A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

RECEIVED NOV 28 1985

TITLE: NEUTRON VIBRATIONAL SPECTROSCOPY: THE USE OF HYDROGEN AS A
STRUCTURAL AND DYNAMICAL PROBE

LA-UR--85-3571

DE86 002401

AUTHOR(S): J. ECKERT

SUBMITTED TO: INTERNATIONAL CONFERENCE ON NEUTRON SCATTERING, SANTA FE, NM,
AUGUST 19-23, 1985

DISCLAIMER

MASTER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. Its views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

**NEUTRON VIBRATIONAL SPECTROSCOPY:
THE USE OF HYDROGEN AS A STRUCTURAL AND DYNAMICAL PROBE**

J. Eckert

Physics Division, Los Alamos National Laboratory, Los Alamos, NM 87545

Abstract

The large incoherent scattering cross-section of hydrogen combined with an exact knowledge of the form of the scattering function can be utilized in neutron spectroscopic experiments to study local structural environments as well as interaction strengths. An important application of this technique is to focus on a particular hydrogen atom, or hydrogenous molecular group in the material, mainly by employing isotopic substitution. Hydrogen is thereby used as a local probe of structure as well as dynamics. Examples include: site geometry and occupancy in metal hydrides, potential well geometry of hydrogen-metal complexes and hydrogen-bonded systems, and dynamical coupling in linear chain hydrogen-bonded materials.

(Invited Paper, International Conference on Neutron Scattering, August 19-23, 1985, Santa Fe, NM; submitted to Physica B)

I. Introduction

Recent advances both in experimental technique and in theoretical understanding represent a crucial step towards realizing the potential of neutron vibrational spectroscopy to be a highly quantitative and important tool. Perhaps the principal advantage of incoherent inelastic neutron scattering (IINS) over related techniques such as Raman Scattering, IR absorption and Electron Energy Loss Spectroscopy is that the scattering cross-section can be calculated exactly from a knowledge of the interatomic forces. The application of this type of calculation has been somewhat inadequate because of approximations used for the Debye-Waller factor and the neglect of multiphonon scattering. Efforts to improve the computational treatment of neutron vibrational spectroscopy include: (1) better understanding [1] of the form of the Debye-Waller factor; (2) procedures to fit the form of the IINS spectra (not just intensities) with normal-coordinate analysis type calculations [2]; (3) inclusion of multiphonon processes [3] in such a calculation; and (4) application of molecular dynamics simulation to compute IINS spectra [4].

Improvements in experimental technique, on the other hand, are largely connected with the advent of spallation sources, whose high flux of epithermal neutrons can be used to build high resolution neutron energy loss spectrometers. This includes high intensity filter detector spectrometers as well as chopper spectrometers (such as the High Energy Transfer Spectrometer at the Spallation Neutron Source at Rutherford). The latter allow measurements at different momentum transfers (Q), albeit at a significant loss in intensity. This type of instrument is necessary for reliable discrimination against multiphonon processes in IINS spectra. Parallel improvements have also been achieved at the hot source spectrometer IN1 of the Institut Laue-Langevin.

The applications of neutron vibrational spectroscopy to be reviewed in this paper are of a slightly less quantitative nature, as the above mentioned advanced computational techniques have yet to become widely available. The unique sensitivity of neutrons to hydrogen can however be utilized by using hydrogen or hydrogenous molecules as probes of their surroundings and thus learn local structural details from spectroscopic data. Site geometries may be determined and potential surfaces mapped out by this use of hydrogen as a local probe. While neutrons are often useful

for their penetrating power, they can nevertheless be made a surface sensitive technique by employing hydrogen adsorbed on a surface which in turn has a small neutron scattering cross-section. Finally, we will discuss examples where hydrogen-containing molecular groups serve as a dynamical probe, i.e., where either intramolecular or intermolecular mode mixing can be identified because of the large intensities of vibrations involving these groups.

II. Site Occupancy of H in Metals

The vibrations of interstitial hydrogen in metals provide rather detailed information on hydrogen-metal interactions but are not usually accessible by any spectroscopic technique other than inelastic neutron scattering. Because the bound hydrogen atom can in many cases be regarded as a localized oscillator [5], the vibrational spectrum (number and positions of lines and their relative intensities) can be interpreted directly in terms of site geometry, relative site occupancy as well as hydrogen-metal forces. This approach has been utilized, for example, to determine the occupancy of octahedral sites in rare earth dihydrides [6,7] and to identify hydrogen trapped at impurity sites [8] with quite high sensitivity. Efforts have also been made to correlate vibrational spectra with multiple site occupancy in intermetallic hydrides such as LaNi_5H_x [9] and ZrCoH_x [10].

In the case of α -phase $\text{LaNi}_5\text{H}_{0.15}$ Hempelmann et al. observed a complex spectrum [Fig. 2 in Ref. 9] between 40 and about 200 meV which suggested that at least two different H sites were occupied. Since available structural data suggests at least two possible space groups for α - LaNi_5H_x , one with two H-sites (P31m) and one with five sites (P6/mmm), one might in fact attempt to make a choice between these possibilities based on the vibrational spectra. The authors used the local oscillator model along with a r^{-1} dependence of the vibrational frequencies on H-Me distance to analyze their data. They started with the assumption that the two extreme frequencies of 57 meV and 165 meV were to be associated with H on the highly distorted 3f octahedral site of space group P6/mmm. H-Ni and H-La force constants were thereby determined and frequencies could then be calculated for H on any sites in the two structures. Hempelmann and collaborators found that the observed spectrum fits best with occupation of

the 3f and 6m sites (P6/mmm) but did not regard their data accurate enough to choose between the two space groups. Nevertheless, this must be regarded as an excellent example of the kind of information that vibrational spectroscopy with H as probe atom can provide, particularly if somewhat better resolution and higher neutron fluxes become available.

Multiple site occupancy can, of course, also occur in a pure metal, and the case of the rare earth dihydrides (REH_2) is particularly noteworthy in this context. Most of these form an fcc CaF_2 structure in which mainly the tetrahedral sites are occupied. One reason why H does not readily go into the larger octahedral sites may be the fact that some metal d-orbitals point at these sites [11] and that therefore the t-sites have lower electronegativity. For o-sites to become occupied some bands associated with these orbitals must then become depleted. In these cases then H atoms indirectly become probes of the electronic structure as well. For those REH_2 , which order antiferromagnetically, occupation of o-sites at compositions of about $X(= \frac{\text{H}}{\text{Me}}) \sim 1.95$ and above causes the magnetic structure to become incommensurate as well [12].

As an example we show in Fig. 1 the low temperature vibrational spectrum of $\text{CeH}_{2.1}$ measured on the Filter Difference Spectrometer (FDS) at the Los Alamos Neutron Scattering Center (LANSCE). These data are part of an effort to study the concentration and temperature dependence of o-site occupancy in $\text{REH}_{2\pm\delta}$ systems [6,7]. The large peak centered near 105 meV as well as the shoulders at higher energies may be associated with t-site hydrogen while the small peak near 70 meV is characteristic of hydrogen on o-sites. From coherent inelastic neutron scattering experiments on $\text{CeD}_{2.12}$ [13] it may be inferred that the structure observed for the t-site peak is the result of dispersion in the optic branches. The asymmetry in the o-site peak, however, appears as a function of temperature. Since the structure of $\text{CeH}_{2.1}$ is thought to remain fcc at low temperatures [13], the observed distortion may result from H moving off the center of the octahedral site, for example, from $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ to (x, x, x) . By integrating the areas under the respective peaks one can then determine that about 8% of the H atoms in $\text{CeH}_{2.1}$ reside on o-sites. It is easily possible to detect o-site occupancy in the order of 1% by this technique [6]. Fig. 1 nicely demonstrates the power of neutron vibrational spectroscopy when

using H as a structural probe to study interstitial site geometry and occupancy.

III. Coordinated Hydrogen Molecule in a Tungsten Complex

While neutrons are often noted for their penetrating power, they may nevertheless be made into a surface-specific probe by the adsorption of hydrogen or other hydrogenous molecules upon a substrate which scatters neutrons weakly. A significant amount of information of the surface structure of metal powders such as Pt-black has, for example, been obtained by studying the vibrations of chemisorbed H and relating the spectra to the surface geometry of the substrate [14]. The interpretation of these data is often facilitated by comparisons with model compounds where the local geometry of the H-Metal atom(s) complex is known. These high surface area metal powders are generally highly reactive so that hydrogen molecules dissociate upon adsorption. A potentially very powerful application of neutron vibrational spectroscopy would ultimately be the study of catalytic reactions. It is in this context that the H_2 -W complex model compound first synthesized and studied by Kubas et al. [16] has such enormous significance. In this compound a hydrogen molecule is bound side-on to the metal without dissociating, but with stretched H-H bond of 0.82 Å (vs. 0.74 Å for the free molecule). Crystal structure as well as IR and Raman spectroscopic studies [15] all confirmed the identity of the bound species as H_2 . The latter work could, however, only identify four of the six normal modes of the H_2 -W system and, in particular, the torsional mode was not located.

Differential spectroscopy had to be employed using the FDS at LANSCE since the ligands that stabilize the molecular structure themselves contain many hydrogen atoms. The bound H_2 molecule can easily be exchanged in solution with D_2 and then a difference taken of the low temperature neutron spectra between the H_2 and D_2 complexes. The experiments were carried out on two different compounds with different ligands and gave consistent results. In both cases two of the modes observed by light scattering ($W-H_2$ stretch and one of the two $\delta(WH_2)$ modes) were also found in the neutron data. In addition, a strong peak at about 330 cm^{-1} was assigned to the H_2 torsion, and some structure above 600 cm^{-1} may well be the second $\delta(WH_2)$ mode. Since the H-H axis is known to be aligned with the P-W-P axis in the

molecule, the hindering potential can to lowest order be taken to have two-fold symmetry. By taking the somewhat longer H-H distance into account a barrier height of approximately 700 cm^{-1} can then be deduced from the observed torsional frequency. Further experiments are in progress to assist in interpreting these neutron vibrational spectra of the bound H_2 molecule.

IV. Hydrogen Bonded Systems

Differential spectroscopy can also be most useful in focussing on the dynamics of H in a hydrogen bond. It is frequently possible to exchange these hydrogen atoms with D and then to obtain directly the vibrational spectrum of the hydrogen bond by subtracting the deuterated spectrum from the protonated one. This technique was used with considerable success to identify certain H-bond vibrations [16,17] which are often used to relate H-bond strength to structural data, such as O-O distance for an $\text{O}\cdots\text{H} - \text{O}$ bond. For very short H-bonds this mode assignment is often difficult with optical spectroscopies [16] because of extensive mode mixing. Thus by focussing on the H-bond by means of isotopic substitution, IINS spectroscopy can provide crucial information on the H-bond potential well.

A most important question in this context is the one of the existence of a lower limit on O-O distance for the formation of an $\text{O} - \text{H}\cdots\text{O}$ bond, as well as that of the shape of the potential well at those short distances. Shown in Fig. 2 is the correlation of the out-of-plane bend $\gamma(\text{OHO})$ versus O-O distance for very short hydrogen bonds given in Ref. 16. While the frequency increases with decreasing $R(\text{OO})$ for distances greater than about $2.44\text{ \AA}$ (as would be expected for a deepening of the potential well), the reverse appears to be the case for even shorter H-bonds. Since other possible structural explanations for this change in the correlation of bending frequency with O-O distance could be ruled out [16], Howard et al. concluded that the dynamics of the H-bond were significantly altered for $R(\text{OO}) < 2.44\text{ \AA}$. This would, of course, imply a change in the H potential well. Since the H-bonds of many of the materials shown in Fig. 2 above and below $2.44\text{ \AA}$ are believed to be the symmetric type [16], this is difficult to understand except by noting that it is very difficult to tell by crystallography if the proton is truly located centrally between the two O atoms or has two slightly separated small minima near the center [18].

Within the available crystallographic information therefore there appears to be room for postulating such changes in the potential shapes, and a detailed theoretical analysis of these observations would be most important for the understanding of very strong H-bonds.

From this example, where by IINS H-bond spectroscopy a pronounced change in the H-bond dynamics was discovered, we will turn to an instance where the H-bond modes mix with skeletal modes of the molecule. This type of coupling can be deduced when a normal mode (as assigned by optical spectroscopy) that does not involve H motion, nevertheless is found to have significant neutron scattering intensity. This type of study is also important for determining the role of heterionic coupling [19] between molecular groups on different molecules in the solid.

Differential spectroscopy was again employed [17] in recent IINS work on Potassium Hydrogen Succinate (KHSu), $\text{KH}(\text{CH}_2\text{COO})_2$, Potassium Fluoride Succinic Acid (KFHSu), $\text{KF}(\text{CH}_2\text{COOH})_2$, and their counterparts with deuterated H-bonds. These two systems have, respectively, strong $\text{O} - \text{H} \cdots \text{O}$ and weak $\text{O} - \text{H} \cdots \text{F}$ bonds which serve to form linear chains of molecules in the crystal. The differential spectra [Fig. 3] for the two compounds reveal rather different H-bond dynamics [17]. In the case of KHSu the stretching mode $\nu_{\text{as}}(\text{OHO})$ is at low frequency because of the short O-O distance and is found to mix with the scissor mode $\delta(\text{CO}_2)$ which introduces pronounced neutron intensity at the position of the latter mode. The H-bond in this case bridges two O atoms of CO_2 groups on neighboring molecules. For the weakly hydrogen bonded chains of KFHSu, on the other hand, the stretching mode is now at much higher frequency (ca. 2000 cm^{-1}) and therefore cannot mix with skeletal modes of the molecule. The differential spectrum of KFHSu, however, does show weak IINS intensity for the same scissor mode $\delta(\text{CO}_2)$. The interpretation in this case must be that this intensity results instead from a riding motion of the adjacent non-centered hydrogen bonding hydrogen. This recent work is part of an extensive study on the role of carboxylate groups in H bond dynamics.

V. Conclusion

The preceding discussion has shown that neutron vibrational spectroscopy can be a very powerful tool and provide important complementary information to other spectroscopies, particularly in cases

where it is possible to focus on part of a molecule, hydrogen atom, or hydrogenous group using the technique of differential spectroscopy. In addition, one may expect that further advances in computational techniques [2-4] as well as source intensities and instrumentation will significantly increase the amount of information one can extract from molecular systems by IINS and that the technique will therefore become much more quantitative.

VI. Acknowledgements

I wish to thank my collaborators without whom much of this work would not have been possible, J. Howard, J. A. Goldstone, D. Richter, D. Tonks, P. M. Richards, E. L. Venturini, J. Tomkinson, A. D. Taylor, G. J. Kubas, P. J. Vergamini, and B. I. Swanson. This work was performed in part under the auspices of the Office of Basic Energy Sciences, U. S. Department of Energy.

References

1. J. Howard, J. M. Nicol, B. C. Boland, J. Tomkinson, J. Eckert, J. A. Goldstone and A. D. Taylor, Mol. Phys. 53, 323 (1984).
2. J. Howard and G. J. Kearley (private communication).
3. J. Howard (private communication).
4. John Anderson, S. J. Ullo and Sidney Yip, Physica B (these proceedings).
5. See, for example, J. Eckert, J. A. Goldstone, D. Tonks and D. Richter, Phys. Rev. B 27, 1980 (1983) and references therein.
6. J. A. Goldstone, J. Eckert, P. M. Richards and E. L. Venturini, Sol State Comm. 48, 475 (1984).
7. J. A. Goldstone, J. Eckert, P. M. Richards and E. L. Venturini, Physica B (these proceedings).
8. A. Magerl, J. J. Rush, J. M. Rowe, D. Richter and H. Wipf in Electronic Structure and Properties of Hydrogen in Metals, edited by P. Jena and C. B. Satterthwaite (Plenum Press, New York, 1983) p. 171.
9. R. Hempelmann, D. Richter, G. Eckold, J. J. Rush, J. M. Rowe and M. Montoya, J. Less Comm. Met. 104, 1 (1984).
10. S. J. C. Irvine, D. K. Ross, I. R. Harris and J. D. Browne, J. Phys. F: Met. Phys 14, 2881 (1984).
11. J. Hauck, J. Less Comm. Met. 94, 123 (1983).
12. R. R. Arons and J. Schweizer, J. Appl. Phys. 53, 2645 (1982).

13. P. Vorderwisch, S. Hautecler and W. D. Teuchert, Solid State Comm. 25, 213 (1978).
14. C. J. Wright in The Structure of Surfaces, Vol. 2, edited by M. A. Von Hove and S. Y. Tong (Springer Verlag, Berlin, 1984) p. 210.
15. G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini and H. J. Wasserman, J. Am. Chem. Soc. 106, 451 (1984).
16. J. Howard, J. Tomkinson, J. Eckert, J. A. Goldstone and A. D. Taylor, J. Chem. Phys. 78, 3150 (1983).
17. J. Howard, J. Tomkinson, A. D. Taylor, J. Eckert and J. A. Goldstone (unpublished work).
18. W. Joswig, H. Fuess and G. Ferraris, Acta Cryst. B 38, 2798 (1982).
19. U. A. Jayasooriya, G. J. Kearley, S. F. A. Kettle and H. J. Lauter, Phys. Stat. Sol. (a) 63, 169 (1981).

Figure Captions

Fig. 1 Hydrogen vibrational spectrum of $\text{CeH}_{2.1}$ at 12 K obtained on the Filter Difference Spectrometer at Los Alamos. The solid line represents a lineshape fit to the data for purposes of integrating the peak intensities. The small peak near 70 meV and large peaks near 105 meV result from hydrogen on octahedral and tetrahedral sites, respectively.

Fig. 2 Correlation of bending frequency $\nu(\text{OHO})$ with O-O distance from Ref. 16. The numbers and letters O - H...O hydrogen bonds in different compounds as discussed in Ref. 16.

Fig. 3 Vibrational spectra of Potassium Hydrogen (Deuterium) Succinate obtained at the Los Alamos Neutron Scattering Center (above) and the differential spectrum which results from subtracting the data for the material with deuterated H-bond from the protonated isomorph [Ref. 17].

Figure 1

Figure 2

FIGURE 2