Different Species of Hydrogen Chemisorbed on Raney Nickel Studied by Neutron Inelastic Spectroscopy

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The chemisorption of hydrogen on Raney nickel has been studied by neutron inelastic spectroscopy at high energy transfer. The main vibration levels at 120 and 140 meV are interpreted as being produced by multi-bonded surface species. A weak band also appears around 280 meV, superposed on the harmonic of the 140 meV peak, which can be attributed to the vibration of a linear form Ni—H. This interpretation is supported by the optical spectra of transition metal hydrides of known structure.

Studies of hydrogen chemisorption on transition metals are made more easily on supported metals because of their large surface area. Unfortunately, the support plays an ill-defined role in the adsorption and there is the possibility of a " spill over " effect. Sophisticated methods such as flash desorption [1] must be used to study the well defined but limited surfaces exposed on mono-crystals. Thus the energies for hydrogen chemisorption on (111), (110) and (100) planes of nickel were found to vary from 85 to 96 kJ mol^{-1}. Infrared studies performed on supported platinum detected several chemisorption states.[2, 3]

Recently, the preparative chemistry of the transition metal hydrides [4, 5] has progressed greatly. The most interesting of these compounds, for comparison with hydrogen chemisorbed on metal catalyst surfaces, are hydrides which have several metal atoms in their molecule. Fortunately, many data on the structure, the metal hydrogen bond length,[6] the position of infrared bands on n.m.r. spectra [7] have been collected. Thus, two types of hydrogen can be detected : terminal hydrogen which is bound to one metal atom and multibonded hydrogen which is bound to two or more metal atoms.

In a previous publication,[8] we described the time-of-flight spectra obtained on the energy-gain side and covering the range 0-140 meV (1200 cm^{-1}). These exhibited rather poor resolution in the region where the bands produced by hydrogen were detected. In the present study, the energy-loss spectra were investigated in the range 80-600 meV (650-4800 cm^{-1}) energy transfer, with better resolution. The measurements were made *in situ* with adsorption on a well defined Raney nickel. Thus we

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can calculate the possible configurations of chemisorbed hydrogen atoms according to the data available for hydrides in the literature and eliminate the species which are not consistent with the experimental spectra.

EXPERIMENTAL

SAMPLES AND PROCEDURE

Raney nickel was chosen to study the chemisorption of hydrogen for several reasons: despite the fact that the sensitivity of neutrons for hydrogen is rather high, a total amount of 10^{21} protons is needed for the measurements. Consequently a high specific area material is necessary. This type of nickel has a surface of 70 to 80 m^2 g^{-1} and 30 to 40 g of nickel provide a sufficient number of protons even with a surface coverage below 0.5.

The preparation of the sample and its characterization were described in the previous paper.[8] It is a polycrystalline material (crystal size 50-70 Å) containing <3.5 % aluminium, in the form of unattacked alloy. The first point which has to be stressed is the very low amount of aluminium hydroxide left in the samples after the successive washing treatments. Pretreatment at 200°C under 10^{-6} Torr leaves traces of water and hydrogen which correspond to less than 0.03 monolayer. The two different samples used for this experiment of adsorption of hydrogen and deuterium were prepared simultaneously and loaded in two different sample holders.

The aluminium sample holder filled with pure nickel is connected to the gas and to the vacuum line. After the first energy scan performed with pure nickel, 190 cm^3 of hydrogen is introduced to the catalyst and the experiment is carried out. A second introduction of H_2 is then carried out to ensure saturation of the surface so that the total amount of gas is 447 cm^3—and the third scan is done. Under these conditions, the two measurements were performed for a surface coverage of respectively 0.42 and 1. The same procedure was followed with deuterium, except that the experiment was performed only at saturation of the surface (515 cm^3 D_2).

THE SPECTROMETER

All the experiments were carried out on the triple axis spectrometer IN1 b installed on the hot source of the high flux I.L.L. reactor in Grenoble. During our experiment, the spectrometer was equipped successively with a copper and a beryllium monochromator. The copper crystal provides a very high flux of 1.1×10^7 neutrons cm^{-2} s^{-1} at the sample. The beryllium crystal provides only half the intensity, but with a better resolution. At 120, 180 and 260 meV, the resolution is 7, 10 and 15 meV with the Be monochromator and 10, 15 and 22 meV with the copper crystal. In each case, several sets of crystallographic planes were used to cover the whole range in energy. For example, with the Be (102) planes, one covers the range 75-200 meV and with the (201), 150 to 450 meV. Energy analysis is performed with a beryllium filter mounted on a 1.8 m arm, rotating around the sample. With this system the scattering angle range is limited to 15-50°. This range is a severe limitation of the instrument: for example if the energy transfer, $E = (\hbar^2/2m)(k_0^2 - k_f^2) = 140$ meV, the momentum transfer Q only varies by 6 % between 23° and 48°. Of course, at higher energy transfer, the situation is still worse and a study of the Q dependence of the intensity distribution would need very high counting times to obtain a low statistical error.

RESULTS

Fig. 1 shows the scattered intensity distribution in the energy transfer range 80-200 meV obtained with the Be monochromator at 23° scattering angle. Curve 1 is the intensity distribution produced by a sample saturated with hydrogen, after subtraction of the background produced by pure nickel shown on curve 3. Curve 2 corresponds to the intensity obtained with a coverage of 0.42. Curves 1 and 2 are very similar and the two peaks at 120 and 140 meV (950-1130 cm^{-1}) have the same ratio in the two cases. On fig. 2 the energy range 200-300 meV is represented.
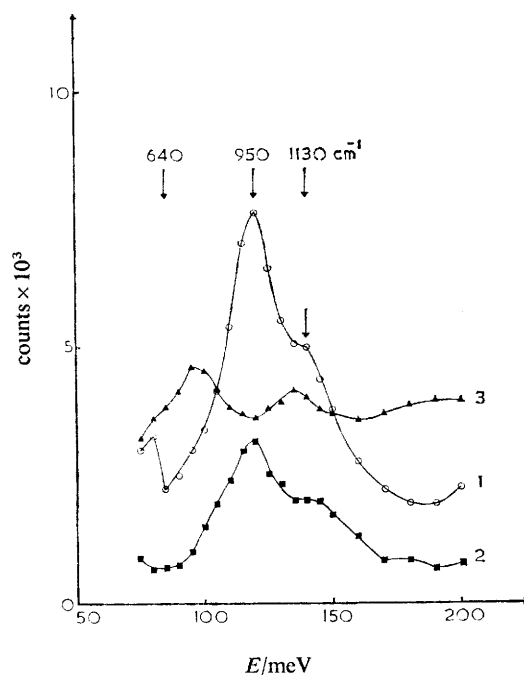
FIG. 1.—Scattered energy distribution using the Be monochromator. $\theta = 23°$. Curve 1: intensity distribution after subtraction of the background, corresponding to the saturation of the surface. Curve 2: intensity distribution corresponding to a coverage of 0.4. Curve 3: background.
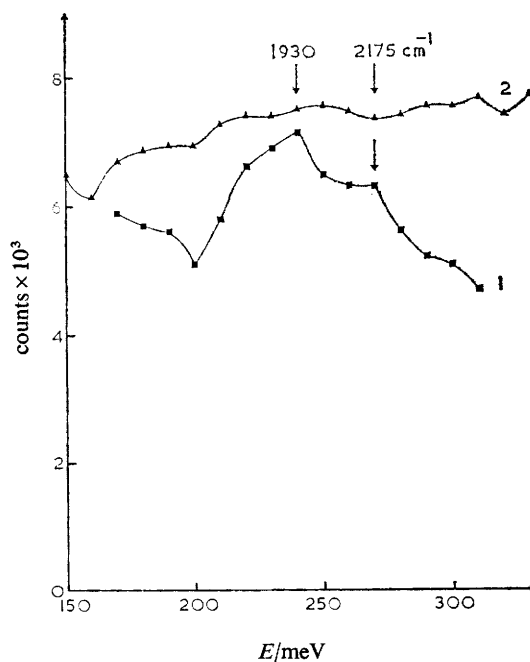

FIG. 2.—Scattered intensity at high energy with the Be monochromator. Curve 1: intensity distribution after background subtraction. Curve 2: background.

Two maxima are detected at 240 and 280 meV (1930 and 2175 cm⁻¹). A comple
mentary run was also performed at the scattering angle 48° between 80 and 200 me
in order to study the Q dependence of the intensity. The whole experiment was als
repeated between 60 and 600 meV with the copper monochromator (fig. 3 and 4)
The same general features appear on these curves despite the poorer resolution
Three equally spaced peaks can be seen on fig. 4 at 240-280, 360-400 and 480-500 meV
Finally fig. 5 shows the intensity distribution obtained using the Be monochromato
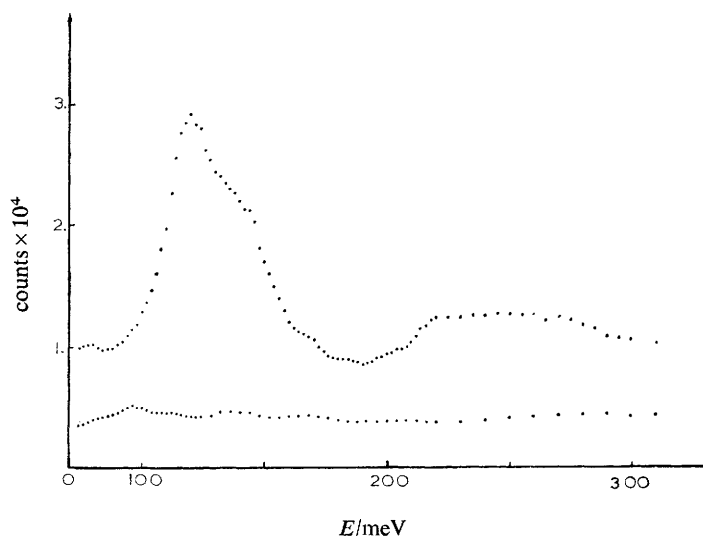after deuterium adsorption. Three peaks appear at 85, 100 and 120 meV.

FIG. 3.—Intensity distribution with the Cu monochromator after background subtraction (curve 1)
background (curve 2).

INTERPRETATION OF THE SPECTRA

The measured spectra reflect the dynamics of light atoms bound to the surface of
metal composed of heavy atoms. They also contain possible changes of the eigen
frequency distribution of Ni microcrystals due to the presence of hydrogen atoms o
their surface, as we have taken the difference between the scattered intensities fror
the loaded and outgassed samples. Computation of the dynamics of adlayers i
possible on the basis of assumed structures and force constants. However, in th
case of the Ni + H system, so little fundamental information is available that lattic
dynamics calculations would contain too many free parameters to be the worthwhil
at the present time.

We proceed, therefore, by testing whether current models for H_yNi_x molecule
are compatible with our neutron results. This could be a starting point for a stric
interpretation.

Successful numerical representation of our data by Gaussian peaks suggests tha
we may assume local harmonic oscillators with a frequency broadened by anharmoni
and many body effects. We have then to ascertain whether the available informa
tion on internal vibration frequencies of H_yNi_x complexes can give rise to neutro
scattering in the region of energy transfer where such scattering is measured.

The general question that arises when one considers the complete energy distribu
tion curves, is just how many of these peaks can be considered as originating in pur

one quantum processes, because fig. 4, for example, does suggest multiple excitations of a harmonic oscillator.

If one again considers the 120-140 meV region [8] our conclusion from time-of-flight measurements was that no multiquantum processes appear. The best way to
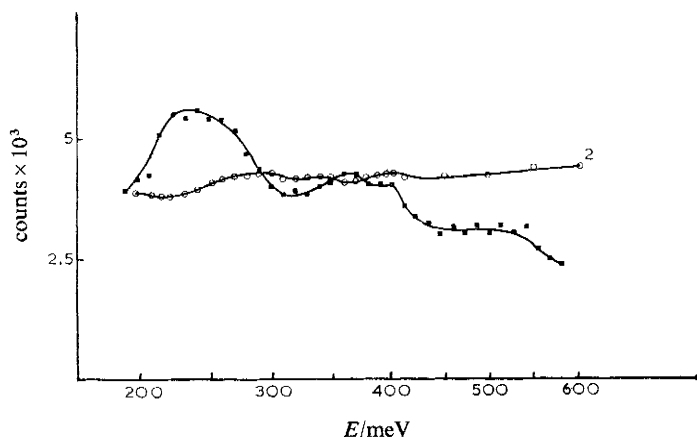

FIG. 4.—Intensity distribution in the 200-600 meV region using the Cu monochromator (curve 1) and background (curve 2).
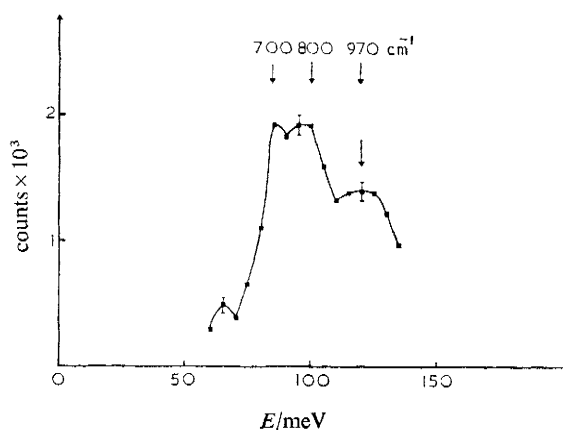

FIG. 5.—Intensity distribution obtained with the Be monochromator for deuterium adsorption.

proceed is to consider the momentum transfer dependence of the intensity: a one quantum process should follow a Q^2 law whereas a two quantum process should vary as Q^4. From table 1, where the intensities measured at $23°$ and $48°$ are compared, it is clear that our experimental values are very close to a Q^2 variation, within the

TABLE 1.—COMPARISON OF EXPERIMENTAL INTENSITY RATIOS AT $48°$ AND $23°$ WITH PREDICTED VALUES FOR ONE QUANTUM AND TWO QUANTUM PROCESSES

$E/$meV	$I_{48°}/I_{23°}$	$(Q_{48}/Q_{23})^2$	$(Q_{48}/Q_{23})^4$
120	1-1.10	1.15	1.32
140	1.05-1.12	1.13	1.28

limits of error. Moreover, these 120-140 meV peaks could hardly be explained by multiple de-excitation of phonons which have a frequency distribution centred at 30 meV. The last argument in this discussion is provided by fig. 5 where the M–D frequencies are seen to occur at 85 and 100 meV in accord with the isotopic ratio.

We now consider the 200-300 meV region in order to decide whether the levels at 240 and 275-280 meV are simply harmonics of the lower frequency vibrations. The order of magnitude of the two quanta scattering contribution compared with the one quantum scattering cross section is the ratio of the recoil energy to the oscillator energy. The scattering cross section law reads :[9]

$$S(\mathbf{Q}, \omega_0) = \exp(-2W) \sum_{-\infty}^{+\infty} \exp(-nZ_0) I_n\!\left(\frac{\hbar Q^2}{2m\omega_0} \operatorname{csch} Z_0 \, \delta\right)(E_i - E_f + n\hbar\omega_0)$$

where $\exp(-2W)$ is the Debye–Waller factor, $Z_0 = \hbar\omega_0/2kT$ and I_n is a modified Bessel function of the first kind. The intensity ratio of the two quantum to one quantum process then reads :

$$R_{2/1} = \exp(Z_0)\!\left[I_2\!\left(\frac{\hbar Q^2}{2m\omega_0} \times \frac{2}{e^{Z_0} - e^{-Z_0}}\right) \Big/ I_1\!\left(\frac{\hbar Q^2}{2m\omega_0} \times \frac{2}{e^{Z_0} - e^{-Z_0}}\right)\right]$$

with $\hbar\omega_0 = 120$ meV and $kT = 25$ meV; $R_{2/1} = 0.36$ and 0.33 respectively for the scattering angles 48° and 40°. A comparison of these figures with the experimental values reported in table 2 is an irrefutable proof that the 240 meV peak is a two quantum process. Concerning the intensity measured at 275-280 meV, the experimental values are greater by 20 % (0.27 and 0.26) than the calculated ones (0.24 and 0.22). This may indicate a small contribution from a one quantum process to this 275-280 meV level.

TABLE 2.—MEASURED INTENSITIES FOR VARIOUS SCATTERING ANGLES

E/meV	intensity $\theta = 23°$	intensity $\theta = 40°$	intensity $\theta = 48°$
120	1	1	1
140	0.66	0.70	0.64
240		0.31	0.33
280		0.27	0.26

In summary it appears that our spectra present two main peaks at 120 and 140 meV and probably a weak maximum at 275-280 meV.

A complete structure determination of hydride complexes of transition metals [5] has been conducted, using in some cases both neutrons and X-ray scattering: the atom positions and the metal hydrogen distances are known. In an optical spectroscopic study, two types of vibration levels were detected. The most frequently reported is situated between 1900 and 2200 cm^{-1} (235-285 meV) as in HNi $(P(OEt)_3)_4^+$ at 1970 cm^{-1} or HPtSPh $(PPh_3)_2$ at 2130 cm^{-1}. In these cases, the H atom is bonded to only one metal atom: it is generally called a terminal hydrogen and has bond length varying from 1.48 (Rh—H) to 1.66 Å (Ir—H). A second type of structure is also reported in which the H atom is bonded to several metal atoms. This is the case for complexes containing Re, Ru or Cr. The metal-to-hydrogen distances generally fall between 1.7 and 2.05 Å and the νM—H frequencies measured by Raman spectroscopy vary from 850 to 1200 cm^{-1}. It is likely that most of the hydrogen chemisorbed on Raney nickel is in this second form.

To support this comparison we have presented in the appendix a calculation of the vibration frequencies based on two types of model. The linear (or terminal)
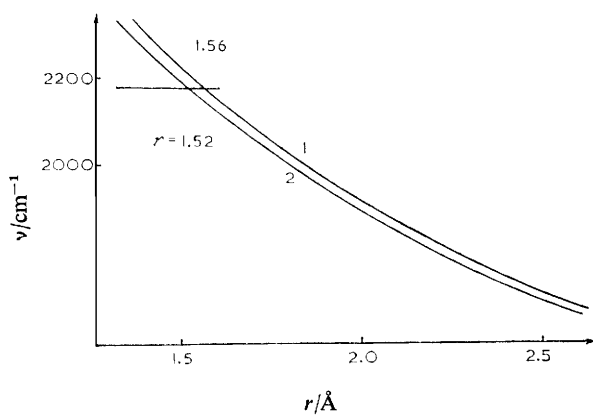
FIG. 6.—Model for linear adsorption (singly bonded H) representing the vibration frequency as a function of the metal to hydrogen distance. For Ni—H curve 1 is (111) or (110) plane and curve 2 is (110) plane.
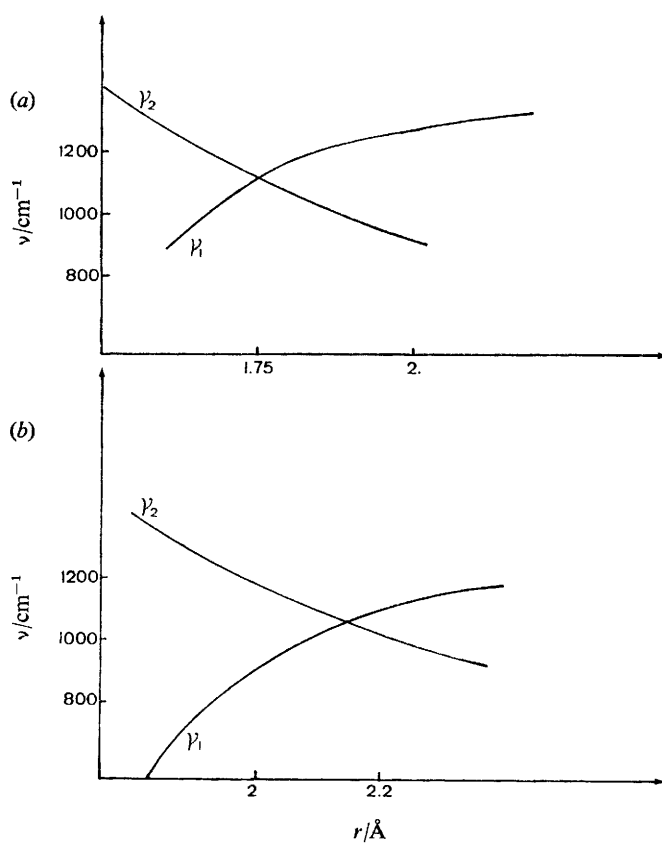
FIG. 7.—Models for multibonded surface species. (a) C_{3v} symmetry, Ni_3H and (b) C_{4v} symmetry, Ni_4H.

nickel–hydrogen model, where the adsorption site is composed of a unique metal atom, which has C_{6v}, C_{4v} or C_{2v} symmetry, depending on the crystallographic plane. The second model corresponding to multibonded species has C_{4v}, C_{3v} or C_{2v} symmetry. To evaluate the frequency νM—H as a function of bondlength we used semi-empirical potential functions. For adsorption energies of molecular hydrogen between 85 and 96 kJ mol^{-1}, $\nu = f(r)$ are reported in fig. 6 and 7.

It is rather surprising to observe on fig. 6 that the unique vibration calculated for the linear form Ni—H, on the (111), (100) and (110) planes has a frequency restricted to the range 2150 and 2000 cm^{-1} when the bond length varies from 1.5 to 1.8 Å. Similarly on fig. 7, two of the three modes calculated for Ni_3H give a level at 900-950 and 1100-1150 cm^{-1}, if the Ni—H distance is 1.7 or 1.8 Å. Finally for C_{4v} symmetry, corresponding to multibonded species on (100) planes, the same frequencies can appear for a Ni—H distance of 2.05 Å.

CONCLUSION

We have shown that on chemisorption of hydrogen on degassed Raney-nickel, most of the protons interact with several nickel atoms, giving rise to vibration levels at 120 and 140 meV. The presence of a small number of atoms in the linear form is not certain but would explain the small intensity detected at 275-280 meV.

If one compares our results with the recent theoretical study of Fassaert and Van der Avoird,[10] several points come to mind : first the metal-hydrogen distances of the linear form and the adsorption energies are consistent with our experimental data (1.5 to 1.6 Å and 2.6 to 2.8 eV). Similarly, our model for multibonded species agrees rather well with the calculated values (1.8 compared with 1.76 Å in C_{3v} symmetry and 1.9 compared with 2.05 Å in C_{4v}). Where the conclusions of these authors do not accord with out experimental study concerns their predictions on stability of the various species. They conclude that the linear form should be much more stable than the multibonded one and it appears that most of our hydrogen is highly coordinated.

Another point concerns the problem of metallic surface determination using hydrogen chemisorption. No indication of strict stoichiometry can be drawn from our study and it would be premature to admit that in this case, each nickel atom can chemisorb one H atom as normally accepted for platinum. These conclusions can finally be compared with the results previously deduced from the magnetic study of this nickel–hydrogen interaction.[11,12] The linear relationship between the volume adsorbed and the saturation magnetisation was interpreted as the formation of one bond per nickel atom. However, the small deviation from linearity observed at the beginning and the end of these curves, together with the fact that a magnetic interaction is a collective phenomenon leads to some restriction of our former conclusions : if statistically each nickel atom adsorbs nearly one hydrogen atom this does not mean that the simple linear form is the main species on the surface.

APPENDIX

With the linear or (terminal) Ni—H model a group theoretical analysis leads to the irreducible representation given in table 3. Solving the secular equations by the GF matrix originated by Wilson,[13] the frequencies of the vibrations are obtained in terms of force constants. By reason of the light mass of the hydrogen atom, the Ni—H

stretching vibrations have a frequency considerably higher than other modes. They were calculated by setting equal to zero the force constants which govern the low frequencies.[14] The relation between frequency and force constant is

$$v^2 = \frac{1}{4\pi^2C^2}(\mu_{Ni}+\mu_{H})f \quad \text{with} \quad \mu = 1/m.$$

These constants can be calculated if the potential energy function is known. Lippincott and Schroeder [15, 16] published a general relation between the potential

TABLE 3

plane symmetry		terminal hydrogen		
		(111) C_{6v}	(100) C_{4v}	(110) C_{2v}
normal modes of vibration	number modes	18 $3A_1^{\ddagger\bullet}+2B_1+B_2+$ $3E_1^{\ddagger\bullet}+3E_2^{\ddagger}$	12 $3A_1^{\ddagger\bullet}+2B_1^++$ $B_2^++3E^{\ddagger\bullet}$	12 $5A_1^{\ddagger\bullet}+A_2^++$ $3B_1^{\ddagger\bullet}+3B_2^{\ddagger}$
vNi—H	number modes	1 A_1	1 A_1	1 A_1

plane symmetry		multibonded hydrogen	
		(111) C_{3v}	(100) C_{4v}
normal modes of vibration	number modes	6 $2A_1^{\ddagger\bullet}+2E^{\ddagger\bullet}$	9 $2A_2^{\ddagger\bullet}+2B_1^++B_2^++2E^{\ddagger\bullet}$
vNi—H	number modes	3 A_1+E	4 A_1+B_1+E

$+$ Raman active. $\bullet$ I.r. active.

energy and the internuclear distances applicable to the ground state of diatomic and polyatomic molecules. This function reads:

$$V = D_e\{1-\exp[-n(\Delta r)^2/2r]\} \cdot [1+af(r)]$$

where D_e is the dissociation energy, corresponding to the minimum of the potential energy curve, $\Delta r = r-r_e$, r_e being the bond length at equilibrium, a is a constant, $f(r)$ a function of r bound to the limit conditions:

$$f(r) \to \infty \text{ for } r \to 0 \quad \text{and} \quad f(r) \to 0 \text{ for } r \to \infty;$$

$af(r)$ is generally small and is neglected by many authors.

n, called internuclear delta function parameter, is defined by imposing conditions for equilibrium:

$$(dV/dr)_{eqn} = 0 \quad \text{and} \quad (d^2V/dr^2)_{eqn} = f$$

hence $n = fr_e/D_e$.

Actually, n is evaluated by Lippincott from the empirical relation:

$$n = n_0(I/I_0)_B^{\frac{1}{2}} \times (I/I_0)_A^{\frac{1}{2}} \qquad (1)$$

where $(I/I_0)_A$ and $(I/I_0)_B$ are the ratios of ionisation potentials of atoms A and B to the values corresponding to atoms in the same row and the first column of the periodic table. Therefore, to determine

$$f_{Ni-H} = \frac{n \times D_{NiH}}{r_e} \qquad (2)$$

one needs the value of the adsorption energy relative to one H atom.

D_{NiH}, the bond energy, can be estimated from the dissociation energy of hydrogen, D_{HH} (421 kJ mol^{-1}) and the heat of adsorption, ΔH_{a}, according to :

$$-\Delta H_{\text{a}} = 2D_{\text{NiH}} - D_{\text{HH}}.$$

For Ni—H, D_{NiH} has been theoretically determined by Stevenson [17] to be equal to 276 kJ mol^{-1}.

The heats of adsorption on (111) and (100) planes (96 kJ mol^{-1}) and on (110) planes (85 kJ mol^{-1}) lead to a bond energy equal to 264 and 258 kJ mol^{-1} respectively.

According to eqn (1) and (2), f_{NiH} for each model can be expressed as a function of the bond length r and introduced into the expressions for the frequencies.

With multibonded species, the frequencies read :

$$\nu_1^2 = \frac{1}{4\Pi^2 C^2}[\mu_{\text{H}} + \mu_{\text{Ni}} + 2\mu_{\text{H}} \cos \alpha](f + 2f')$$

$$\nu_2^2 = \frac{1}{4\Pi^2 C^2}[\mu_{\text{H}} + \mu_{\text{Ni}} - \mu_{\text{H}} \cos \alpha](f - f'), \text{ in } C_{3v} \text{ symmetry,}$$

and

$$\nu_1^2 = \frac{1}{4\Pi^2 C^2}[\mu_{\text{H}} + \mu_{\text{Ni}} + \mu_{\text{H}}(\cos \beta + \cos \alpha)](f + f' + 2f'')$$

$$\nu_2^2 = \frac{1}{4\Pi^2 C^2}[f + f' - 2f'']\mu_{\text{Ni}}$$

$$\nu_3^2 = \frac{1}{4\Pi^2 C^2}[\mu_{\text{H}} + \mu_{\text{Ni}} + \mu_{\text{H}} \cos \beta](f + f') \text{ in } C_{4v} \text{ symmetry.}$$

Using the central force approximation, $f' = f'' = 0$ and $f = \frac{1}{3}f_{\text{x}}$ or $\frac{1}{4}f_{\text{x}}, f_{\text{x}}$ being the force constant calculated in the case of terminal hydrogen, one obtains ν as a function of r.

Fig. 6 and 7 show this representation of the vibration frequency as a function of the metal to hydrogen distance.

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