Raman, FTIR, Photoacoustic-FTIR and Inelastic Neutron Scattering Spectra of Alkaline Earth and Lanthanide Salts of Hexahydridoruthenate(II), A_2RuH_6, (A = Ca, Sr, Eu) and Their Deuterides

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Received: April 4, 2008; Revised Manuscript Received: May 21, 2008

The vibrational spectra (Raman, photoacoustic and Fourier transform infrared and inelastic neutron scattering) of the calcium, strontium and europium salts of hexahydrido- and hexadeuteridoruthenate(II) have been analyzed. All observed fundamental modes and overtone and combination bands are assigned. Density functional theory calculations of the vibrational frequencies assist in the analysis.

Introduction

Complex metal hydride salts are among the materials receiving much attention as potential hydrogen storage systems.[1] A promising candidate is Mg_2FeH_6, due to a high hydrogen-to-metal storage ratio. The structural and vibrational spectroscopic properties of this complex[2,3] and of other ternary metal hydrides of the alkaline earth salts of the Group 8 metal hydrides, A_2MH_6 (M = Ru, Os), have been reported.[4–6] The infrared and Raman spectra of the ruthenium salts[5,6] and the pressure dependences of the Raman vibrational peaks have been described earlier[7] and the wavenumbers of the strongest peak in the infrared spectrum of alkaline earth and lanthanide salts of the Group 8 metal hexahydrides correlates with the ionization energies of the cation and central metal atom for both the ruthenium and osmium salts.[8] Recently, Daku and Hagemann have assigned the fundamental modes of Ca_2RuH_6/D_6 based on wavenumbers derived from density functional theory (DFT) calculations.[9]

For such high symmetry compounds the number of modes observable by Raman and infrared spectroscopic methods is reduced by the principle of mutual exclusion and by the high degeneracy of some of the vibrational modes. Parker and coworkers[3] have emphasized the benefit of using multiple vibrational spectroscopic methods: infrared, Raman and neutron inelastic scattering (INS), and applied this approach in the case of Mg_2FeH_6/D_6. An assignment of the vibrational spectra of the ruthenium species $[RuH_6/D_6]^{4-}$ is reported in the present work for the calcium, strontium and europium salts using these different techniques plus photoacoustic infrared spectroscopy (PAIR) and DFT calculations.

Experimental Section

The compounds were prepared by literature methods[10] and their purity was confirmed by X-ray powder diffraction and infrared and Raman spectroscopy. Raman spectra were obtained using an InVia Renishaw spectrometer[11] with a solid-state NIR laser (785 nm) at 1.5 or 3 mW power and an argon-ion laser (514.5 nm) at 1.25 or 2.5 mW as the samples tended to decompose at this wavelength. FTIR spectra were measured in KBr pellets using an ABB Bomem spectrometer at 2 cm^{-1} 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^{-1} resolution.

INS spectra were obtained using the filter analyzer neutron spectrometer (FANS)[12] 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. Only the calcium and strontium salts were measured, as the neutron absorption cross-section is prohibitively high for europium. Ca_2RuH_6 samples were studied at 4 and 295 K over the range from 40 to 240 meV (323−1936 cm^{-1}) and Sr_2RuH_6 at 10 K from 45 to 200 meV (363−1614 cm^{-1}).

First-principles DFT calculations were performed within the plane-wave implementation of the generalized gradient approximation (GGA) to the density-functional theory in the PWscf package.[13] A Vanderbilt-type ultrasoft potential was used with Perdew-Burke-Ernzerhof exchange correlation. A cutoff energy of 400 eV and a 2 × 2 × 2 k-point mesh (generated using the Monkhorst−Pack scheme) were found to be sufficient for the total energy to converge to within 0.07 meV/atom. Structural relaxation was first performed with the starting input from the neutron powder diffraction results[8] on the deuterated complex: $a_0 = 7.226$ Å, $r(Ru-D) = 1.704$ Å. The dynamical calculations were then performed on the optimized structure using the supercell method with finite difference. A 2 × 2 × 2 supercell was used and the full dynamical matrix was obtained from a total of 10 symmetry-independent atomic displacements (0.02 Å).

Results and Discussion

There are 15 internal vibrations for an octahedral ion such as $[MH_6]^{4-}$ but the high symmetry reduces these to only six

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10.1021/jp803013h CCC: $40.75

TABLE 1: Vibrational Wavenumbers (cm^{-1}) and Assignments for Ca_2RuH_6/D_6

Raman		IR		PAIR		INS-H				
						exptl				
H	D	H	D	H	D	4 K	295 K	calcd	assignment	
				2736	1952				$\nu_1 + \nu_4$	T_{1u}
				2686	1912				$\nu_2 + \nu_4$	T_{1u}
				2271	1599				$\nu_2 + \upsilon_{lib}$	T_{1u}
1833	1311						1834	1854	ν_1	a_{1g}
		1769	1262	1765	1252				$\nu_4 + \nu_5$	T_{1u}
1754	1274					1758	1741	1819	ν_2	e_g
		1729	1229	1728	1228				$\nu_5 + \nu_6$	T_{1u}
		1564	1125	1565	1129	1558	1551	1600	ν_3	t_{1u}
		1395	998	1404	1011	1405	1404		$\nu_6 + \nu_{lib}$	T_{1u}
						1056	1022		$2\nu_{lib}$	
		896	646	900	645	887	889	836	ν_4	t_{1u}
871	618					867	858	801	ν_5	t_{2g}
ia	ia	ia	ia	ia	ia	867	858	785	ν_6	t_{2u}
ia	ia	ia	ia	ia	ia	537	528	451	ν_{lib}	t_{1g}
201	199						194	ν_{trans}	t_{2g}	
							175	ν_{trans}	t_{1u}	

TABLE 2: Vibrational Wavenumbers (cm^{-1}) and Assignments for Sr_2RuH_6/D_6

Raman		IR		PAIR		INS		
H	D	H	D	H	D	H	assignment	
				2676	1980		$\nu_1 + \nu_4$	T_{1u}
				2618	1868		$\upsilon_2 + \nu_4$	T_{1u}
				2223	1594		$\nu_2 + \nu_{lib}$	T_{1u}
1782	1265						ν_1	a_{1g}
		1737	1239	1735	1229		$\nu_4 + \nu_5$	T_{1u}
1731	1235						ν_2	e_g
		1700	1211	1707	1215		$\nu_5 + \nu_6$	T_{1u}
		1487	1075	1474	1073		ν_3	t_{1u}
		1371	987	1380	995	1384	$\nu_6 + \nu_{lib}$	T_{1u}
						1075	$2\nu_{lib}$	
		879	634	885	636	890	υ_4	t_{1u}
850	602					856	υ_5	t_{2g}
ia	ia	ia	ia	ia	ia	856	ν_6	t_{2u}
ia	ia	ia	ia	ia	ia	561	υ_{lib}	t_{1g}

modes; a_{1g}, e_g, t_{1g}, $2t_{1u}$, and t_{2u}. The g-modes are Raman active and the u-modes are infrared active except for the t_{2u} mode, which is inactive in both the Raman and infrared spectra. Thus, three peaks should appear in the Raman spectrum and two in the infrared. The crystal structures of the hexahydridoruthenate compounds have been reported, space group *Fm*3*m* (No. 225).[8,10,14] In the solid-state cubic lattice, the ruthenium atoms occupy the Wyckoff 4a sites of octahedral symmetry and so there is no site splitting but there are additional lattice modes; t_{1g}(ia), t_{2g}(R), t_{1u}(IR) and t_{1u}(ia). Therefore, there should be an additional mode observable in both the infrared and Raman spectra, except that the wavenumbers may be too low to be detected. The advantage of the inelastic neutron scattering method is that the normal vibrational selection rules no longer apply and all vibrations are allowed.

The measured wavenumbers are listed in Tables 1–3, together with the calculated values for the calcium salt. The spectra of all compounds are very similar and the peaks of the deuterated compounds showed the expected wavenumber ratio of $\sqrt{2}$. Since more complete results are available for the calcium salt the analysis of this complex will be discussed first. The spectra of the hydrogen species are shown in Figure 1 for the different spectroscopic methods and also the calculated 1-phonon and 2-phonon INS spectra. The assignment of the three Raman and two infrared internal bands is fairly routine. However, the infrared spectra show additional, less intense, peaks on either side of the intense fundamental, ν_3, and the PAIR spectra display bands in the frequency region above 2000 cm^{-1}. The INS spectra show complementary peaks to those in the infrared and Raman spectra, plus strong features at 528 and 1022 cm^{-1} and 561 and 1075 cm^{-1} for the calcium and strontium salts, respectively. These peaks are not present in the Raman and infrared spectra and are, therefore, assignable to either the inactive bending motion, ν_6, or to the inactive librational mode, υ_{lib}, and an overtone. The most intense peak in the INS spectrum of the calcium salt, at 858 cm^{-1}, must be an overlap of υ_5 (871 cm^{-1}, Raman) with another fundamental. The wavenumbers of the inactive lattice mode t_{1g} (the librational motion of the $[RuH_6/D_6]^{4-}$ ion) were obtained by calculation for the calcium salt at 451 cm^{-1} and this mode is assigned to the INS peak at 528 cm^{-1} with an overtone at 1022 cm^{-1}. The ν_6 band, therefore, is coincident with ν_5.

The selection rules for combination bands require a u-mode to be in combination with a g-mode and the resultant, therefore, must be an infrared-active vibration. Thus the weak additional peaks in the infrared spectra can be assigned as combination bands of ν_3, ν_4 or ν_6 with one of the Raman-active fundamentals, Tables 1–3. Similar combinations were reported for the spectra of Mg_2FeH_6/D_6[3] and Rb_2PtH_6/D_6[15] and observed but not assigned for K_2PtH_6/D_6.[16] The Raman-active t_{2g} translational lattice mode, calculated to be at 194 cm^{-1} for the calcium salt, should not show an isotope effect and were observed at 201 and 199 cm^{-1} for the hydrido- and deuterido salts, respectively.

TABLE 3: Vibrational Wavenumbers (cm^{-1}) and Assignments for Eu_2RuH_6/D_6

Raman		IR		PAIR			
H	D	H	D	H	D	assignment	
				2628	1858	$\nu_1 + \nu_4$	T_{1u}
				2538	1806	$\nu_2 + \nu_4$	T_{1u}
				2295	1647	$\nu_2 + \upsilon_{lib}$	T_{1u}
1785	1271					ν_1	a_{1g}
		1727	1227	1721	1218	$\nu_4 + \nu_5$	T_{1u}
1713	1229					ν_2	e_g
		1691	1205	1694	1204	$\nu_5 + \nu_6$	T_{1u}
		1462	1064	1473	1064	ν_3	t_{1u}
		1373	988	1376	995	$\nu_6 + \nu_{lib}$	T_{1u}
		874	634	882	636	ν_4	t_{1u}
840	595					ν_5	t_{2g}

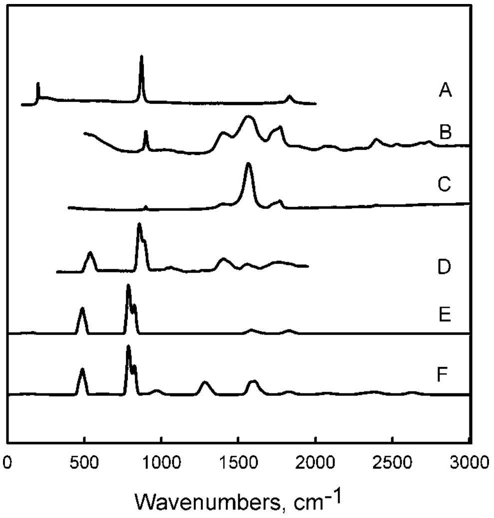

Figure 1. Vibrational spectra of Ca_2RuH_6: (A) Raman, (B) PAIR, (C) IR, (D) INS, (E) calculated 1-phono INS spectrum, and (F) calculated 2-phonon INS spectrum.

TABLE 4: Mulliken Population Analysis of Charge Densities for A_2RuH6 where A = Mg, Ca, Sr

	Mg_2RuH_6	Ca_2RuH_6	Sr_2RuH_6
A	+1.80	+1.97	+1.94
Ru	−1.91	−2.12	−1.94
H	−0.28	−0.30	−0.32

Using these assignments for the calcium salt and the consistent similarities between the spectra allows the spectra of the strontium and europium salts to be assigned, Tables 2 and 3. The INS spectrum of the strontium salt shows the same prominent librational mode and an overlap of the υ_5 and υ_6 peaks as does the calcium compound. A determination of the inactive ν_6 mode in the europium salt, which could not be measured by inelastic neutron scattering, was obtained from the difference, 851 cm^{-1}, between the combination band at 1691 cm^{-1} and the Raman ν_5 fundamental at 840 cm^{-1}. Similarly, $\upsilon_{lib} = 582$ cm^{-1} was calculated from the difference between the PAIR overtone at 2295 cm^{-1} and υ_2 at 1713 cm^{-1}. The wavenumbers of the combination bands in the PAIR spectrum of the strontium salt are slightly larger than the sum of the fundamentals. This is unusual as the effect of anharmonicity usually leads to a lower wavenumber sum. However, the strong similarity between the spectra of all the compounds supports the assignments.

Except for υ_1, the wavenumbers of all internal modes of the alkali metal ruthenium hexahydrido salts follow the order Ca > Sr > Eu and for the hexahydrido salts of different central metal atoms the M-H stretching modes are Pt > Fe > Ru. The bending modes have similar values for all the salts, between 800 and 900 cm^{-1}, regardless of the central metal atom. Two modes, υ_3 and υ_4, involve motions of the central atom and might be expected to show a mass effect but no effect is observed, probably due to the more dominant role of the counterion in determining the vibrational wavenumbers.[4,8] The librational wavenumbers for the ruthenium salts are much larger than are those reported for Mg_2FeH_6 and Rb_2PtH_6.[3,15]

The results of the DFT calculations of the Mulliken population analysis for the magnesium, calcium and strontium salts are given in table 4. These values confirm that charge transfer from the ruthenium hexahydrido anion to the alkaline earth cation occurs.[8] However, the population values are quite different from those calculated for the alkali metal series of $[PtH_6]^{2-}$ salts,[15] where, although the alkali metal ion charges were less than unity, the hydrogen atoms carried small positive charges. The negative charge on the hydrogen atoms of the ruthenate salts indicates that they retain hydridic character in agreement with the ionic character of the metal−hydrogen bond determined from the deuterium nuclear quadrupole coupling constants.[8]

Acknowledgment. The financial support of the NSERC (Canada) is acknowledged. R.O.M. acknowledges support from Trinity College Scovill Chair Research Fund. Prof. Hans Hagemann is thanked for a copy of his paper in advance of publication.

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JP803013H