Microscopic investigation of hydrogen-storage materials

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Abstract

Material investigation, at microscopic level, can be carried out using spectroscopic techniques like neutron or light scattering. Optical spectroscopy techniques (e.g. Raman Scattering) are sensitive to the vibrational dynamics and are generally used to probe optically transparent media. In the case of optically dense specimens, or metals, only the surface can be accessed, with a substantial decrease in detection efficiency. This problem does not affect thermal neutrons, for which almost all materials are transparent. In addition, due to the exceptionally high neutron scattering cross section for protons, neutron scattering techniques are extremely useful to investigate bulk microscopic properties of materials that are promising for hydrogen storage.

Atomic Storage: ionic metal hydrides

Complex ionic hydrides are promising materials for effective hydrogen storage in a solid matrix. In this context a better **knowledge of the metal-hydrogen ionic bond** is extremely important both for understanding the present proposed materials (cf. the poster by A. Albinati et al.) and for design/engineering of even better materials.
To this aim, we have started an experimental program using **Inelastic Neutron Scattering** (INS) measurements on polycrystalline alkali hydrides (LiH, NaH, KH, RbH and CsH) and on the heaviest alkaline earth hydrides (CaH_2, SrH_2, and BaH_2) at *T*=20 K using **TOSCA-II** [1], a crystal-analyzer inverse-geometry spectrometer.
Raw spectral data were subtracted of the empty can contributions and corrected for **multiple scattering, self-absorption** and **heavy-ion scattering**. Finally, the processed data, ***S(Q,E)***, were analyzed through an **iterative multiphonon procedure**, aiming to extract the Hydrogen-projected Density of Phonon States (H-DoPS) $Z_H(E)$.
A quantitative comparison could be established between the present experimental results on **alkali hydrides** and lattice-dynamics calculations (see Fig. 1) [2] (LiH being a quantum system, has been considered apart [3]). Work is in progress on a similar task for alkaline earth hydrides (see Fig. 2).
It is evident that the agreement between the simulated and the present INS $Z_H(E)$ is much improved with respect to previous experimental determinations, so that some of the observed discrepancies were surely due to experimental imperfections.

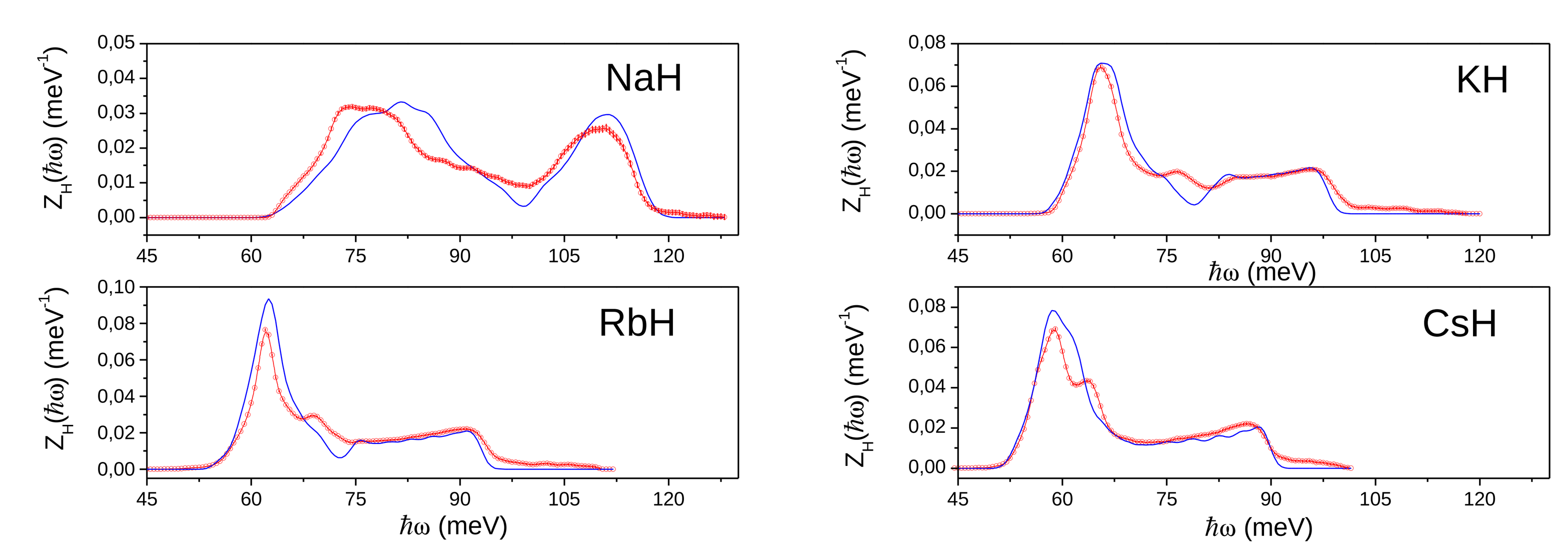

Fig. 1: measured INS spectra of alkali hydrides and *ab-initio* calculations

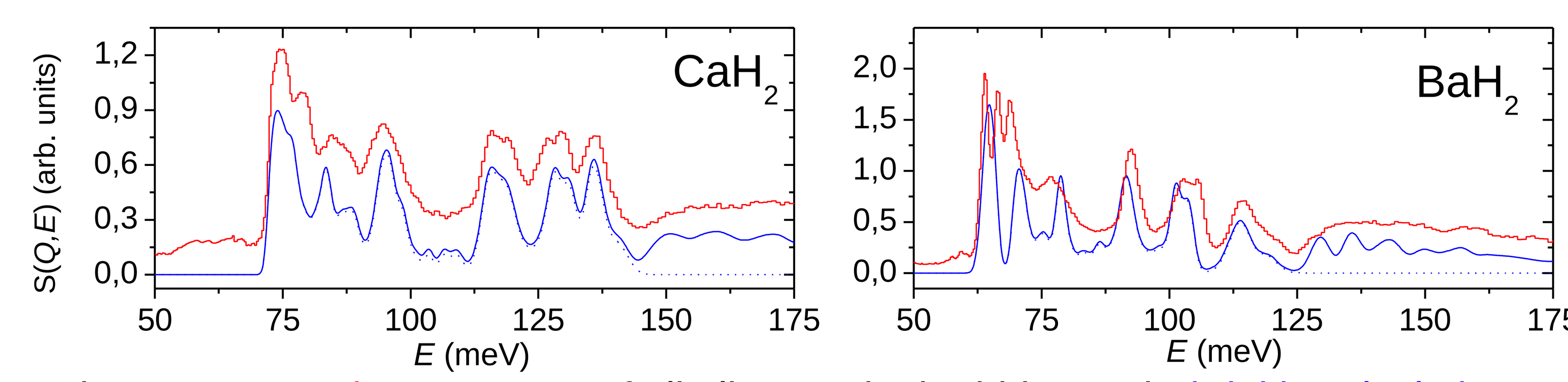

Fig. 2: measured INS spectra of alkaline earths hydrides and *ab-initio* calculations

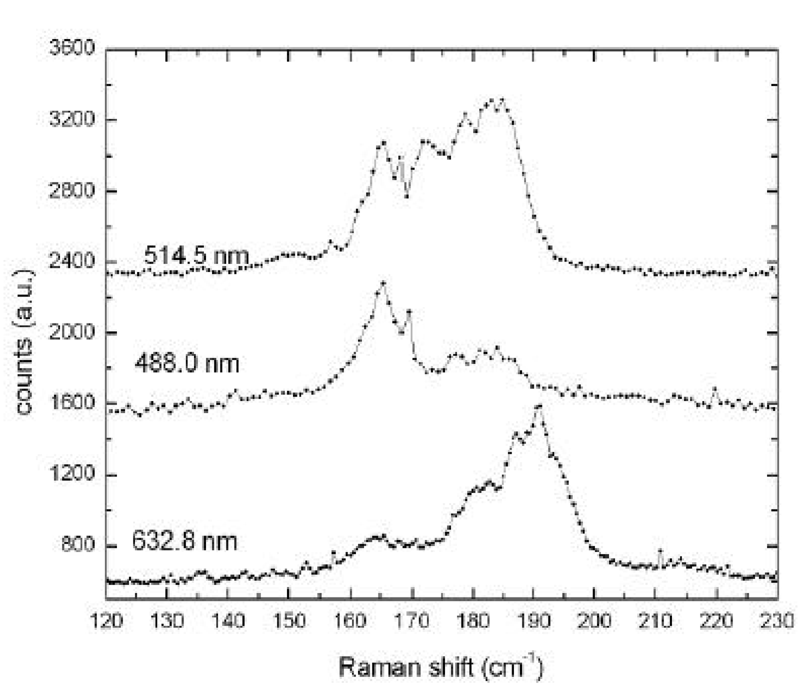

Fig. 3: Raman spectrum of SWCN

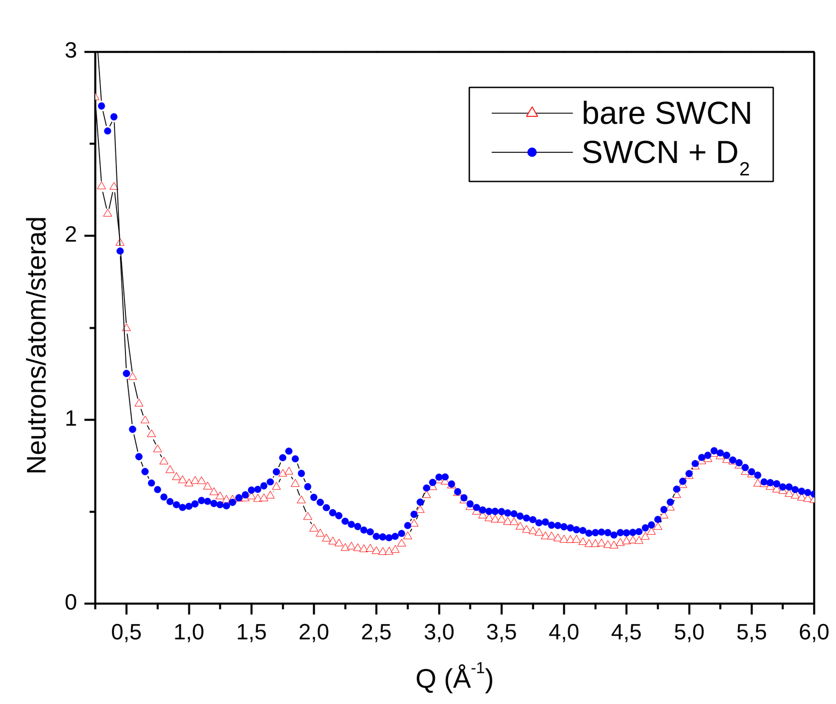

Fig. 4: SWCN+D2 neutron diffraction

Molecular Storage: carbon nanotubes

Carbon nanotubes are also promising for hydrogen storage in molecular form. In this case too, a detailed knowledge of the microscopic interaction between the carbon substrate and molecular hydrogen is of fundamental importance (cf. the poster by K.D. Ross et al.). To this aim, we have started an experimental program using both **Light Scattering** and **Neutron Diffraction**. Fig. 3 shows the Raman spectra of single walled carbon nanotubes from which we were able to obtain microscopic information on the substrate. In Fig. 4 we show a diffraction pattern collected on SANDALS, a liquid and amorphous systems neutron diffractometer, on a carbon nanotube sample "charged" with deuterium.
Data analysis, for which we are planning to use **Reverse Monte Carlo** simulation techniques, is presently ongoing.

Conclusion

We have reported **new INS measurements** on **alkali hydrides** and **alkaline earth hydrides**. The experimental data give direct information on the Hydrogen-projected Density of Phonon States (H-DoPS) and are to be compared with ab-initio calculations of the same quantity. The comparison gives an overall good agreement between theory and experiment for the alkali hydrides. For the alkaline earth hydrides, work is in progress.
Raman optical spectroscopy and neutron diffraction are used to investigate the interaction of molecular hydrogen with the carbon nanotubes substrate. The two techniques give similar results as far as the microscopic features of the substrate are concerned (i.e. diameter size and distribution). However, more sophisticated techniques (simulations) are needed in order to interpret the data from the hydrogen-nanotube system.

Ongoing collaborations:

1. **HYTRAIN** (http://www.hytrain.net): Marie Curie Research & Training Network on Hydrogen Storage (U.E. FP6)
2. **Firenze HYDROLAB** (http://www.iccom.cnr.it/hydrolab/): Programma di Ricerca Avanzata per la Produzione Immagazzinamento e la Produzione dell'Idrogeno
3. **Università di Milano**, Dipartimento di Chimica Strutturale e Stereochimica Inorganica (Prof. A. Albinati)
4. **Università di Padova**, Dipartimento di Ingegneria Meccanica, Settore Materiali (Prof. G. Principi)
5. **Università di Trento**, Dipartimento di Fisica (Prof. R. Vallauri)

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