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The Interaction between Benzene and Nickel. A Neutron Inelastic Spectroscopy Study

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Neutron inelastic spectroscopy has been used to study benzene chemisorption on Raney nickel precovered with hydrogen. From the valence force field determination, it is concluded that, as on the bare surface, the molecule is adsorbed flat on the surface and is preferentially attached on top of a single metal atom. The determination of the force constants shows that the ring undergoes relatively mild perturbations. This stable form is considered as a precursor for the activated complex whose formation is the limiting step in hydrogenation and exchange reactions.

INTRODUCTION

Benzene hydrogenation has often been used as a test reaction on nickel catalysts. Kinetic measurements, however, are insufficient to provide a clear understanding of the reaction mechanism. Recently van Meerten *et al.* (*1*) studied benzene hydrogenation and H–D exchange, and to explain their kinetic results they concluded that the activated complex should be a dissociative π-adsorbed state. However, they were unable to take into account the exact force constants derived from a force field analysis of the adsorbed molecule. Ideally, any proposed mechanism should be compatible with the results of spectroscopic studies and with other types of measurements such as radiotracer studies (*2*) and magnetic measurements (*3*). Recent progress achieved on single crystals using LEED and electron energy loss spectroscopy (*4*) should also be considered.

In a recent study of benzene adsorbed on Raney nickel (*5*) using neutron inelastic spectroscopy, we proposed a model for the adsorbed complex. The advantage of this method compared to optical spectroscopy lies in the fact that no selection rules hold. Moreover, one can use the large differences in the inelastic cross sections of the various nuclei to favour the molecule under study. Nickel, for example, has an incoherent cross section 15 times lower than that of hydrogen. Therefore we were able to determine the structure of benzene on bare nickel, showing that the molecule is adsorbed flat on the surface at a distance of 2.5 ± 0.5 Å and that the metal–ring interaction produces a 20% weakening of the C–C force constants.

The purpose of this paper is to report a study of benzene chemisorption on a hydrogen-precovered nickel and to consider the consequences of the calculated structure for the hydrogenation mechanism.

EXPERIMENTAL

A. Samples

The chemisorption of benzene was studied on Raney nickel. This material is well suited for neutron studies as it can be cleaned of all hydrogenous molecules at 600

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K without excessive sintering. One can thus easily adsorb the minimum amount of 10^{-2} mole benzene in the 25-cm^2 beam.

The preparation of the wet nickel from Al–Ni alloy and its characterization have already been described (*6*). Eighty grams of the metal is introduced in a quartz reactor, disposed on a series of 12 stainless-steel platelets, and connected to the cryopump. After 48 h at 600 K, the vacuum is better than 10^{-7} Torr. The powder is then transferred to the aluminum sample holder and separated from the reactor with a torch. The bare sample (I) is introduced in the cryostat at 77 K for the neutron background measurement. The sample is then warmed at 300 K and 8×10^{-5} mole benzene per gram of nickel is introduced (coverage 0.8 $\theta_{\max}$) on this bare nickel, through a break seal. The neutron experiment is repeated.

A second experiment (sample II) was performed by first covering the metal with hydrogen ($\theta = 0.5$) and then introducing 4×10^{-5} mole benzene per Ni gram. The energy scan is then repeated at 77 K.

We have checked that for such hydrogen coverage, subsequent benzene chemisorption does not displace hydrogen and does not produce any cyclohexane. On the other hand, the metal surface is free from any contamination by CO or O_2 which had been removed by our cryopump (over 1000 liters s^{-1}). We have also verified that the system is stable for several hours at 300 K, after benzene chemisorption. A fortiori, no surface reaction can occur during the experiment, at 77 K.

B. Neutron Inelastic Scattering Spectra

The neutron spectra were obtained at the Institut Laue Langevin using the beryllium filter spectrometer IN 1 B; this instrument has been described elsewhere (*5*).

The scattering from the sample can be analyzed simply in terms of incoherent scattering because of the large incoherent cross section (σ_H) and the low mass (m_H) of the protons. The differential cross section can then be written, in the isotropic approximation (*7*), and for energy loss spectra:

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{\text{inc.}} = \frac{k}{k_0} \sum_d \frac{\sigma_H}{4\pi} \exp(-2W_d) \frac{K^2 C_d^2(\lambda)}{m_H \omega_\lambda} \delta(\omega - \omega_\lambda).$$

In this equation, K, the neutron momentum transfer, is defined as $K = k - k_0$, where k and k_0 are, respectively, the final and incident wave vectors, $\exp(-2W_d)$ is the Debye–Waller factor, and we have recently shown that this factor can be neglected in the comparison between experimental and calculated spectra (*20*).

The intensities of the vibrational modes ω_λ are thus directly related to the vectors $C_d(\lambda)$, which describe the displacement of the dth proton in the λth normal mode.

These vectors can be computed from a normal coordinate analysis using the method of Wilson *et al.* (*9*). We have used the same geometry and the same coordinates for the surface complex as in our previous work (*5*). The geometry of the surface complex with the definition of the internal coordinates is shown in Fig. 1 (this adsorption geometry is discussed later).

RESULTS

A. Determination of the Spectra

The spectrum of solid benzene shown in Fig. 2a was recorded first. The subtraction of a weak background produced by the aluminium container is the only correction applied to the raw data.

The observed intensities of the vibrations of solid benzene presented in Fig. 2a are slightly different from those reported in our previous work (*5*). This is due to the faster cooling of a thinner sample which yields a perfectly amorphous structure. The agreement with the calculated spectrum of Fig. 2b is thus better because of the absence of preferential orientation of the molecules in respect to the neutron momentum transfer. We have also checked that the calculated neutron spectra derived from other force

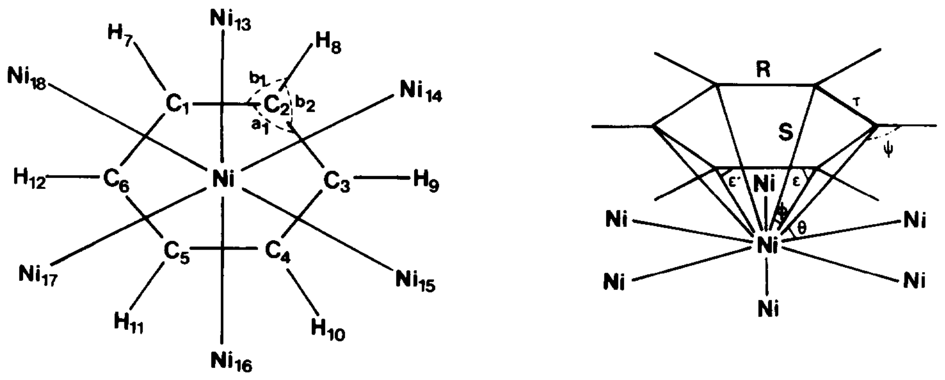

FIG. 1. Geometry and definition of internal coordinates for adsorbed benzene.

fields proposed for this molecule (*10, 11*) were almost identical to the spectrum of Fig. 2b, the assignment of the vibrational modes being the same for all authors.

The spectrum of benzene adsorbed on bare nickel shown in Fig. 4a is identical to that reported in Ref. (*5*). It is obtained by subtracting the spectrum of pure nickel from the intensity scattered by the benzene-covered metal. The spectrum of nickel itself does not interfere with that of benzene. Indeed, the nickel phonons are centered around 160 cm^{-1}, well away from the lowest vibrations of benzene. Thus any modification of these phonons upon chemisorption has little influence on the subtraction. Obtaining the spectrum of benzene chemisorbed on the hydrogen-covered surface is more delicate as a modification of the structure of hydrogen may occur upon benzene adsorption. To check this possibility, we have, in a separate experiment, recorded the spectrum of chemisorbed hydrogen in the presence of perdeuterobenzene. The incoherent cross section of deuterium is so low that the measured intensity can be attributed only to hydrogen. H–D exchange on the surface is avoided by performing the adsorption of H_2 at 250 K.

Figure 3b shows the scattering curve measured in this experiment. It can be compared with the results (reported in Ref. (*21*)) of Fig. 3a for the adsorption of hydrogen on the bare surface. No modification of the vibrational frequencies of the bands at 120 and 140 meV is detected; only a slight narrowing and a small modification of their relative intensity are noticed. Thus, it is justified to consider that the contribution of benzene can be obtained by subtracting the spectrum of hydrogen-covered nickel from the intensity measured with the sample containing benzene and hydrogen (Fig. 5a).

B. Interpretation of the Spectra

On comparing the spectra of solid benzene (Fig. 2a), and of benzene on bare nickel (Fig. 4a) and hydrogen-covered nickel (Fig. 5a), it is obvious that no direct assignment of the vibrational modes can be made. The original approach in Ref. (*5*) was based on electron loss spectroscopy results, obtained on single crystals (*12*). The spectra measured upon adsorption on (111) and (100) planes were almost identical, which is a strong indication for bonding of the molecule flat on the surface on top of one, or possibly two, metal atoms. We have therefore adopted $C_6H_6Cr(CO)_3$ as a model (*8*) and have been able, by changing only a few force constants, to transfer its force field to the case of chemisorbed benzene. The calculated spectrum is shown in Fig. 4b. The vibrational frequencies are indicated by spikes whose intensity is derived from the normal coordinate analysis, the convolution with a Gaussian resolution function producing the smooth spectrum. In case I, 15% of

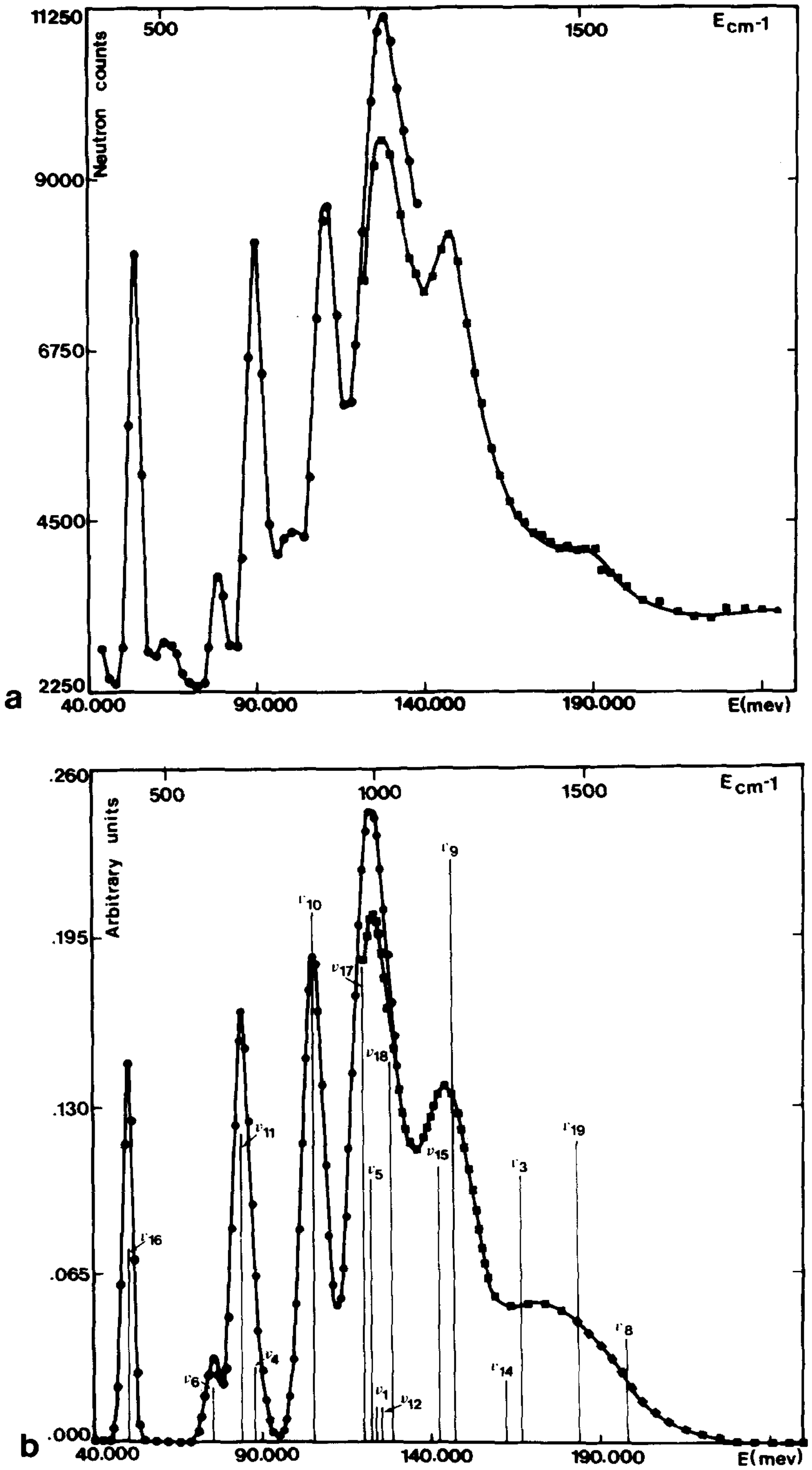

FIG. 2. (a) Experimental neutron spectrum of solid benzene at 77 K. (b) Calculated spectrum from the force field reported in Ref. (*18*). ●, (200) monochromator reflexion; ■, (220) reflexion.

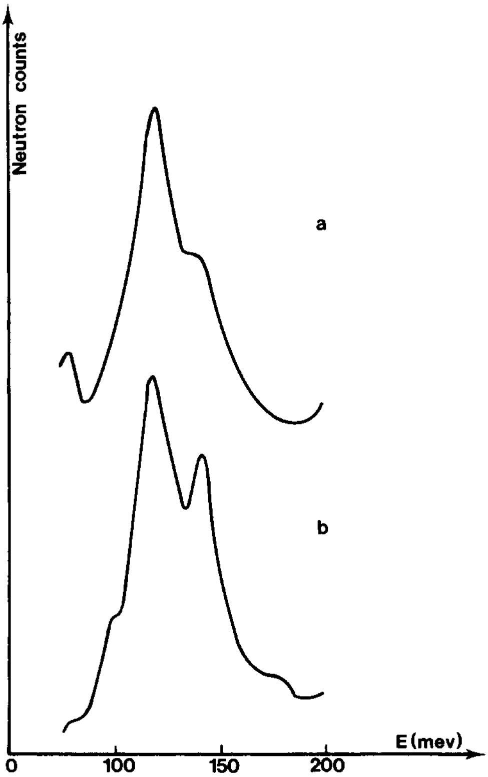

FIG. 3. Observed neutron spectrum of hydrogen on Raney nickel: (a) Bare surface (*21*); (b) upon co-adsorption with perdeuterobenzene.

the intensity was found to correspond to chemisorbed hydrogen produced by dehydrogenation of the benzene.

We shall discuss later the inadequacy of dissociative models and how they fail to reproduce the experimental data.

If we turn to the case of benzene adsorbed on nickel precovered with hydrogen (Fig. 5a), we notice that the large composite band has shifted up from 110 to 125 meV. The most intense vibrations situated in that region are the out-of-plane bending modes. ν_{10} was taken as 105 meV, with ν_{11} unresolved on its low-frequency side. Unlike case I, the ν_{18} (C–C) stretching mode cannot be pointed out; its intensity added to the other γ vibrations ν_{17} and ν_5 gives the maximum at 125 meV. Therefore the (C–C) stretching and (C–C) bond interaction force constants cannot be determined with precision. However, the γ vibrations being placed by modifying the ψ and ψ_T force constants (see Table 1), values for the (C–C) stretching and (C–C) bond interaction force constants equal to those for $(C_6H_6)Cr(CO)_3$, give a good fit and explains the slight increase of the frequency of the band at 150 meV (this band is made up of the ν_9 and ν_{15} modes which have a contribution from (C–C) stretch in their potential energy distribution). The (Ni–C) frequencies are slightly decreased so that the (Ni–C) stretching force constant is reduced to 1.3 mdyn $Å^{-1}$ (cf. 1.5 for C_6H_6/Ni).

The complete modifications of the force field are given in Table 1. Again, the usual restriction on the uniqueness of the force field is stressed. For example, the (C–C) stretching and (C–C) interaction force constants have globally increased (compared to case I) but as these two force constants are related, a drop in one can be compensated by an increase in the other so that one value cannot be cited alone. However, this force field is useful in that it gives quantitative agreement with the observed neutron intensities.

The calculated frequencies of benzene adsorbed on hydrogen-precovered nickel are given in Table 2; they are compared to those of free benzene and of benzene adsorbed on bare nickel. We have investigated the influence of the ring-to-nickel plane distance on the vibrational frequencies and we have found that this distance was of the same order, namely, 2.5 ± 0.5 Å, as in our study of C_6H_6 adsorbed on bare nickel (for details see Ref. (*5*)).

The calculated neutron spectrum is shown in Fig. 5b. The agreement with the experimental spectrum of Fig. 5a is satisfactory.

DISCUSSION

A. Possibility of Other Geometries for the Surface Species

The fairly good agreement obtained between the experiment and the spectrum cal-

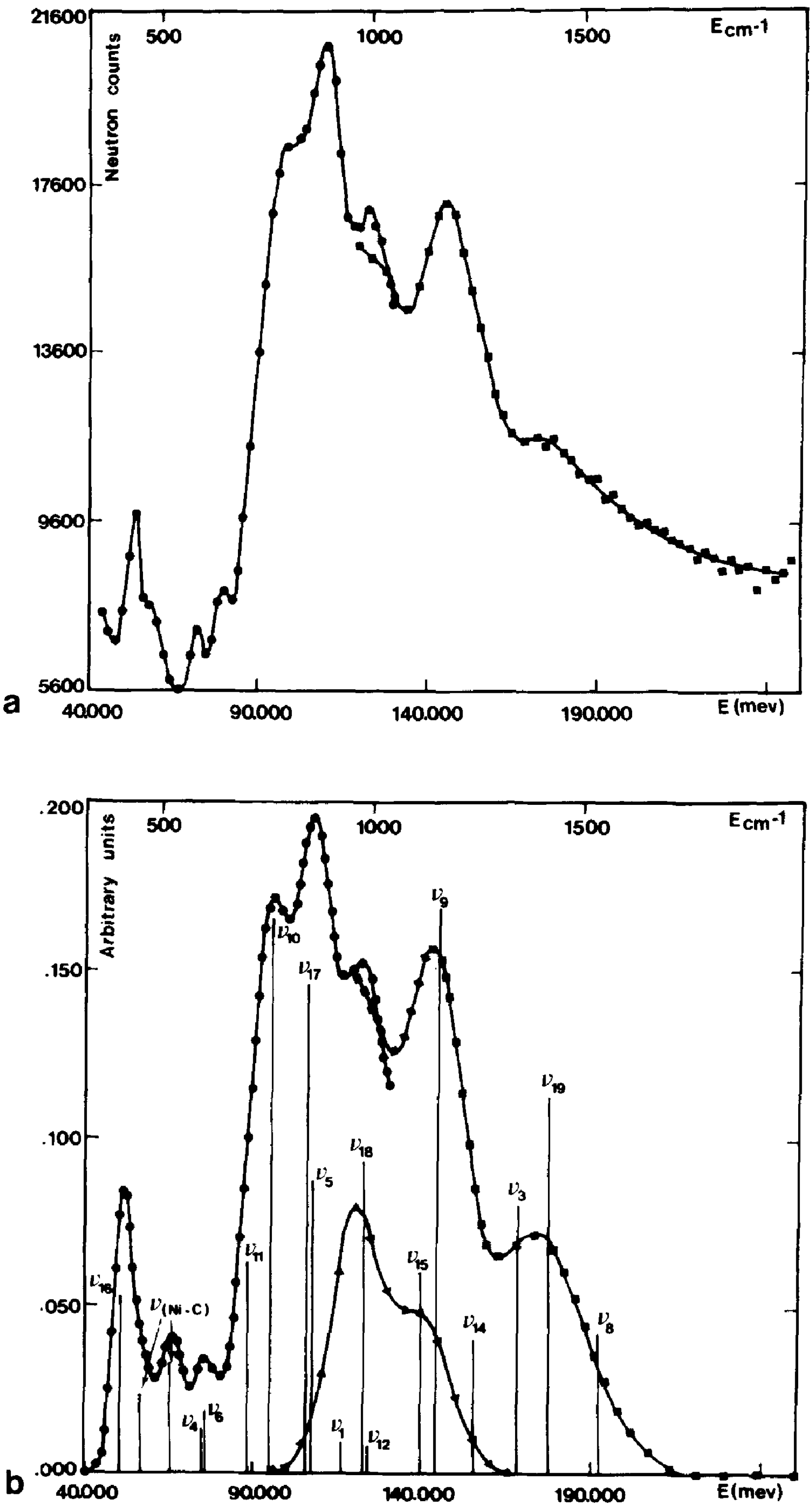

FIG. 4. (a) Experimental spectrum for benzene chemisorbed on bare nickel. (b) Calculated spectrum from Ref. (5).

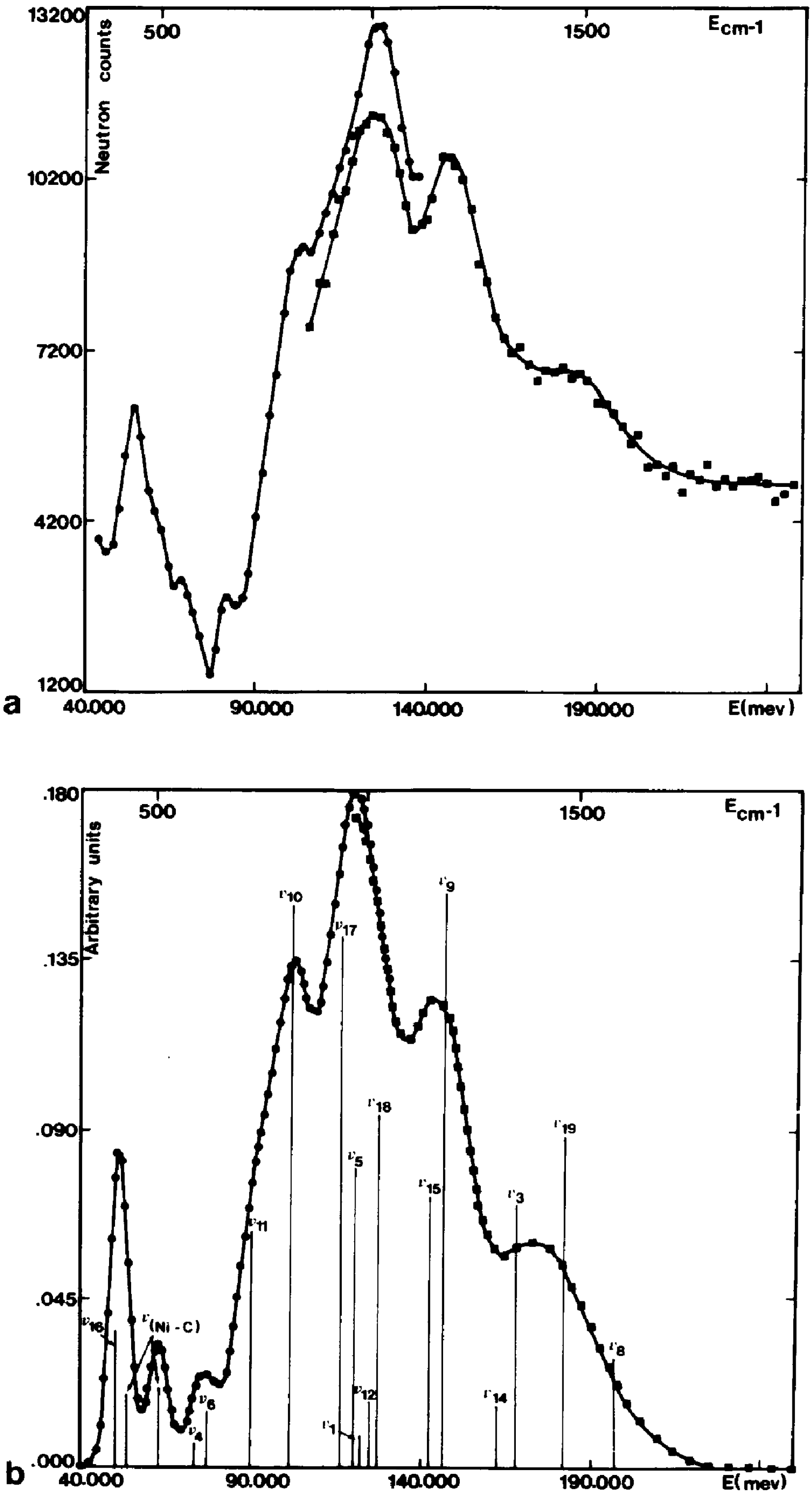

FIG. 5. (a) Experimental spectrum for benzene chemisorbed on hydrogen-covered nickel. (b) Calculated spectrum resulting from the force field of Table 1.

TABLE 1

Force Field of Benzene Adsorbed on Hydrogen-Precovered Nickel Compared with Free Benzene, Benzenetricarbonyl-chromium, and Benzene Adsorbed on Bare Nickel

Force constant definition[a]	Value in C_6H_6 (*16*)	Value in $(C_6H_6)Cr(CO)_3$ (*8*)	Value in C_6H_6/Ni (*5*)	This work
R	6.031	5.65	5.0	5.65
$R_i R_{i+1}$	0.843	0.70	0.60	0.7
S		0.75	1.50	1.3
θ		0.40	0.40	0.4
ψ		0.215	0.13	0.15
$\Phi = \epsilon = \epsilon'$		0.25	0.25	0.25
$R_\epsilon = -R'_\epsilon$		−0.20	−0.20	−0.20
$\gamma_i \psi_i$		0.07	0.07	0.07
$S\tau_i = -S\tau_{i-1}$		0.05	0.05	0.05
$\delta_i \Phi_{i-1} = -\delta_i \Phi_{i+1} = -\delta_i \epsilon_i$ $= \delta_i \epsilon'_i = -\delta_i \epsilon'_{i-1} = \delta_i \epsilon_{i+1}$ $= \alpha_i \Phi_i = \alpha_i \Phi_i = -\alpha_i \epsilon_i$ $= -\alpha_i \epsilon'_i = \alpha_i \epsilon'_{i-1} = \alpha_i \epsilon_{i+1}$		0.045	0.045	0.045
$\epsilon_i \tau_i = -\epsilon'_i \tau_i = \gamma_i \epsilon_i$		0.11	0.17	0.17
$\psi_i \tau_i = -\psi_i \tau_{i-1}$		−0.01	−0.025	0.0
$\gamma_i S_i = \gamma_i S_{i+1} = -\gamma_i S_{i+2}$ $= -\gamma_i S_{i+3}$		−0.01	−0.06	−0.06

[a] The valence force constants are expressed in millidynes per angstrom, the deformations in millidyne angstrom per square rad, and the bond-angle interactions in millidynes per rad.

culated on the basis of a flat, nondissociated molecule, does not constitute a proof of uniqueness for such a geometry. It is thus worthwhile to consider, for example, models involving a partial dehydrogenation of the molecule, such as a di-σ bonding. In this case, the degeneracy of the E vibrations should be lifted and several modes should appear in the range 20–50 meV. To verify that their neutron intensities are high enough to be detected, we have calculated the spectrum produced by a benzene molecule in which two H atoms in *ortho* positions have been replaced by Ni atoms. For this purpose, we have used the force field determined by Scherrer (*11*) for the series of chlorobenzene molecules. The resulting spectrum (Fig. 6) shows the presence of several intense vibrational modes below 300 cm^{-1} (which are not present in our experimental results) and a large modification to the intensity distribution between 800 and 1400 cm^{-1}. More generally, any lowering of the symmetry of the surface complex would result in such modifications of the calculated spectrum. We conclude, a posteriori, that our model is the most satisfactory.

With the usual restrictions concerning the uniqueness of the force field, the picture which comes out is of a benzene molecule keeping its symmetry with only slight variations of the C–C force constants. Only the metal–carbon force constants are higher than in $(C_6H_6)Cr(CO)_3$ but lower than on bare nickel. Let us consider now how this model for the chemisorbed complex fits with other experimental results.

TABLE 2

Vibrational Frequencies (cm^{-1}) of Adsorbed Benzene on Bare and Hydrogen-Precovered Raney Nickel Compared to Those of Free Benzene (Wilson Notation)

Notation	Free C_6H_6 (*18*)	C_6H_6/Ni (*5*)	C_6H_6/Ni + H_2 (This work)	$\sum_H C_d^2 \times 10^2$
8	1595	1545	1590	32.5
19	1479	1439	1463	98.4
3	1346	1357	1357	79.1
14	1309	1253	1306	17.8
9	1177	1163	1177	170.2
15	1146	1128	1149	82.2
18	1035	992	1030	105.2
12	1010	1003	1003	19.9
1	993	939	985	10.1
5	991	868	970	90.3
17	969	857	937	158.7
10	849	768	817	167.6
4	707	610	727	71.2
11	675	714	622	17.9
6	607	613	593	7.2
16	404	411	408	40.1
ν(Ni-C)		529	508	24.4
ν(Ni-C)		459	432	20.1
Def.		92	92	13.3
Def.		89	89	6.9
Def.		43	43	0.
Def.		42	42	0.

B. Comparison with Other Spectroscopic Data

As we have shown in Ref. (*5*), our force field yields a reasonable assignment of the electron energy loss spectra obtained on single crystals by Lehwald *et al.* (*4*) and Bertolini and Rousseau (*13*). We were even able to calculate the vibrations of C_6D_6 which fit well with experimental results of these authors. This demonstrates that the neutron technique, in which all the vibrational modes are active, is very powerful for determining the force field of the ad-

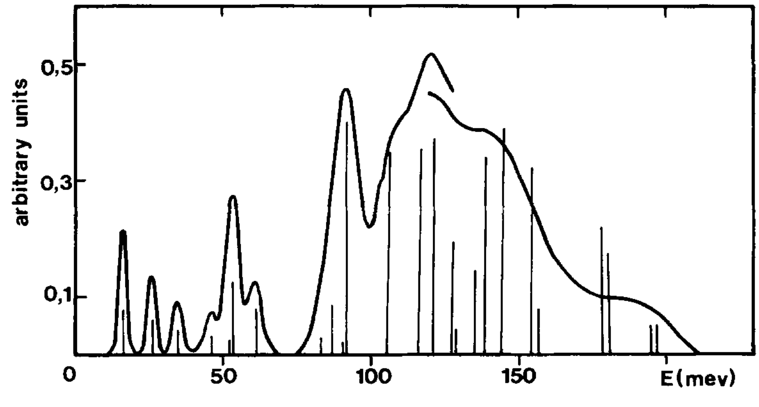

FIG. 6. Calculated neutron spectrum for 1,2-C_6H_4 Ni_2.

sorbed molecule and the structure of the surface complex. On the other hand, although the assignment of the spectra obtained from electron energy loss is difficult, such spectra provide helpful information concerning the modification of the surface complex structure on the different crystallographic planes.

Infrared studies of benzene chemisorption on supported catalysts have mainly been carried out on platinum samples. The strong absorption of the support below 1000 cm^{-1} severely restricts the observation range and the conclusion of Sheppard *et al.* (*14*), for example, based on the slight modifications of the $\nu_{\mathrm{C-H}}$ frequency, is not clearly in favour of a π or σ complex. The use of an "electronic" probe such as CO preadsorbed on the sample, by Primet and Mathieu (*19*), has led to more precise figures for the magnitude of the electronic transfer between various substituted aromatic hydrocarbons and the metal. However, their arguments for rejecting the σ complex are not fully convincing.

Thus, at the present time, optical spectroscopy brings indications which are not contradictory with our findings.

C. Compatibility with Other Experiments

Magnetism has proved to be a sensitive tool in the study of chemisorption on nickel. Candy *et al.* (*15*) have found a variation of saturation magnetization of 4.6 Bohr Magneton (B.M.) per adsorbed benzene molecule on bare nickel and only 1.5 B.M. on a hydrogen-covered surface. A precise geometry is certainly impossible to extract from these figures. Indeed, magnetism which is a collective phenomenon, reflects the magnitude of the electronic transfers. More precisely, it indicates that the filling of the incomplete 3*d* subband of Ni concerns an "ensemble" of several atoms on the free surface and that this effect is strongly reduced when the metal is already covered by hydrogen. This influence of C_6H_6 on a large area of the surface is corroborated by the LEED structure determined by Bertolini *et al.* (*12*) on Ni (111) and (100), who found that the molecule occupies 50 and 55 $\mathrm{Å}^2$, respectively. In no case can one conclude from magnetic studies that σ complexes are formed on the surface.

Candy *et al.* (*16*) in their volumetric study of benzene hydrogenation with labeled molecules have concluded that hydrogen and benzene compete on the surface and that only 80% of the benzene is hydrogenated to cyclohexane at 300 K. This fraction is in low interaction with nickel as each molecule is replaced on the surface by one H atom.

All these observations are in agreement with our findings. On bare nickel total dehydrogenation of a small fraction of the aromatic molecules occurs and this is the first stage. When the coverage is increased, the benzene molecules still undergo large perturbations which result in a strong carbon–nickel coupling but without C–H rupture. The present study shows that when the surface is covered by hydrogen, the perturbation of the ring is less and the carbon–nickel force constant is lowered. However, the precision of our determination of the ring-to-surface distance is not sufficient to assess whether or not benzene forms an adlayer on top of a homogeneous hydrogen layer.

D. The Activated Complex in Benzene–Hydrogen Reactions

With our symmetrical model, it is difficult to account for the production of C_6H_5D in benzene–deuterium exchange; this is the reason why many authors have postulated for the reaction intermediates complexes such as those in Fig. 7. Such diagrams involve a partial loss of the aromatic character and in any case a change in symmetry which is not compatible with the observed low-energy vibrations. However, it has been shown (*17*) that for chemisorbed atoms like hydrogen, the mean residence time on a given site is of the order of 10^{-9} s; thus how can we explain that the rate for the hydrogenation or exchange re-

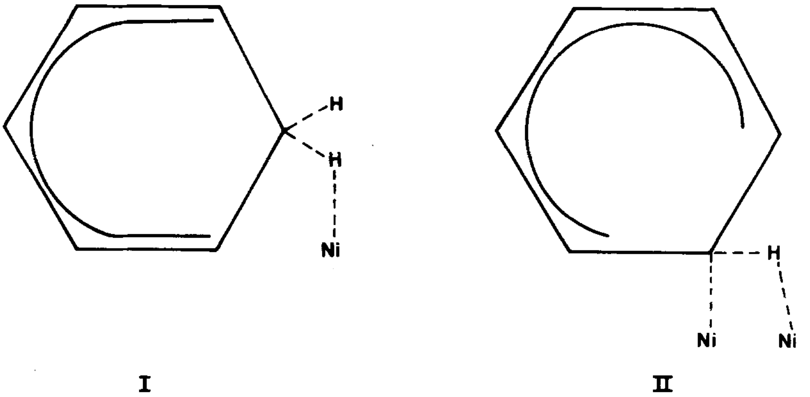

FIG. 7. Models for associative (I) and dissociative (II) π complexes of benzene on nickel.

action is only of the order of one molecule per second per surface atom?

The only possibility seems to be that the stable chemisorbed state corresponds to our picture and that a complex of type I (Fig. 7), for example, is formed but with a very short lifetime. Its formation would then be the rate-controlling step for the reaction and its concentration is so low that there is no hope of detecting its presence in the adsorbed phase.

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