# Raman, FTIR, Photoacoustic-Infrared, and Inelastic Neutron Scattering Spectra of Ternary Metal Hydride Salts $A_2MH_5$ , (A = Ca, Sr, Eu; M = Ir, Rh) and Their Deuterides

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## **S** Supporting Information

**ABSTRACT:** The vibrational spectra of the ternary metal hydride (deuteride) salts,  $A_2MH_5$  and  $A_2MD_5$ , where A = calcium, strontium and europium and M = iridium(I) and rhodium(I), have been assigned using Raman, Fourier transform infrared, photoacoustic infrared, and inelastic neutron scattering spectroscopies and density functional theory (DFT) calculations. The wavenumbers of the infrared-active stretching vibrations depend upon the ionization energies of the central metal atom and the cation. The phase transition in calcium pentahydridoiridate(I) was studied as a function of temperature and pressure.



Complex metal hydride salts are among the materials receiving much attention as potential hydrogen storage systems.<sup>1</sup> A proposed candidate is Mg<sub>2</sub>FeH<sub>6</sub>, due to a high volume density. The structure and vibrational spectra have been reported for this compound<sup>2,3</sup> and other ternary metal hydride salts of the group 8 transition metals,  $A_2MH_6$  (A = alkaline earth and lanthanide and M = Ru, Os), have been extensively studied.<sup>4-12</sup> The isoelectronic metal hydrido- anions of the neighboring group 9 transition metals, Co, Rh, and Ir, (A<sub>2</sub>MH<sub>5</sub>), are unusual in that they are pentacoordinated with square-pyramidal molecular structures. The preparation, properties, and structures of the hydrides of iridium and rhodium with calcium, strontium, and europium,  $1^{3-21}$  including the mixed salts with Ca-Eu and Sr-Eu, <sup>17,18</sup> have been reported. Neutron diffraction studies have shown that the room-temperature crystal structures are face-centered cubic with the K<sub>2</sub>PtCl<sub>6</sub> structure, space group Fm3m, but disordered such that the six octahedral sites have 5/6 occupancy.<sup>16,20</sup> Transitions to the ordered low-temperature tetragonal structures, space group I4/ mmm, occur for the calcium and strontium salts where the unit cell is approximately half the volume and contains two formula units instead of four.<sup>16,17,20</sup> The four basal (equatorial) positions are fully occupied, the apical (axial) sites are half occupied and the structure is disordered along the c axis. The transition in the calcium salt occurs between 295 and 275 K



and in the strontium salt between 200 and 140 K (but is still incomplete at 4 K). In the europium salt, the transition temperature is 200 K, and transitions also occur in the mixed crystal salts of europium with calcium and strontium.<sup>18</sup> The room-temperature structure of Mg<sub>2</sub>CoH<sub>5</sub>, (tetragonal, space group *P4/mmm*), is ordered with the apical hydrogen positions alternating up and down, and the transition between the cubic disordered state and the tetragonal ordered structure occurs at a much higher temperature of 498 K.<sup>22</sup> In all cases, the apical bond length is longer than are those in the equatorial plane.<sup>19,20,22</sup> A deuterium NMR study has shown that the disorder in the high-temperature phases of Ca<sub>2</sub>IrD<sub>5</sub> and Ca<sub>2</sub>RhD<sub>5</sub> is dynamic in nature and the metal–hydrogen bonds have high ionic character.<sup>21</sup>

Parker and co-workers<sup>3</sup> have emphasized the benefit of using multiple vibrational spectroscopic methods, infrared, Raman, and inelastic neutron scattering (INS), and applied this approach in the case of  $Mg_2FeH_6/D_6$  and  $Mg_2CoH_5/D_5$ .<sup>3,23</sup> The advantage of the INS method is that the normal vibrational selection rules no longer apply, i.e., all vibrations are allowed, and for hydrogenous materials, the spectrum is dominated by modes involving hydrogen displacements. It was observed in

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the study of the ruthenium salts<sup>8</sup> that photoacoustic infrared spectroscopy (PAIR) spectra showed increased intensity of the combination bands, which assisted in the assignment of such bands. The analysis of the vibrational spectra of the calcium and strontium pentahydridoiridate(I) and calcium pentahydridorhodate(I) salts, and their corresponding deuterido species, are reported in the present work, using all four of these spectroscopic techniques together with variable-temperature and variable-pressure studies of the phase transition in calcium pentahydridoiridate(I).

## EXPERIMENTAL SECTION

The compounds were prepared by literature methods.<sup>14–16</sup> Calcium, strontium, and europium were purified by vacuum distillation and subsequently reacted with hydrogen or deuterium to form the respective binary hydrides (deuterides). The binary compounds were then mixed with iridium or rhodium and heated in an atmosphere of hydrogen or deuterium to give the ternary metal hydrides (deuterides). Their purity was confirmed by X-ray powder diffraction and infrared and Raman spectroscopy. No impurities were detected. Raman spectra were obtained using an InVia Renishaw spectrometer with a solid-state NIR laser (785 nm) at 10 mW power and an argon ion laser (514.5 nm) at 1.25 or 2.5 mW power as the samples tended to decompose at the shorter wavelength. (Certain commercial suppliers are identified in the paper to foster understanding. Such identification does not imply recommendation or endorsement by the NIST.) FTIR spectra were measured in KBr pellets using an ABB Bomem spectrometer at 2 cm<sup>-1</sup> resolution. PAIR spectra were recorded using a Bio-Rad FTS6000 spectrometer equipped with a MTEC 300 PA detector in rapid scan mode at 4 cm<sup>-1</sup> resolution. For variable-pressure studies, the samples were contained in stainless-steel gaskets in a Diamond Anvil Cell (DAC) from High Pressure Diamond Optics, Tucson, AZ. Ruby fluorescence was used as the pressure calibrant.<sup>24</sup> The spectra were measured at each pressure after 15 min for equilibration and then again at ambient pressure after completing a series of runs up to a maximum of 5.6 GPa. The Raman spectra were recorded and fitted using Renishaw WiRE 2.0 software. Because of their sensitivity to air and moisture, the samples were stored under argon and handled in glove bags under dry nitrogen.

Inelastic neutron scattering spectra were obtained using the Filter Analyzer Neutron Spectrometer (FANS)<sup>25</sup> at the NIST Center for Neutron Research with the Cu(220) monochromator and horizontal divergences of 20' of arc for both the in-pile and monochromatic-beam collimators. Ca<sub>2</sub>IrH<sub>5</sub> spectra were measured at 4 K (323 to 2094 cm<sup>-1</sup>) and at 270 and 300 K (309 to 1169 cm<sup>-1</sup>). Sr<sub>2</sub>IrH<sub>5</sub> spectra were measured at 15 K (363 to 2065 cm<sup>-1</sup>) and at 135 and 210 K (363 to 1024 cm<sup>-1</sup>). These temperatures were chosen to cover the region of the phase transition.<sup>16</sup> Ca<sub>2</sub>RhH<sub>5</sub> spectra were measured at 4 K (309 to 2065 cm<sup>-1</sup>) and at 300 K (328 to 1170 cm<sup>-1</sup>).

First-principles calculations were performed within the planewave implementation of density functional theory (DFT) using the PWscf package.<sup>26</sup> Vanderbilt-type ultrasoft potentials were used with the Perdew–Burke–Enzerhod exchange correlation. A cutoff energy of 554 eV and a  $6 \times 6 \times 4$  *k*-point mesh (generated using the Monkhorst–Pack scheme) were found to be sufficient for the total energy to converge to within 0.1 meV/atom. Structural optimizations were performed by fixing unit cell constants to low-temperature values determined from neutron powder diffraction results for Sr<sub>2</sub>IrD<sub>5</sub> (4.2 K, I4/mmm tetragonal structure with a = b = 5.530 Å and c = 7.796 Å<sup>16</sup>),  $Ca_2IrD_5$  (20 K, tetragonal structure with a = b = 5.0314 Å and c = 7.4373 Å<sup>20</sup>), and Ca<sub>2</sub>RhD<sub>5</sub> (10 K, *Fm*3m cubic structure with  $a = b = c = 7.248 \text{ Å}^{27}$ ). For each compound, an artificially ordered structure was created such that one of the two apical hydrogen sites along the *c* direction was assumed to be vacant, while the other was fully occupied. This permitted a periodic phonon calculation to be performed for an arrangement of identically oriented square pyramidal IrH54- anions. The dynamical calculations were performed on the optimized structures using the supercell method with finite displacements. For each compound, a  $2 \times 2 \times 2$  supercell was used and the full dynamical matrix was obtained from a total of ten symmetryindependent atomic displacements (0.02 Å). Optical-mode vibrational wavenumbers for all three compounds generated by DFT calculations are tabulated in the Supporting Information in addition to animations of the different vibrations, as exemplified for Sr<sub>2</sub>IrH<sub>5</sub>.

For all figures in this article, vertical error bars associated with the data denote  $\pm 1\sigma$ . Where no error bars are shown, the standard uncertainty is commensurate with the scatter in the data.

#### RESULTS AND DISCUSSION

Assignment of the Vibrational Peaks. Square-pyramidal coordination geometry is uncommon, and cases with hydride ligands only are restricted to very few examples. There are nine internal vibrations for a MH<sub>5</sub> square pyramid with  $C_{4y}$ symmetry;  $3A_1 + 2B_1 + B_2 + 3E$ . All species are Raman-active but only the A1 and E modes are infrared-active. Thus, nine peaks should appear in the Raman spectrum and six in the infrared, with four stretching vibrations and five bending motions. The stretching modes occur above  $1000 \text{ cm}^{-1}$ , bending between 1000 and 600 cm<sup>-1</sup>, and librational modes below 600 cm<sup>-1</sup>. The existence of four molecules per unit cell<sup>19,21</sup> would introduce u- and g-modes and, therefore, the exact coincidence of vibrational wavenumbers in the infrared and Raman spectra is not expected, but the molecular symmetry,  $C_{4w}$  is retained in the octahedral sites in the crystal, and no site splitting occurs. There should be additional modes observable due to lattice modes in the solid, except that the wavenumbers may be too low to be observed. Below the phase transitions, the tetragonal form occurs with only two molecules per unit cell. Again, the molecular and site symmetry remain the same. The observed peaks are assigned according to the following principles: (i) the normal modes and their activity governed by Raman-infrared symmetry selection rules; (ii) in inelastic neutron scattering all modes are active, intensities are dictated by their degeneracy and the magnitude of the hydrogen displacements, and both intensities and frequencies are often predictable by first-principles phonon calculations; (iii) a peak should appear in both the hydrogen and deuterium spectra with the expected ratio of approximately  $\sqrt{2}$ ; and (iv) combination bands and overtones are enhanced in the photoacoustic IR spectra.

Calcium Pentahydrido- and Pentadeuteridoiridate(l). The Raman, FT-IR, and PAIR spectra of  $Ca_2IrH_5$  and  $Ca_2IrD_5$  are shown in Figures 1–3 and the INS spectra of  $Ca_2IrH_5$  in Figure 4.

The measured wavenumbers are listed in Table 1 for room-temperature Raman and infrared spectra. The neutron diffraction study  $^{20}$  of Ca<sub>2</sub>IrD<sub>5</sub> at 4 K gave the apical Ir–D



Figure 1. Raman spectra of  $Ca_2IrH_5$  (upper, red) and  $Ca_2IrD_5$  (lower, black).



Figure 2. FTIR spectra of  $Ca_2IrH_5$  (upper, red) and  $Ca_2IrD_5$  (lower, black).



Figure 3. PAIR spectra of  $Ca_2IrH_5$  (upper, red) and  $Ca_2IrD_5$  (lower, black).

bond length of 1.805(6) Å, much longer than the equatorial Ir-D bond lengths of 1.681(3) Å. The apical bonds are, therefore, much weaker (more ionic<sup>21</sup>) than are the equatorial bonds and are decoupled from the in-plane vibrations, creating an effective  $D_{4h}$  symmetry for the equatorial plane (see Table 1). Modes  $\nu_1$ and  $\nu_9$  (the numbering system is that used by Nakamoto<sup>28</sup>) involve motion of the apical hydrogen and, therefore, should be active under  $C_{4v}$  symmetry. For the stretching modes, the strong Raman peak at 1972  $\rm cm^{-1}$  is absent in the infrared spectrum, and the strong peak at 1691 cm<sup>-1</sup> in the infrared spectrum appears as a very weak peak in the Raman spectrum at 1697 cm<sup>-1</sup> and disappears at temperatures below 200 K. The 1442 cm<sup>-1</sup> peak is both Raman and infrared-active and is assigned to the apical hydrogen stretch,  $\nu_1$ , (A<sub>1</sub>), and the 1972 cm<sup>-1</sup> peak is assigned to the Raman-active symmetric in-plane stretch,  $\nu_2$  (which is not infrared-active under  $D_{4h}$  symmetry) and the 1691 cm<sup>-1</sup> peak to the asymmetric in-plane stretch  $\nu_{7}$ , which is an E mode under  $C_{4v}$  symmetry and both infrared- and



**Figure 4.** INS spectra of  $Ca_2IrH_5$  at 4 and 270 K (below the phase transition) and 300 K (above the phase transition) compared to DFT calculations for the 1-phonon (in red) and 1 + 2-phonon INS spectra (in black). Horizontal bars beneath the spectra denote the fwhm instrumental resolution.

Raman-active but would be  $E_u$  under  $D_{4h}$  symmetry. The location of the remaining stretching mode,  $\nu_4$  (B<sub>1</sub>), was not obvious, but the DFT calculations indicate that it is very close to the  $\nu_2$  mode.

In the bending mode region, the strongest peaks of the INS spectra occur between 800 and 900 cm<sup>-1</sup>. The 809 cm<sup>-1</sup> peak has a shoulder at 785 cm<sup>-1</sup> in the 4 K spectrum but is better resolved at 300 K, and these two peaks correspond to the two overlapping peaks in the Raman spectrum at the same wavenumbers. The 782 cm<sup>-1</sup> peak is both Raman and infrared active and is assigned to  $\nu_{9}$  as it involves motion of the apical hydrogen atom. The bending mode at 810 cm<sup>-1</sup> is Ramanactive only and is assigned to the A<sub>1</sub> mode,  $\nu_3$ , on the basis of the DFT calculations (see Supporting Information), even though it does not appear in the infrared spectrum. The peak at 886 cm<sup>-1</sup> is also Raman active only and is assigned as the B<sub>2</sub> mode,  $\nu_6$ , equivalent to the  $\nu_2$  mode with  $B_{1g}$  symmetry under  $D_{4h}$  symmetry. There remain two bending vibrations to be assigned, and the INS spectra at 4 and 300 K showed peaks at 915 and 739 cm<sup>-1</sup>, which were not observed in either the Raman or infrared spectra. Since the peak at 739 cm<sup>-1</sup> is of much lower intensity, it is assigned to  $\nu_5$  and the 911 cm<sup>-1</sup> peak to  $\nu_9$  as the former would be the B<sub>2u</sub> vibration and both infrared and Raman-inactive under  $D_{4h}$  symmetry. Again, the DFT calculations support these assignments.

The PAIR spectra, Figure 3, are dramatically different in appearance from the FT-IR spectra due to the increased intensities of combination bands. The selection rule for combination bands is a Raman-active band combining with an infrared band (u-  $\times$  g-) and thus the combination bands must be infrared-active. The bands adjacent to the strong infrared peak at 1691 cm<sup>-1</sup> can be assigned as combinations or overtones; 1967, 1805, 1565 cm<sup>-1</sup>, and peaks above 2000 cm<sup>-1</sup> are similarly assigned to combinations, in Table 1, with the requirement that the peaks are assigned in both hydrogen and deuterium spectra with the expected isotopic ratio. Weak broad peaks in the Raman spectra of Ca<sub>2</sub>IrD<sub>5</sub> observed at 813, 1628, 1810, and 1969 cm<sup>-1</sup> are due to residual hydrogen and are not

Table 1.	Vibrational	Wavenumb	ers and .	Assignments for	Ca <sub>2</sub> IrH <sub>5</sub> a	ind Ca <sub>2</sub> IrD <sub>5</sub>	(Numbering	of the Modes	According to
Nakamot	o <sup>28</sup> )			U			· · · · ·		C C

		Ca <sub>2</sub> IrH <sub>5</sub>				$Ca_2IrD_5$		assignr	nents
Raman	FTIR	PAIR	INS 4 K	INS 300 K	Raman	FTIR	PAIR	$C_{4\nu}$	$D_{4h}$
		2900					2063	$\nu_{2} + \nu_{8}$	
		2784					1984	$\nu_2 + \nu_3$	
		2560					1837	$\nu_6 + \nu_7$	
		2477					1760	$\nu_7 + \nu_9$	
		2226					1585	$\nu_1 + \nu_9$	
1972			1976		1406			$\nu_2, A_1$	$\nu_1$ , A <sub>1 g</sub>
		1969				1395	1405	$\nu_4$ , B <sub>1</sub>	$\nu_4, B_2_g$
	1805	1811	1818			1282	1288	$2\nu_8$	
1697	1691	1694	1655		1216	1212	1213	ν <sub>7</sub> , Ε	$\nu_7$ , E <sub>u</sub>
1619	1614								
	1565	1586	1584			1134	1133	$2\nu_9$	
1484					1064				
1442	1438	1446	1407		1038	1033	1041	$\nu_1$ , A <sub>1</sub>	
	1312	1313	1325			925	937	$\nu_9 + \nu_L$	
			1060	1075				$2 u_{ m L}$	
			915	910				ν <sub>8</sub> , Ε	$\nu_7$ , E <sub>u</sub>
886			887	879	629			$\nu_6$ , B <sub>2</sub>	$\nu_2, B_{1g}$
810			809	810	578			$\nu_3$ , A <sub>1</sub>	$\nu_{3}$ , $A_{2u}$
782	788	783	785	784	557	553	556	ν <sub>9</sub> , Ε	
			739	729				$\nu_5$ , A <sub>1</sub>	$\nu_5, B_{2g}$
			546	546	483			$ u_{ m L}$	
532		525	520	530	376		378	$ u_{ m L}$	
465		456		503				$ u_{ m L}$	

listed in Table 1. The peaks appearing below 600 cm<sup>-1</sup> are librational modes, in particular, the peak at 546 cm<sup>-1</sup> with a shoulder at 530 cm<sup>-1</sup>, which occurs in both the Raman and INS spectra. DFT calculations indicate that the lowest wavenumber mode is a torsional oscillation about the  $C_4$  axis.

Strontium Pentahydrido- and Pentadeuteridoirididate(I). The Raman spectrum of strontium pentahydroiridate(I) could not be obtained due to decomposition under laser irradiation, even at 785 nm. Thus, the assignments are based on the infrared spectra and INS spectra only. The results are given in Table 2.

The INS spectra in Figure 5 are similar to those of the calcium salt in Figure 4 except for the 525 cm<sup>-1</sup> peak, which is more clearly defined from the shoulder at 556 cm<sup>-1</sup>, and the shoulder at 863 cm<sup>-1</sup> is also better resolved.

*Calcium Pentahydrido- and Pentadeuteridorhodiate(l).* Raman and FT-IR spectra were measured at room temperature and INS spectra at 4 and 300 K. The results are given in Table 3. The peaks in the INS spectra, Figure 6, are broader and less defined than those of the calcium and strontium iridium salts but are similar in appearance. The assignments are given in Table 3.

Spectra were also measured for other ternary metal hydride salts,  $Eu_2IrH_5$  and  $Sr_2RhH_5$ , but were not of good quality due to sample sensitivity to air and moisture and decomposition under laser irradiation. Only the strongest peaks were observable and are listed in Table 4.

**Dependence of Vibrational Wavenumbers on Ionization Energies.** In earlier studies of the vibrational spectra of the group 8 ternary metal hydrides,  $A_2MH_6$ , the wavenumbers of the infrared-active metal-hydrogen stretching mode,  $T_{1u}$ , were shown to be dependent on the sum of the second ionization energy of the cation (alkaline earth or lanthanide) and the first ionization energy of the central metal atom (Ru, Table 2. Vibrational Wavenumbers and Assignments  $(C_{4\nu})$ : Sr<sub>2</sub>IrH<sub>5</sub>

FTIR	PAIR	INS 15 K	INS 135 K	INS 210 K	assignment
	2852				$\nu_2 + \nu_8$
	2491				$\nu_6 + \nu_7$
2025	2031				$\nu_1 + \nu_9$
1937		1944			$\nu_2$ , A <sub>1</sub>
		1944			$\nu_4$ , B <sub>1</sub>
	1750	1790			$2\nu_8$
1626	1617	1656			ν <sub>7</sub> , Ε
1369	1370	1394			$\nu_1$ , A <sub>1</sub>
1256	1289	1283			$\nu_5+\nu_{\rm L}$
		1105			$2 u_{ m L}$
918	917				
		902	909	910	ν <sub>8</sub> , Ε
		865	866	866	ν <sub>6</sub> , Β <sub>2</sub>
		800	796	790	$\nu_3$ , A <sub>1</sub>
765	769	787			ν <sub>9</sub> , Ε
		742	745	747	ν <sub>5</sub> , B <sub>1</sub>
		555	554	549	$ u_{ m L}$
		525	522	525	$ u_{ m L}$
		451	434		$ u_{ m L}$

Os).<sup>8,29,30</sup> This relationship is due to a weakening of the metal—hydrogen bond by electron transfer to the counterion. In the present work, the dependence of the infrared active metal—hydrogen stretching modes,  $\nu_1$  and  $\nu_7$ , on the difference between the second ionization energy of the cation and the first ionization energy of the transition metal atom is shown in Figure 7.

A least-squares fit to the points for  $\nu_1$ , the apical hydrogen stretch, gave a slope of  $6.3 \times 10^{-3}$  and an intercept of 1272 cm<sup>-1</sup> ( $R^2 = 0.980$ ) for the hydrogen species and  $4.7 \times 10^{-3}$  and



**Figure 5.** INS spectra of  $Sr_2IrH_5$  at 15 and 135 K (below the phase transition) and at 210 K (above the phase transition) compared to DFT calculations for the 1-phonon (in red) and 1 + 2-phonon INS spectra (in black). Horizontal bars beneath the spectra denote the fwhm instrumental resolution.

Table 3. Vibrational Wavenumbers and Assignments  $(C_{4\nu})$ : Ca<sub>2</sub>RhH<sub>5</sub> and Ca<sub>2</sub>RhD<sub>5</sub>

	С	a <sub>2</sub> RhH <sub>5</sub>	$Ca_2RhD_5$			
Raman	FTIR	INS 4 K	INS 300K	Raman	FTIR	$C_{4 \mathrm{V}}$
		1955				$\nu_1+\nu_{\rm L}$
1806		1803		1275		$\nu_2$ , A <sub>1</sub>
	1736	1733			1258	ν <sub>7</sub> , Ε
1620	1626			1144		
	1567	1583			1128	$2\nu_9$
1442	1461	1406		1047		$\nu_1, A_1$
1263		1231	1149	961		$\nu_9+\nu_{\rm L}$
	1209				872	
	1048	1059	1068		782	$2 u_{ m L}$
			948			ν <sub>8</sub> , Ε
	867	886	883			$\nu_6, B_2$
802		800	805	577		$\nu_3$ , A <sub>1</sub>
	786		769		554	ν <sub>9</sub> , Ε
		687	696			$\nu_5$ , B <sub>1</sub>
			636			
558	554	550				$ u_{ m L}$
			578			
434		530	529			

931 cm<sup>-1</sup> ( $R^2 = 0.977$ ) for deuterium. There is also a trend evident for  $\nu_7$ , the in-plane hydrogen stretch, with, respectively, values of the slopes and intercepts of  $3.6 \times 10^{-3}$  and 1583 cm<sup>-1</sup> ( $R^2 = 0.819$ ).

Note that the Raman-active modes, e.g., the in-plane symmetric stretch,  $\nu_2$ , do not involve a change in dipole moment and do not depend upon the ionization energies. Thus, the dependence of the stretching modes on the ionization energies of the group 9 ternary metal hydride salts indicates the transfer of electron density from the anion to the cation.

Temperature and Pressure Dependence of the Raman Spectra of Calcium Pentahydroiridate(I). All the group 9 iridium ternary metal hydride salts exhibit phase



**Figure 6.** INS spectra of  $Ca_2RhH_5$  at 4 and 300 K compared to DFT calculations for the 1-phonon (in red) and 1 + 2-phonon INS spectra (in black). Horizontal bars beneath the spectra denote the fwhm instrumental resolution.

Table 4. Vibrational Wavenumbers and Assignments  $(C_{4\nu})$ : Sr<sub>2</sub>RhH<sub>5</sub> and Eu<sub>2</sub>IrH<sub>5</sub>

	$\mathrm{Sr}_{2}\mathrm{RhH}_{5}$			$\mathrm{Eu}_{2}\mathrm{IrH}_{5}$		
Raman	FTIR	PAIR	Raman	FTIR	PAIR	
					2105	
			1818			$\nu_2$
		1765		1772		$ u_4 $
	1656		1616	1619	1599	$\nu_7$
	1450	1439		1511	1523	
1313			1381	1391	1378	$\nu_1$
				1230	1246	
	867			751	761	



**Figure 7.** Wavenumber dependence of the metal—hydrogen stretching modes on ionization energies (second ionization energy of the cation minus the first ionization energy of the metal atom). Filled circles  $\nu_1$  and empty circles  $\nu_7$ .

transitions from the face-centered-cubic structure to a tetragonal phase. In the neutron powder diffraction study<sup>20</sup> of  $Ca_2IrD_5$ , the change in unit cell dimensions occurred between 295 and 275 K, which is in agreement with differential scanning calorimetry results,<sup>21</sup> where the onset of the transition occurred at 286 K but was not complete until 240 K. The deuterium NMR line shapes showed a narrow line at room temperature followed by broadening and the appearance of Pake doublets with the narrow line absent at about 253 K. The changes in the

Raman spectra of  $Ca_2IrH_5$  with temperature occur below 147 K with the largest changes occurring for  $\nu_3$ , which increases from 810 cm<sup>-1</sup> to 817 cm<sup>-1</sup>, and  $\nu_9$ , which increases from 785 cm<sup>-1</sup> to 802 cm<sup>-1</sup>. The apical Ir–H stretch actually decreases from 1444 cm<sup>-1</sup> at 172 K to 1441 cm<sup>-1</sup> at 148 K. A change in the wavenumbers of the lattice modes might be expected with the transition to the tetragonal phase, but there are only increases of about 2–3 cm<sup>-1</sup>. The INS spectra show little change in wavenumbers but only in line broadening.

The pressure dependence of the wavenumbers for  $Ca_2IrH_5$  are given in Table 5 and shown in Figures 8 and 9 for the bending and stretching regions, respectively.

Table 5. Pressure Dependence  $(d\nu/dP, cm^{-1} GPa^{-1})$  of Wavenumbers  $(cm^{-1})$  in the Raman Spectra of Ca<sub>2</sub>IrH<sub>5</sub>

below 3 GPa $d\nu/dP$	above 3 GPa $d\nu/dP$
7.97	2.29
8.96	-0.47
14.2	8.07
13.50	5.95
10.7	3.33
-1.51	-9.53
8.88	1.97
	below 3 GPa du/dP 7.97 8.96 14.2 13.50 10.7 -1.51 8.88



**Figure 8.** Wavenumber dependence on pressure for the bending mode region of  $Ca_2IrH_5$ .

For all the measured dependences, there is a clear break in the slopes at 3.1 GPa due to the phase transition from the facecentered-cubic to the tetragonal structure. In general, the slopes



Figure 9. Wavenumber dependence on pressure for the stretching mode region of  $Ca_2IrH_5$ .

are lower in the tetragonal phase. The pressure dependence of  $\nu_1$  is negative in both phases, and the bending modes  $\nu_3$  and  $\nu_9$  are the most sensitive to pressure. These are also the motions that are most sensitive to temperature. The values of  $d\nu/dP$  for the A<sub>2</sub>RuH<sub>6</sub> salts (A = Ca, Sr, Eu)<sup>10</sup> range from 17 to 27 cm<sup>-1</sup> GPa<sup>-1</sup> for the A<sub>1g</sub> stretch, from 24 to 25 cm<sup>-1</sup> GPa<sup>-1</sup> for the E<sub>g</sub> stretch, and 9.5 to 10.7 cm<sup>-1</sup> GPa<sup>-1</sup> for the T<sub>2g</sub> bend, i.e., in all cases larger than the wavenumber dependences measured for the pentahydrides in the present study.

## ASSOCIATED CONTENT

#### Supporting Information

Table of vibrational wavenumbers for  $Ca_2IrH_5$ ,  $Sr_2IrH_5$ , and  $Ca_2RhH_5$  generated by DFT calculations; animations of the fundamental optical modes for  $Sr_2IrH_5$ ; full authorship of refs 25 and 26. This material is available free of charge via the Internet at http://pubs.acs.org.

### AUTHOR INFORMATION

#### Notes

The authors declare no competing financial interest.

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