h} symmetry, all the 3-fold degenerate T modes split to an E mode and either an A or B mode. Thus the T_{2g} mode splits to Raman-allowed B_{2g} and E_g modes and the librational T_{1g} mode splits to A_{2g} and E_g modes, the latter of which is allowed. Additional modes are also allowed in the infrared; however, there are no bands observed. In the INS spectrum, with the assumption of D_{4h} symmetry, there is a small improvement in the quality of the fit in the bending mode region but at the cost of a more complex force field. These effects are only observed for the hexahydrido complex; thus deuteration must stabilize the symmetric form because the energy cost to displace the heavier deuterium atoms is too great. The major difficulty with this explanation is that there is no apparent driving force why a totally symmetric $^1A_{1g}$ electronic ground state should split.

Conclusions

The combination of the three types of vibrational spectroscopy, infrared, Raman, and INS, has enabled all of the internal, and most of the external, modes of Mg_2FeH_6 and Mg_2FeD_6 to be observed and assigned, as well as some of the modes of Mg_2FeD_5H. As an aid to the assignment a reliable, empirical force field has been developed. The spectra also show evidence for a dynamic distortion of the hexahydrido complex, an effect that is not observed for the deuterated species.

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