

Structural and vibrational properties of Ca_2FeH_6 and Sr_2RuH_6 H. Hagemann^{a,*}, V. D'Anna^a, L.M. Lawson Daku^a, S. Gomes^{b,1}, G. Renaudin^{b,1}, K. Yvon^b^a Département de Chimie Physique, Université de Genève, 30, quai E. Ansermet, CH 1211 Geneva 4, Switzerland^b Laboratoire de Cristallographie, Université de Genève, 24, quai E. Ansermet, CH 1211 Geneva 4, Switzerland

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ABSTRACT

The structural and vibrational properties of the isostructural compounds Ca_2FeH_6 and Sr_2RuH_6 are determined by periodic DFT calculations and compared with their previously published experimental crystal structures as well as new experimental vibrational data. The analysis of the vibrational data is extended to the whole series of alkaline-earth iron and ruthenium hydrides A_2TH_6 ($\text{A}=\text{Mg}, \text{Ca}, \text{Sr}$; $\text{T}=\text{Fe}, \text{Ru}$) in order to identify correlations between selected frequencies and the T–H bond length. The bulk moduli of Ca_2FeH_6 and Sr_2RuH_6 have also been determined within DFT. Their calculated values prove to compare well with the experimental values reported for Mg_2FeH_6 and several other compounds of this structure.

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1. Introduction

The title compounds belong to the class of so-called complex transition (T) metal hydrides that derive their name from the presence of T metal hydrido complexes in the structure. For $\text{T}=\text{Fe}, \text{Ru}, \text{Os}$ their general formula is A_2TH_6 ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$), and their hydrido complexes have octahedral shape and the composition $[\text{TH}_6]^{4-}$. Their structural and physical properties have been studied abundantly in the past, in particular in view of their potential as hydrogen storage materials (for a critical and comprehensive review see [1]). Their prototype Mg_2FeH_6 was discovered in the 1980s and characterized with respect to a variety of properties [2], including structural, vibrational and hydrogen sorption properties. The compound turned out to have one of the highest hydrogen density known among condensed materials (i.e. more than twice that of liquid hydrogen), but was thermally too stable for reversible hydrogen storage applications at room temperature. Later, however, it was shown to be of interest as a material in thermal heat energy storage systems [3]. As to the vibrational properties of the A_2TH_6 series several members have been studied in the past, such as Mg_2FeH_6 or Ca_2RuH_6 [4–9]. A recent review [10] summarizes the data available so far. In this paper we present the vibrational spectra of two less well studied members, Ca_2FeH_6 and Sr_2RuH_6 , and compare the results of DFT calculations and calculated bulk moduli to those of other members in this series.

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2. Experimental

2.1. Sample preparation

Mixtures of the binary hydrides (deuteride) CaH_2 , CaD_2 and SrH_2 and metallic Fe and Ru powders (Johnson Matthey, 99.99%) with molar ratio 2:1 were pressed to pellets to prepare the three ternary hydrides (deuteride) Ca_2FeH_6 , Ca_2FeD_6 and Sr_2RuH_6 , respectively. The starting materials were prepared by hydrogenation (deuteration) of metallic calcium powder (STREM 99.9%) and strontium powder (STREM 99.9%) at 775 K under a hydrogen (deuterium) pressure of 20 bar for two days. All materials were handled in an argon-filled glove-box since they were sensitive to air and moisture. The three pellets were placed in nickel crucibles and sintered in an autoclave at 775 K under a hydrogen (deuterium) pressure of 150 bar for four days. X-ray powder diffraction showed that the samples were single-phase and contained the expected ternary hydride (deuteride) having a cubic Fm-3m symmetry with K_2PtCl_6 -type structure [11,12].

2.2. Vibrational spectra

The Raman spectra of Ca_2FeD_6 were collected on a Kaiser Holospec f/1.8 spectrograph with a 50- μm slit ($\sim 3\text{--}4\text{ cm}^{-1}$ resolution) that was equipped with a liquid nitrogen cooled CCD camera, using a 488 nm Ar laser excitation with a power of ca 15 mW. These spectra were subject to a very strong background. In the case of Ca_2FeH_6 , no Raman spectrum could be observed due to the very strong background. The new Raman spectrum of Sr_2RuH_6 was measured using a Renishaw InVia Raman microscope using 785 nm excitation.

FTIR spectra were obtained using a Paragon 1000 (Perkin-Elmer) instrument equipped with a Golden Gate Single Reflection Diamond ATR set-up (P/N 10 500 Graseby-Specac Series).

The powder samples to be analyzed were pressed against the ATR crystal with a calibrated strength in an Ar filled glove-box and protected by an airtight protective polyethylene film during measurement.

2.3. Computational methods

The computational study of Ca_2FeH_6 and Sr_2RuH_6 was done within DFT [13,14], using the ABINIT [15–17] package which is based on plane waves and pseudopotentials.

For both systems, the calculations were performed in the Generalized Gradient Approximation (GGA) [18,19] using norm conserving Troullier–Martins [20] and optimized Rappe–Rabe–Kaxiras–Joannopoulos (RRKJ) [21] pseudopotentials in the separable Kleinman–Bylander form [22], generated with the FHI98PP [23] and OPIUM [24] programs.

Convergence studies performed on both systems led to the choice of a $10 \times 10 \times 10$ Monkhorst–Pack grid [25] and a kinetic energy cut-off of 60 hartree for the two systems.

The optimizations were performed with the crystal symmetry kept fixed to Fm-3m (number 225) space group; the Wyckoff positions of the alkaline-earth (Ca, Sr), transition metal (Fe, Ru) and H atoms are 8c, 4a and 24e, respectively. The structures of the compounds were fully relaxed by letting simultaneously evolve the cell parameter (a) and the reduced coordinate x_{H} of the hydrogen atom, which is the only adjustable internal coordinate.

In order to calculate the bulk moduli of Ca_2FeH_6 and Sr_2RuH_6 , their equations of state have been determined by optimizing their structures for fixed values of the lattice parameter (see below).

For both systems at ambient pressure, their phonons were calculated at the gamma point, within density-functional perturbation theory [26,27]. The symmetry analysis of these frequencies were performed with the ABINIT “get_irreps.py” utility, which makes use of the symmetry information available from the Bilbao Crystallographic Server [28,29].

Phonon calculations were also performed for Ca_2FeD_6 and Sr_2RuD_6 .

3. Results and discussion

3.1. Experimental vibrational spectra

The members of the series A_2TH_6 ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$) based on $\text{T}=\text{Fe}, \text{Ru}, \text{Os}$ have fully ordered structures. They crystallize in the Fm-3m (no. 225) space group with $Z=4$ and contain a fcc lattice of $[\text{TH}_6]^{4-}$ anions separated by A^{2+} cations in tetrahedral voids [1]. Recently, some partially disordered members of this series have been reported for manganese ($\text{T}=\text{Mn}$) and some rare earths ($\text{A}=\text{Y}, \text{Er}, \text{Dy}$) [29–31]. Interestingly, while these hydrides display octahedral $[\text{MnH}_6]^{4-}$ complexes, their general composition is AMn_2H_6 . Given that the disorder occurs on the A site, the compounds must be formulated as $(\text{A}, \text{Mn})\text{MnH}_6$. For the sake of comparison, they will be included in the considerations below.

The symmetry analysis shows the following optical modes:

- Internal modes of the octahedral $[\text{MH}_6]^{4-}$ anions: $\text{A}_{1g}+\text{E}_g+2\text{T}_{1u}+\text{T}_{2g}+\text{T}_{2u}$; A_{1g} (ν_1), E_g (ν_2) and T_{1u} (ν_3) are stretching modes, T_{1u} (ν_4), T_{2g} (ν_5) and T_{2u} (ν_6) are bending modes;
- libration mode of $[\text{MH}_6]^{4-}$ anions: T_{1g}
- translational motions of the cation against the anion: T_{1u} and T_{2g} .

The IR active modes transform as T_{1u} , the Raman active modes as $\text{A}_{1g}, \text{E}_g, \text{T}_{2g}$.

Fig. 1 presents the IR spectra of CaH_2 , Ca_2FeH_6 and Ca_2FeD_6 . A weak band at 1000 cm^{-1} for Ca_2FeH_6 is probably due to a CaH_2 impurity. 3 strong bands are observed for Ca_2FeH_6 at 924, 1442 and 1570 cm^{-1} , while only two IR active fundamentals (ν_3 and ν_4) are expected. The band at 1442 cm^{-1} can be assigned to the combination of ν_6 +libration (ca $900+540 \text{ cm}^{-1}$), which is enhanced by Fermi resonance, in agreement with previous results for Ca_2RuH_6 and Sr_2RuH_6 [8]. In the case of Mg_2FeH_6 , this combination mode is not observed. Indeed, the corresponding frequency would be expected at $460+836=1296 \text{ cm}^{-1}$, which appears to be too different from the frequency of the allowed ν_3 band at 1746 cm^{-1} to give rise to a Fermi resonance.

The weak features around 1860 and 1900 cm^{-1} also arise from combination tones ($\nu_5+\nu_6$ and $\nu_4+\nu_5$, respectively). It is interesting to note that the relative intensity of the ν_4 band is extremely weak for Mg_2FeH_6 [9], while it is stronger for Ca_2FeH_6 (see Fig. 1) and Ca_2RuH_6 [9,33]. The IR spectrum of Ca_2FeD_6 shows the expected isotopic shifts. The Raman spectrum of Ca_2FeD_6

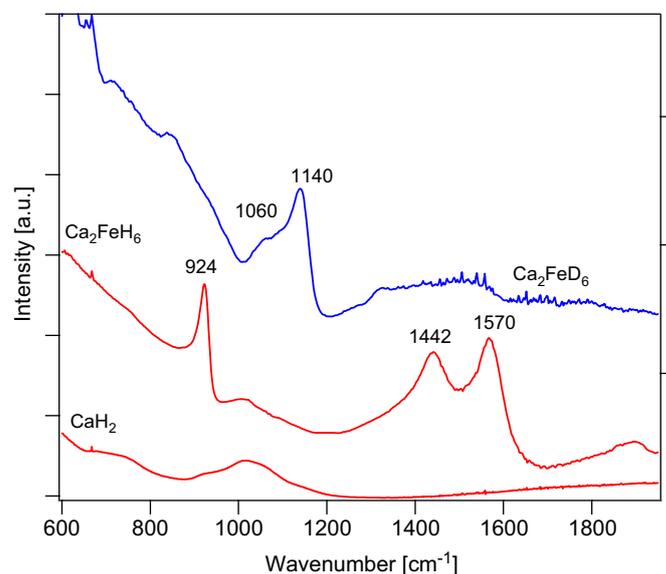


Fig. 1. IR spectra of CaH_2 , Ca_2FeH_6 and Ca_2FeD_6 (blue) at room temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

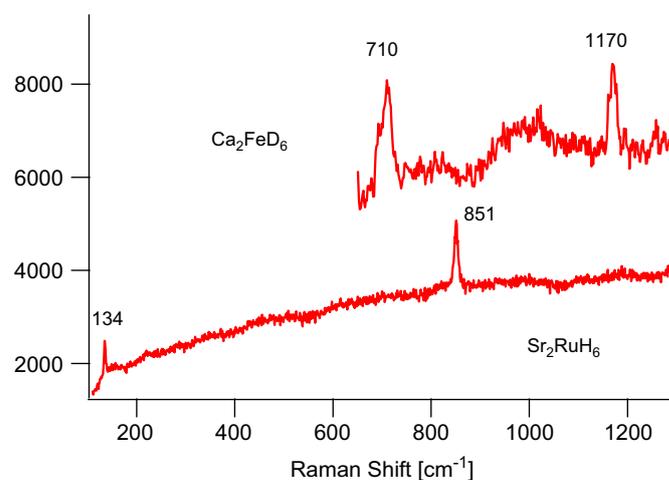


Fig. 2. Raman spectrum of Sr_2RuH_6 (as obtained with the Renishaw instrument) and Ca_2FeD_6 (obtained with the Holospec Monochromator, a strong background was subtracted for clarity) at room temperature.

(see Fig. 2) shows two bands at 1170 (A_{1g} (ν_1)) and 710 cm^{-1} (T_{2g} (ν_5)). For Mg_2FeD_6 , the relative intensity of the ν_5 band was also found to be very weak [9], in contrast to the spectrum in Fig. 2.

Fig. 2 presents the Raman spectrum below 1000 cm^{-1} of Sr_2RuH_6 . Besides the previously reported T_{2g} bending mode (ν_5) at 851 cm^{-1} [5,8], the translational T_{2g} mode at 134 cm^{-1} is observed for the first time.

The experimental data are collected in Table 1.

3.2. Theoretical calculations

Table 2 compares the calculated structures of Ca_2FeH_6 and Sr_2RuH_6 with the experimental structures reported by [4,11,34,35]. The agreement for the lattice parameter a is excellent. The Fe(Ru)–H bond length is calculated to be about 0.04–0.05 Å larger than the experimentally reported value, which reflects the usual GGA overestimate of the structural parameters.

Table 1 includes the theoretically calculated vibrational frequencies for Ca_2FeH_6 and Sr_2RuH_6 and their deuterated analogs. The agreement between theory and experiment is quite good; the slight underestimation of the experimental values can be ascribed to the tendency of the GGA calculations towards slightly smaller force constants (also related to the overestimated structural parameters).

As recently shown in our study of Ca_2RuH_6 [7], the frequency of the librational mode is particularly sensitive to the surroundings of the $[\text{MH}_6]^{4-}$ complex and to pressure, thus making its theoretical determination quite challenging. Thus noticeably different values were predicted at the LDA and GGA levels for the librational frequency of Ca_2RuH_6 [7]. This explains the discrepancy observed between experiment and theory for the librational frequency of Sr_2RuH_6 , which is calculated at 478 cm^{-1} and was observed at 561 cm^{-1} by Barsan et al. [8].

It is interesting to note that the splitting between ν_1 and ν_3 is much smaller for the Fe compounds than for the Ru compounds.

Kritikos and Noréus [4] have shown a correlation between IR active stretching frequencies and unit cell parameter. We have previously [5] attempted to correlate Ru–H stretching frequencies with Ru–H bond length using Badger's rule, however the correlation was not very satisfactory. Using both experimental [4–10]

and theoretical results from the literature and from this study, we have plotted IR and Raman active stretching modes against the M–H bond length in Fig. 3. The frequency of the IR active ν_3 mode appears to decrease systematically with increasing M–H bond length (as highlighted by the dashed lines in Fig. 3), however, the data point for Sr_2RuH_6 does not appear to follow this trend. A possible explanation may be that the reported experimental Ru–H bond length [12] (1.69(1) Å) is in fact too short. A bond length of ca 1.715 Å would bring this value in line with the other results (see Fig. 3). The DFT calculations on Sr_2RuH_6 and Ca_2RuH_6 support this suggestion, as the calculated Ru–H bond length is larger in the Sr compound than in the Ca compound, while the vibrational frequencies for both stretching modes (ν_1 and ν_3) are smaller for the Sr compound (see the open symbols in Fig. 3).

Finally, we have studied theoretically the pressure dependence of the crystal structure of Ca_2FeH_6 and Sr_2RuH_6 . The calculated pressure–volume curves could be fitted using a Vinet equation of state [35]. The results are summarized in Table 3 and compared with experimental values of similar compounds [32,36]. The calculated bulk moduli of Ca_2FeH_6 and Ca_2RuH_6 are very close. In the case of Ca_2RuH_6 we had seen that under pressure the $[\text{RuH}_6]^{4-}$ octahedron is not compressed very much compared to the entire lattice [7]. The bulk modulus reflects thus mainly the interaction between the Ca^{2+} ions and the relatively rigid $[\text{MH}_6]^{4-}$ anions.

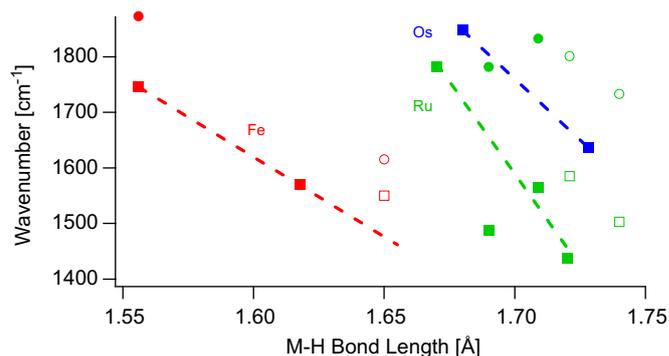


Fig. 3. M–H stretching frequencies vs. M–H bond lengths.

Table 1
Observed and calculated vibrational frequencies (cm^{-1}). The frequency of the librational band at 540 cm^{-1} was estimated from the combination band at 1442 cm^{-1} (see text). The experimental data for Sr_2RuH_6 were taken from [8].

	M–H (D) stretching modes			M–H (D) bending modes			Librations	Translations
	A_{1g} (R) ν_1	E_g (R) ν_2	T_{1u} (IR) ν_3	T_{2g} (R) ν_5	T_{1u} (IR) ν_4	T_{2u} (IA) ν_6		
Ca_2FeH_6 (Ca_2FeD_6)								
Experimental	(1170)		1570 (1142)	(710)	924 (681)		ca 540	
Calculated	1615 (1143)	1584 (1121)	1550 (1113)	934 (661)	877 (633)	839 (539)	505 (357)	202 (203)
Sr_2RuH_6 (Sr_2RuD_6)								
Experimental [8]	1782 (1265)	1731 (1235)	1487 (1075)	850 (602)	879 (634)	856	561	134 (this work)
Calculated	1733 (1226)	1706 (1207)	1503 (1073)	793 (561)	839 (600)	799 (565)	478 (338)	131 (131)

Table 2
Crystal structures of Ca_2FeH_6 and Sr_2RuH_6 : comparison of theory with experiment.

	a (Å)		x_{H}		M–H (Å)		V (Å ³)	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
Ca_2FeH_6	7.036(1)	7.032	0.230[11]	0.234	1.618(5)	1.6451	348.319	347.726
Sr_2RuH_6	7.608[4]	7.627	0.223[12]	0.228	1.69[12]	1.7359	440.54	443.67

Note: In the case of Ca_2FeD_6 the experimental values are in fact the values of $\text{Ca}_{1.98}\text{Mg}_{0.02}\text{FeD}_6$ [11].

Table 3
Experimental and theoretical bulk moduli of A_2MH_6 compounds.

Compound	B_0 (GPa)	B_0'	a (Å)
Mg_2FeH_6 [36]	75.4(4)		6.446
	76.3		
YMn_2D_6 [32]	68.05	6.28	6.708
$DyMn_2D_6$ [32]	83.8	4.59	6.720
$HoMn_2D_6$ [32]	73.2	5.85	6.677
$ErMn_2D_6$ [32]	76.1	5.20	6.6797
Ca_2FeH_6 (GGA)	59.7	4.28	7.032
Ca_2RuH_6 (GGA) [7]	58.5	4.0	7.253
Sr_2RuH_6 (GGA)	49.7	4.29	7.627

Comparing the experimental and theoretical values of the bulk moduli vs. unit cell parameters, it can be noted that the value of the bulk modulus is larger for smaller unit cell dimensions (or molar volumes), in agreement with trends reported for other systems [37].

4. Conclusions

The structural vibrational and elastic/mechanical properties of Ca_2FeH_6 and Sr_2RuH_6 have been studied and compared with the properties of other compounds of this family. The agreement between experimental and theoretical values for structural parameters and vibrational frequencies is generally good. The calculated bulk moduli appear to be very reasonable compared to the available experimental data of related systems. Periodic DFT calculations appear therefore to be quite reliable to calculate these properties for other systems in this family of compounds where experimental data are lacking.

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