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Excitation and desorption of physisorbed H$_2$ via the $^2\Sigma_u$ electron scattering resonance.

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Our high-resolution electron energy-loss measurements concern physisorbed H$_2$ and comprise differential cross sections for excitation of the internal H$_2$ modes and the H$_2$-surface bonding mode and their combinations and extend over the electron impact energy range of the classical low-energy H$_2$ $^2\Sigma_u$ resonance. Comparison with corresponding data for excitation of the internal modes of gas phase H$_2$ reveals that strong elastic electron reflectivity from the Cu(100) substrate profoundly distorts the inelastic scattering pattern for physisorbed H$_2$. We find that this influence can be corrected for and that the resulting peak cross sections agree with the H$_2$ gas phase data, in accordance with theoretical predictions for excitation of the internal H$_2$ vibration. We have used corrected cross sections for the rotational mode spectra of physisorbed H$_2$, HD and D$_2$ in a model concerning electron induced desorption via rotation-translation energy conversion. These spectra include transitions from the ground state as well as excited levels of the physisorption potential well. H$_2$ and HD can desorb from all levels while D$_2$, for energetic reason, can only desorb from the excited levels. This model gives a satisfactory account of the observed desorption cross sections and predicts characteristic velocity distributions of the desorbing molecules. The cross section data for H$_2$ and HD reveals that direct bound-free transitions also contribute to the electron induced desorption.

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I. INTRODUCTION

Physical adsorption of molecules on metal surfaces results in a weak perturbation of the molecular electron structure. The properties of the adsorbed molecules resemble closely those of the gas phase species as manifested by their internal vibrational energies which are almost identical [1]. For physisorbed H$_2$, which is of prime concern in this paper, even the rotational motion is very close to that of the free molecule [2]. However, the physisorbed molecule is attached to the substrate surface and the free translational motion in space is lost and replaced by a confined motion in the shallow physisorption potential well. The lateral motion along the surface may be essentially free [3].

High-resolution electron energy-loss spectroscopy (HREELS) has proven to be a powerful tool to study these properties of physisorbed molecules [4]. Resonance excitation of the internal molecular modes via temporary negative ion formation results, as for the gas phase species [5], in a spectacular enhancement of the excitation probability with characteristic dependencies on electron impact energy and scattering angle. The molecule-surface bonding mode is also resonance excited [6] and the adsorbed molecule may even desorb in a direct bound-free transition by this mechanism.

Physisorbed H$_2$ offers a unique situation in this context since the internal modes as well as the molecule-surface bonding mode and their various combinations can be observed. Detailed, rotationally resolved EELS spectra for gas phase H$_2$ [7], obtained over a wide energy range of the classical H$_2$ $^2\Sigma_u$ shape resonance, provide a crucial reference frame. This resonance corresponds to an electron captured for a short time ($< 10^{-15}$s) in the lowest unoccupied orbital of H$_2$. The electron capture cross section is large with concomitant large inelastic scattering probabilities which peak around 3eV electron impact energy. Excitation of the internal H$_2$ modes is due to the forces that the trapped electron induces on the nuclear coordinates and the coupling between the internal vibration and rotation results in a large cross section for excitation of the vibration-rotation mode [8]. Theoretical models have given accurate accounts of the measured inelastic electron scattering cross sections [9]. For physisorbed H$_2$, resonance excitation of the molecule-surface bonding mode is due to the attractive image force between the short-lived H$_2^-$ ion and the substrate [6]. The ion will experience an acceleration towards the surface and obtain an impulse and may as a consequence decay into an excited vibrational state of the molecule surface potential well and even desorb. We have found that the cross sections for excitation of these modes and their combinations with the internal H$_2$ modes are large.

In the gas phase, electron capture in the $^2\Sigma_u$ resonance results in dissociative electron attachment i.e. H$_2^-$ → H + H$^+$, but the probability is very small due to the short life-time of this H$_2^-$ state and the comparatively slow motion of the nuclei [5]. For H$_2$ physisorbed on a metal surface, a similar short resonance life time will for the same reason prohibit enhanced dissociation of the...
molecule. Theoretical calculations for H$_2$ physisorbed on a simple free-electron metal surface [10] shed light on this scenario. In the H$_2$ $2\Sigma_u^+$ resonance is lowered in energy due to the image charge interaction between the temporary H$_2$ ion and the metal substrate. The resonance width, and hence the resonance life time, is only weakly affected by the proximity to the metal and the probability for inelastic electron scattering is similar to that for H$_2$ gas. Cross sections for excitation of the internal vibration of physisorbed H$_2$ were calculated for a split angular space where electrons that enter from the vacuum and scatter inelastically, either return directly to vacuum and can be detected by spectroscopic means or scatter into the metal and are assumed to escape detection. Low-energy electrons may be strongly backscattered by the substrate, with drastic consequences for the inelastic electron scattering from an adsorbed layer of molecules as we show here for the H$_2$-Cu(100) system. We find that the resulting multiple scattering contributions to the observed EELS differential cross sections for excitation of the internal H$_2$ vibration and rotation modes can be accounted for by an incoherent scattering model. Correcting for these contributions reveals that the peak cross sections for excitation of physisorbed H$_2$ and gas phase H$_2$ are within experimental accuracy the same, i.e. in accordance with the calculations discussed above. This observation has interesting consequences regarding quantitative EELS measurements. Here we have used corrected EELS rotation cross sections to evaluate experimental cross sections for electron induced desorption of H$_2$ via rotation-translation energy transfer [11]. Resonance excitation of the H$_2$ rotation mode is strongly coupled to the vibrational motion of the molecule in the physisorption potential well. We find that a plausible desorption scenario includes transitions from the vibrational ground state as well as excited vibrational states, and that desorption occurs with a probability of unity.

The paper is organized in the following way. In Sec. II we describe the experimental procedure, the general features of the H$_2$-Cu(100) EELS spectrum and the measurements of the related differential EELS cross sections. Characteristic differences between gas-phase H$_2$ and physisorbed H$_2$ are briefly discussed in Sec. III A. In Sec. III B we describe the elastic electron scattering. The differential cross sections for excitation of the internal H$_2$ vibration and rotation modes via the $2\Sigma_u^+$ resonance are presented and discussed in Sec. III C-E. Resonance excitation of the H$_2$-Cu(100) bonding mode is detailed in Sec. III F and in Sec. III G we discuss electron induced desorption of H$_2$, HD and D$_2$ physisorbed on the Cu(100) surface. In Sec. IV we give some concluding remarks.

II. EXPERIMENTAL

The experiments discussed in this paper were carried out in an ultrahigh vacuum apparatus operating at a base pressure of $1 \times 10^{-11}$ Torr. The x-ray aligned (< 0.2°) Cu(100) specimen was cleaned in situ by standard methods involving argon ion bombardment and annealing. Using 4 K helium gas as a cryogen, the specimen could be cooled to a temperature around 10 K and it was heated resistively. Substrate surface properties were monitored by low energy electron diffraction (LEED) and high-resolution electron-energy-loss spectroscopy (EELS). Before hydrogen adsorption the specimen was heated to 900 K and rapidly cooled (< 3 min) to 10 K. The hydrogen adsorption was monitored by mass spectroscopy, work function measurements and EELS. The physisorbed H$_2$ monolayer has a density of $n_s = 0.70 \times 10^{15}$ molecules/cm$^2$ [12]. and the H$_2$ molecules occupy a ground state level with a binding energy of 25.5 meV in the physisorption potential well [13]. A slow rate of infrared photodesorption induced by radiation from the surrounding vacuum chamber wall at room temperature [14] was counteracted by an applied H$_2$ pressure in the low $10^{-9}$ Torr range.

The EELS spectrum in Figure 1 shows the characteristic inelastic electron scattering events from a dense monolayer of H$_2$ adsorbed on the Cu(100) surface. These
include the H$_2$-Cu(100) bonding mode, the internal H$_2$ modes and the combinations of these modes. The corresponding loss energy ranges are:

(i) 0 – 40 meV, which involves excitations of the bonding mode, like the $n = 0 \rightarrow 1$, $n = 0 \rightarrow 2$ and $n = 0 \rightarrow 3$ transitions at 9 meV, 15 meV and 20 meV and transitions to free continuum states above 25.5 meV.

(ii) 40 – 70 meV involves the H$_2$ $j = 0 \rightarrow 2$ rotation mode at 44 meV and its combinations with the $n = 0 \rightarrow 1$, and $n = 0 \rightarrow 2$ modes at 53 meV and 59 meV.

(iii) 490 – 590 meV involves the $\nu = 0 \rightarrow 1$ internal H$_2$ vibration at 511 meV and its combinations with the $n = 0 \rightarrow 1$ mode at 520 meV, the $j = 0 \rightarrow 2$ mode at 552 meV and the $j = 0 \rightarrow 2$, $n = 0 \rightarrow 1$ mode at 561 meV.

All these transitions are marked in the EELS spectrum which was obtained at an incident electron energy, $\epsilon_i = 3$ eV. The inset in Fig. 1 shows the electron scattering geometry. The angle of incidence relative to the Cu(100) surface normal is $\theta_i = 47.7^\circ$ in all measurements reported here. The scattering angle relative to the incident electron beam is $\theta_s = 91.4^\circ$. However, $\theta_s$ has been varied in the range 91.4$^\circ$ – 103.4$^\circ$ around the specular direction at 95.4$^\circ$ in search of possible dipole excited contributions to the inelastic scattering pattern [15]. Regarding the loss energy range (i) we find that the corresponding observations of the H$_2$-Au(110) bonding mode and the H$_2$ rotation mode in the confined single molecule configuration of a scanning tunneling microscope are quite remarkable [16].

Our prime objective in this work is to determine accurate differential cross sections for inelastic scattering of low-energy electrons (1 – 9 eV) from the physisorbed H$_2$ molecules and to compare our observations with corresponding data for gas phase H$_2$ [7]. For this purpose we have calibrated the EELS spectrometer [17] by measuring the incident electron beam current from the electron monochromator, $i_i$, and the transmission of the elastic current, $i_{00}$, that hits the analyzer after specular reflection from the clean Cu(100) surface. The specular electron reflectivity $R = i_{00}/i_i$, versus incident electron energy, $\epsilon_i$, is shown in Fig. 2 and is discussed in more detail in the subsection dealing with elastic electron scattering. In the present context we note that $R$ versus $\epsilon_i$ in Fig. 2 is in satisfactory agreement with the specular reflectivity obtained by our LEED instrument. The EELS analyzer electron multiplier gives the specular elastic intensity in terms of the count rate $i_{00}$ c/s and we define the analyzer transmission as $T = i_{00}/i_{00}$.

The differential cross section, $d\sigma/d\Omega$, for inelastic electron scattering is determined from the count rate, $I_{h\omega}$, for the characteristic scattering events (i) - (iii) presented above. The short range electron scattering cross section is given by [18]

$$I_{h\omega} = \frac{n_s}{R \cos \theta_i} \int \frac{d\sigma}{d\Omega} \cdot d\Omega$$  \hspace{1cm} (1)

where $\Omega_s = k \cdot \Delta \theta_s^2$ is the acceptance angle of the EELS spectrometer, which we have determined from the full width at half maximum, $\Delta \theta_s$, of the specular elastic beam. From Eq. 1 and the relations $R = i_{00}/i_i$ and $T = I_{00}/i_{00}$ we have

$$\frac{d\sigma}{d\Omega} = \frac{I_{h\omega}}{T} \cdot \frac{1}{i_i} \cdot \frac{\cos \theta_i}{n_s} \cdot \frac{1}{k \cdot \Delta \theta_s^2}$$  \hspace{1cm} (2)

The angular width $\Delta \theta_s$ depends on the electron energy $\epsilon_i$ and varies from 2.3$^\circ$ – 1$^\circ$ for $\epsilon_i$ in the range 1 – 9 eV. Our spectrometer calibration shows that the product $T \cdot \Delta \theta_s^2$ is approximately constant over this $\epsilon_i$ range, which means that low $T$ values at low $\epsilon_i$ are characteristic features of the spectrometer, related to the angular dependence of the image transfer in the electron optical system [17].

III. RESULTS AND DISCUSSION

A. General

In this section we will present and discuss measured cross sections for scattering of low energy electrons from physisorbed H$_2$ in relation to detailed data for gas phase H$_2$ obtained by Linder and Schmidt [7]. The latter data include differential cross sections, $d\sigma/d\Omega$, for elastic scattering and rotational, vibrational and combined vibrational-rotational inelastic scattering measured in a cross-beam experiment with an incident electron beam, an H$_2$ gas beam and an electron analyzer and concern electron beam energies in the range 1.5-10 eV and electron scattering angles ranging from 20$^\circ$ to 120$^\circ$ relative to the direction of the incident electron beam. Our data for physisorbed H$_2$ were obtained for incident electron beam energies of 1 – 9 eV and final scattering angles around 90$^\circ$.

Firstly, we note some important aspects regarding the two H$_2$ systems. The physisorbed molecule is known to be weakly perturbed by the interaction with a noble metal surface like Cu(100) [1, 2] and its rotational and vibrational motion differs marginally from that of a free molecule. However, the physisorbed H$_2$ molecule is embedded in the tails of the spilling out metal electrons, which may screen long range electron interaction related to polarization of the molecule. The short-lived H$_2$ $2\Sigma_u^+$ resonance, which is of immediate relevance in the electron energy range of concern here, will be influenced by the proximity of this temporary negative ion to the metal surface [10]. Furthermore, we note that:

(i) The density of a full monolayer of H$_2$ is around $0.7 \times 10^{15}$ molecules/cm$^2$ with a mean separation of 3.6 Å while the molecules are far apart in the gas phase experiment.

(ii) Gas phase H$_2$ has the relevant thermal population of para- and ortho-molecules (i.e. even and odd rotational quantum states). Physisorbed H$_2$ occupies predominantly the j=0 rotational ground state due to ortho-para conversion at active Cu surface sites [19].
B. Elastic scattering

We noted above in remark (iv), that the elastic scattering from the clean Cu(100) surface is dominated by an energy gap in the substrate electron band structure. Figure 2a shows the specular elastic electron reflectivity versus incident electron energy $\epsilon_i$ from the clean Cu(100) surface and from this surface covered with a full monolayer of physisorbed H$_2$. The reflectivity from the Cu(100) surface is large, $R \sim 0.65$ at $\epsilon_i = 1$ eV, and falls off smoothly with increasing electron energy to $R \sim 0.05$ at $\epsilon_i = 8$ eV. The corresponding data for the H$_2$-Cu(100) system in Fig. 2a also shows large values of the reflectivity but with pronounced structure with peaks and valleys caused by interference between the elastic scattering from the H$_2$ overlayer and the substrate and a strong energy and angular dependence of the elastic scattering from the H$_2$ molecules.

Figure 2b shows the differential cross section data $\frac{d\sigma}{dt}$, from Ref. [7] for elastic scattering from gas phase H$_2$ at 20° and 90° scattering angles. We note that forward scattering ($20^\circ$) is weak at 1 eV and increases drastically in the range 1.5 - 4.5 eV while 90° scattering is stronger at 1 eV and decreases slowly with increasing electron energy. This elastic scattering pattern of H$_2$ will influence not only the elastic but also the inelastic electron scattering from the H$_2$ - Cu(100) system. We also note that the cross section for elastic scattering from H$_2$ is large compared to those for inelastic scattering [7].

C. The H$_2$ $\nu = 0 \to 1$ vibration

The differential cross sections for excitation of the H$_2$ vibration and rotation via the $2\Sigma_u$ resonance depend on the initial H$_2$ rotation state. Theoretical predictions [21] give the relative magnitude $\frac{d\sigma}{dt} \propto 6 \cdot \cos^2 \theta_s$ for the rotational excitations $j = 0 \to 2$ and $j = 1 \to 3$ respectively. This relation also holds for the $\nu = 0 \to 1$, $j = 0 \to 2$ and $\nu = 0 \to 1$, $j = 1 \to 3$ combination modes [8]. The angular dependence of the cross section for the $\nu = 0 \to 1$ vibration with $j$ unchanged is characterized by p-wave scattering with a deep minimum at the scattering angle $\theta_s = 90^\circ$. From the resonance model in Ref. [8] we have for $\nu = 0 \to 1$, $j = 0 \to 0$; $\frac{d\sigma}{dt} \propto 6.25 \cdot \cos^2 \theta_s$ and for $\nu = 0 \to 1$, $j = 1 \to 1$; $\frac{d\sigma}{dt} \propto (1.5 + 6.75 \cdot \cos^2 \theta_s)$. The former case corresponds to H$_2$-Cu(100) with a $j = 0$ adsorption state as noted above, while the latter is a reasonable approximation for H$_2$ gas with a population of $j = 1$ around 70%. Hence, at $\theta_s = 90^\circ$ we would expect a vanishing $\nu = 0 \to 1$ cross section for physisorbed H$_2$ and a minimum but finite cross section for H$_2$ gas. The experimental data discussed below show a strikingly different pattern.

Figures 3a and 4a show the electron energy dependence
shown in Figs. 3b and 4b. The energy dependence of these observations can be found from the angular dependence, discussed above, suggest the opposite relation. The corresponding values, $\frac{d\sigma^\nu}{d\Omega}$, for the $\nu = 0 \rightarrow 1$, $j = 0 \rightarrow 2$ combination mode in Fig. 4b differ by only a factor of 2. A qualitative understanding of these observations can be found from the angular dependence of the $H_2$ gas phase cross sections which are shown in Figs. 3b and 4b. The energy dependence of

$$\frac{d\sigma^\nu}{d\Omega}$$ in Fig. 3b reveals a strong variation with scattering angle related to the $^2\Sigma_u^+$ resonance [8]. The peak cross section at $20^\circ$ is almost a factor of 10 larger than at $90^\circ$ while this ratio for $\frac{d\sigma^\nu}{d\Omega}$ in Fig. 4b is only $\sim 1.3$. We note that the data in Ref. [7] indicate that the $20^\circ$ data are reasonable approximations to the values expected at $0^\circ$ scattering angle. The crosses at 3.5 eV denote $0^\circ$ values which we have obtained by extrapolation of the data in Ref. [7].

These observations suggest a simple scenario where strong inelastic scattering in the forward direction from the physisorbed $H_2$ molecules contributes efficiently to the cross section $\frac{d\sigma^\nu}{d\Omega}$ in Fig. 3a. The large values of the specular elastic reflectivity from the Cu(100) substrate discussed above, provides an obvious mechanism. The specific outcome of such a process will depend on whether the inelastic-elastic scattering pattern is dominated by coherent or incoherent scattering channels. The specular elastic reflectivity from $H_2$-Cu(100), shown in Fig. 2a, is dominated by strong interference phenomena, a consequence of coherent scattering. Regarding the inelastic electron scattering a dynamical scattering calculation is required in order to understand the role of coherent versus incoherent contributions to the observed cross

FIG. 3. Differential EELS cross sections, $\frac{d\sigma^\nu}{d\Omega}$, versus incident electron energy for excitation of the $H_2$ $\nu = 0 \rightarrow 1$ vibration with rotational state, $j$, unchanged. (a) For $H_2$-Cu(100), $j = 0$ and $\theta_s = 91.4^\circ$ and $H_2$ gas, thermal $j$ population [7]. $\theta_s = 90^\circ$. (b) For $H_2$ gas, thermal $j$ population [7], $\theta_s = 20^\circ$ and $90^\circ$, the cross ($\times$) at $\epsilon_i = 3.5$ eV denotes the extrapolated value of $\theta_s = 0^\circ$.

FIG. 4. Differential EELS cross sections, $\frac{d\sigma^\nu}{d\Omega}$, versus incident electron energy for excitation of the $H_2$ $\nu = 0 \rightarrow 1$, $j = 0 \rightarrow 2$ combination mode. (a) $H_2$-Cu(100) at $\theta_s = 91.4^\circ$ and $H_2$ gas [7] at $\theta_s = 90^\circ$. (b) $H_2$ gas at $\theta_s = 20^\circ$ and $90^\circ$, the cross ($\times$), at $\epsilon_i = 3.5$ eV denotes the extrapolated value at $\theta_s = 0^\circ$ [7].
The ratio of channels. Hence from Fig. 2b we obtain elastic reflection (90\degree) scattering in the forward direction (0\degree) and we have, as noted above, converted the j = 1 \to 3 data in Ref. [7] to j = 0 \to 2 values using the relation for \( \sigma^d_2 \) at 3.5 eV incident electrons and 90\degree and 0\degree scattering angles which enter the scattering channels a), b), c) in Fig. 5 and contribute to the corresponding EELS cross sections \( \frac{d\sigma^i}{d\Omega} \), \( \frac{d\sigma^e}{d\Omega} \) for \( \text{H}_2\text{-Cu}(100) \). R and T are the elastic specular reflectivity of the substrate and the elastic transmission through the \( \text{H}_2 \) layer respectively.

<table>
<thead>
<tr>
<th>( \theta_s )</th>
<th>( \frac{d\sigma^i}{d\Omega} ) (10\textsuperscript{-18} cm\textsuperscript{2}/sr)</th>
<th>( \frac{d\sigma^e}{d\Omega} ) (10\textsuperscript{-17} cm\textsuperscript{2}/sr)</th>
<th>R T</th>
<th>( \frac{d\sigma^i}{d\Omega} ) (10\textsuperscript{-18} cm\textsuperscript{2}/sr)</th>
<th>( \frac{d\sigma^e}{d\Omega} ) (10\textsuperscript{-17} cm\textsuperscript{2}/sr)</th>
</tr>
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<tbody>
<tr>
<td>a) 90\degree</td>
<td>0.8</td>
<td>1.7</td>
<td>1.4</td>
<td>-</td>
<td>1.7</td>
</tr>
<tr>
<td>b) ( \sim 0\degree )</td>
<td>7.8</td>
<td>2.2</td>
<td>1.9</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>c) ( \sim 0\degree )</td>
<td>7.8</td>
<td>2.2</td>
<td>1.9</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>( \Sigma(a</td>
<td>b</td>
<td>c) )</td>
<td>5.7</td>
<td>3.4</td>
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</tr>
</tbody>
</table>

The estimated contributions listed in Table I clearly demonstrate the importance of inelastic scattering in the forward direction. The direct channel a) at 90\degree gives no contribution to the \( j = 1 \) initial state of physisorbed \( \text{H}_2 \). The channels b) and c) give substantial contributions resulting in an estimated total value of \( \frac{d\sigma^i}{d\Omega} \) of 4.4 \times 10\textsuperscript{-18} cm\textsuperscript{2}/sr which is about 80\% of the measured value 5.7 \times 10\textsuperscript{-18} cm\textsuperscript{2}/sr for the \( \text{H}_2\text{-Cu}(100) \) system. Regarding the \( \nu = 0 \to 1, j = 0 \to 2 \) combination mode, direct 90\degree inelastic scattering is the important channel. The extra contributions from b) and c) increase the summed cross section to 2.9 \times 10\textsuperscript{-18} cm\textsuperscript{2}/sr which is about 85\% of the value 3.4 \times 10\textsuperscript{-18} cm\textsuperscript{2}/sr observed for \( \text{H}_2\text{-Cu}(100) \).

We believe that our simple incoherent scattering model captures the essential physics including strong inelastic e-\( \text{H}_2 \) scattering in the forward direction and strong elastic electron reflection from the Cu(100) substrate.

### D. The \( \text{H}_2 \) j = 0 \to 2 rotation

Figure 6a shows the electron energy dependence of the cross section for the \( j = 0 \to 2 \) rotational excitation of physisorbed \( \text{H}_2 \) at 91.4\degree scattering angle. The corresponding \( \text{H}_2 \) gas phase data were measured at 90\degree [7] and we have, as noted above, converted the \( j = 1 \to 3 \) data in Ref. [7] to \( j = 0 \to 2 \) values using the rela-
is clearly the dominating channel, but the contributions from \(b\), and \(c\), increase the estimated peak cross section to \(2.4 \cdot 10^{-17} \text{cm}^2/\text{sr}\) which is about 80\% of the observed value \(3.0 \cdot 10^{-17} \text{cm}^2/\text{sr}\) for \(\text{H}_2\) physisorbed on the \(\text{Cu}(100)\) surface. This result is consistent with our observations for the \(\nu = 0 \rightarrow 1, j = 0 \rightarrow 2\) vibration-rotation mode, listed in Table I and discussed above.

Summarizing our observations regarding the peak cross sections, at 3.5 eV, for excitation of the \(j = 0 \rightarrow 2\) mode and the \(\nu = 0 \rightarrow 1, j = 0 \rightarrow 2\) combination mode, we find that the data for gas phase \(\text{H}_2\) and \(\text{H}_2\) physisorbed on \(\text{Cu}(100)\) yield quantitatively similar results, provided that the contributions from direct and indirect inelastic scattering are included in the description of \(e-\text{H}_2\) scattering for the \(\text{H}_2-\text{Cu}(100)\) system.

E. The \(^2\Sigma_u^+\) resonance

In the preceding sections we discussed the EELS differential cross sections for resonance excitation of the internal modes of gasphase and physisorbed \(\text{H}_2\). We found that the differential cross sections for both \(\text{H}_2\) states show an electron energy dependence with a characteristic maximum around \(3-4\) eV, due to the \(^2\Sigma_u^+\) resonance. The magnitude of the peak cross sections differs significantly between the two states due to the influence of multiple electron scattering processes in the case of physisorbed \(\text{H}_2\). This phenomenon is spectacular for the \(\text{H}_2\) \(\nu = 0 \rightarrow 1\) internal vibration as discussed in III C. For physisorbed \(\text{H}_2\) we observe a narrow peak at 4 eV with a full width at half maximum around 2 eV. The maximum cross section is about an order of magnitude larger than for \(\text{H}_2\) gas which shows a broad, \(\sim 7\) eV, resonance peak at 3 eV.

Theoretical calculations for \(\text{H}_2\) gas and \(\text{H}_2\) physisorbed on a metal surface [10] reveal a simpler scenario. The calculated cross sections, (Fig. 4 in Ref. [10]), show similar electron energy dependencies for the \(\nu = 0 \rightarrow 1\) vibrational excitation, with a maximum around 3 eV, a width around 6 eV and similar peak cross sections. We believe that the prime difference between these results and our observations derives from the electron scattering properties of the metal surface. The theoretical calculations split the angular space of inelastic electron scattering in two parts, electrons that scatter directly into vacuum and can be detected by spectroscopy and electrons that enter the metal substrate and escape such detection. However, this picture changes if the electrons are efficiently backscattered by the metal substrate, which is the case for the \(\text{Cu}(100)\) surface as discussed above. This effect may be dramatic in EELS measurements due to the angular dependence of the scattering cross section. Resonance excitation of the \(\text{H}_2\) \(\nu = 0 \rightarrow 1\) mode via \(^2\Sigma_u^+\) is dominated by \(p\)-wave scattering with a deep minimum at \(90^\circ\) scattering angle and an intense forward scattering lobe. The consequence of this scattering pattern and the strong electron reflectivity of the \(\text{Cu}(100)\) surface is an intense

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**FIG. 6.** Differential EELS cross sections, \(d\sigma/d\Omega\), versus incident electron energy for excitation of the \(\text{H}_2\) \(j = 0 \rightarrow 2\) rotation. (a) \(\text{H}_2-\text{Cu}(100)\) at \(\theta_2 = 91.4^\circ\) and \(\text{H}_2\) gas [7] at \(\theta = 90^\circ\). (b) \(\text{H}_2\) gas at \(\theta_2 = 20^\circ\) and \(90^\circ\), the cross \((\times)\) at \(e_t = 3.5\) eV denotes the extrapolated value at \(\theta = 0^\circ\) [7].
The H$_2$-Cu(100) data shown in Fig. 3 represent the other extreme where the observed $\nu = 0 \to 1$ cross section correspond exclusively to multiple scattering events and the observed electron energy dependence is augmented by different scattering processes as discussed in relation to fig. 5. The resonance peak is as a consequence narrow and shifted to a higher energy which is incompatible with the expected image charge shift. The influence of multiple scattering is less pronounced for other inelastic channels like the H$_2$-Cu(100) $j = 0 \to 2$ rotation excitation shown in Fig. 6. In this case the resonance maximum is observed $\sim 3.5$ eV and is shifted to lower energy by $\sim 1$ eV as compared to the data for H$_2$ gas. This downshift may be related to the image charge interaction, but the quick fall off with increasing electron energy is partly due to the decreasing elastic reflectivity of the Cu(100) substrate. Hence, a quantitative analysis of how the H$_2$ $^2\Sigma_u$ resonance is influenced by the metal substrate in our case clearly requires a separation of the scattering processes involved.

### F. The H$_2$-Cu(100) vibration

The vibrational motion of H$_2$ in the physisorption potential well is a characteristic feature of the H$_2$-Cu(100) system. The fundamental $n = 0 \to 1$ transition is observed at 9 meV in the EELS spectrum in Fig. 1 and is also observed in the $j = 0 \to 2$, $n = 0 \to 1$ and the $\nu = 0 \to 1$, $n = 0 \to 1$ transition is observed at 9 meV in the EELS spectrum in Fig. 1 and is also observed in the $j = 0 \to 2$, $n = 0 \to 1$ and the $\nu = 0 \to 1$, $j = 0 \to 2$, $n = 0 \to 1$ combination modes at 53, 520 and 561 meV respectively. The corresponding differential scattering cross sections, which are shown in Fig. 7, reveal a dependence on electron impact energy with an apparent minimum in the center of the resonance peak. This feature is not observed for the pure internal H$_2$ mode (see e.g. Figs. 4a and 6a) but seem to be related to excitation of the H$_2$-Cu(100) bonding mode. We have not found any obvious mechanism that would result in such a structure and conclude that more detailed experimental observations including different scattering angles may provide key information in this context.

Regarding resonance enhanced excitation of the H$_2$-Cu(100) bonding mode we will consider predictions from a theoretical model [6, 23] which involves an adsorbed molecule and its temporary negative ion interacting with a metal surface. During this short-lived electron state the ion will experience an acceleration towards the metal surface and obtain an impulse due to the attractive image force and may as a consequence decay into an excited level, $n$, of the physisorption potential well. The cross section for such an event can be expressed as a product of the cross section for electron capture in the resonance and a factor, $P_n$, representing the probability to decay into level $n$. Explicit expressions for $P_n$ have been derived for a truncated harmonic oscillator. From Ref. [23] we have

![Graph](image-url)
where $\epsilon_0$ and $\Gamma$ are the resonance energy and width respectively and $\hbar \omega_0$ is the oscillator energy. The quantity $\lambda$ is given by

$$\lambda = \frac{F}{(2m \hbar \omega_0^3)^{1/2}}$$

(4)

where $m$ is the molecular mass and $F = e^2/4\pi$ is the image force acting on the molecular ion located at distance $z$ above the metal surface. The energy spread of the incident electrons beam is small ($\sim 4$ meV) compared to the resonance width ($\sim 3$ eV) and integration of Eq. 3 with respect to the variable $\epsilon$ gives

$$P_n/P_0 \simeq P_n(\epsilon)/P_0(\epsilon)$$

(5)

Elastic scattering is the dominant channel and we assume that $P_0 \simeq 1$. We use the following input parameters for H$_2$ physisorbed on Cu(100): The $n = 0 \rightarrow 1$ transition gives $\hbar \omega_0 = 8.9$ meV, the equilibrium adsorbate position is $z = (2.41 - 0.77) \ \AA$ outside the Cu(100) image reference plane [24] and we use a resonance width of 3.2 eV from the $j = 0 \rightarrow 2$ energy dependence in Fig. 6a. The calculated transition probability at resonance maximum is $P_1 = 8 \cdot 10^{-2}$. Relating $P_0$ to the $j$-H$_2$ gas phase elastic scattering cross section $14 \cdot 10^{-16}$ cm$^2$ at resonance maximum [7] we estimate a total cross section $8 \cdot 10^{-2} \cdot 1.4 \cdot 10^{-16}$ cm$^2$ = $1.12 \cdot 10^{-16}$ cm$^2$ for the $n = 0 \rightarrow 1$ transition. We have no apriori knowledge about the angular distribution of this inelastic electron scattering process, and simply assume that the distribution is isotropic. Hence we get $\frac{d\sigma}{d\Omega} = \frac{1}{4\pi} \cdot 1.12 \cdot 10^{-16} = 0.89 \cdot 10^{-17}$ cm$^2$/sr.

The measured electron energy dependence of $\frac{d\sigma}{d\Omega}$ is shown in Fig. 7a. From the $j = 0 \rightarrow 2$ data in Fig. 6a and the $\nu = 0 \rightarrow 1$, $j = 0 \rightarrow 2$ data in Fig. 4a we judge that the $^2\Sigma_u$ resonance energy is around 3.5 eV. From Fig. 7a we find that the average $n = 0 \rightarrow 1$ peak cross section in the energy range $2 - 5$ eV is around $2.1 \cdot 10^{-17}$ cm$^2$/sr. The calculated cross section is $0.89 \cdot 10^{-17}$ cm$^2$/sr. This direct contribution to the $n = 0 \rightarrow 1$ cross section correspond to channel a) in Fig. 5. With use of the values for $R$ and $T$ in Table I we find that contributions from channel b) and c) in Fig. 5 results in an increase of the calculated cross section to $= 1.4 \cdot 10^{-17}$ cm$^2$/sr, i.e. about 70% of the measured cross section, which suggests that the theoretical model provides a reasonable quantitative description of this excitation mechanism.

G. Electron-induced desorption of H$_2$

We have previously reported experimental observations of electron-induced desorption of H$_2$, HD, and D$_2$ physisorbed on the Cu(100) surface [11, 25] and the present work is of specific interest in this context. Here we summarize our earlier arguments and discuss their implications in perspective of the cross section measurements presented in the previous paragraphs. The desorption cross sections, $\sigma_d$, are shown in Fig. 8a, and reveal that the desorption proceeds via the $^2\Sigma_u$ electron scattering resonance. These data also provide specific information concerning the resonance excited channels responsible for the desorption process. The cross sections are large and peak around 3 eV with similar values for H$_2$ and HD, which are about a factor of 3 larger than for D$_2$. The electron energy dependence of $\sigma_d$ is similar for H$_2$ and HD but is different for D$_2$. The cross sections for H$_2$ desorption are consistently somewhat larger than those for HD.

In Ref. [11] we argued that these observations show that the desorption process involves two different channels. One channel is characteristic for H$_2$ and HD and is due to resonance excitation of the $j = 0 \rightarrow 2$ rotation mode and subsequent desorption via rotation-translation conversion. Fig. 9a shows the EELS cross sections, $\sigma_d$, for excitation of the $j = 0 \rightarrow 2$ mode of H$_2$, HD and
The desorption data in Fig. 8a show that $\sigma_d$ for $D_2$ is larger than for $H_2$ and the EELS data in Fig. 8b provide no obvious explanation of this observation. In Ref. [11] we proposed that this difference is due to resonance excitation of the molecule-surface bonding mode to free continuum states, a desorption mechanism that depends on the molecular mass as discussed in Sec. III F. Such transitions contribute, for example to the slowly decreasing intensity, above the $H_2$ desorption threshold at 25.5 meV, in the EELS spectrum in Fig. 1. The corresponding EELS cross section, $\frac{d\sigma}{d\Omega}$, was obtained by integrating the EELS intensity, using a simple fit. These data are shown in Fig. 7a and peak around 3 eV, as expected for the $H_2$ $^2\Sigma_u^+$ resonance. Assuming an isotropic angular
distribution we find a peak cross section \( \sigma_p = 1.13 \times 10^{-16} \text{ cm}^2 \). Correcting for the multiple scattering contributions, as discussed above, and assuming that the probability for desorption of \( \text{H}_2 \) from the continuum state is 1 we arrive at an estimated desorption cross section \( \sigma_d^c = 0.6 \cdot \sigma_p \cdot 1 = 0.68 \times 10^{-16} \text{ cm}^2 \).

For HD and D\(_2\), the energy range above the desorption threshold is obscured by the \( j = 0 \rightarrow 2 \) rotation transition and its combinations with the \( \text{H}_2\)-Cu(100) bonding mode and the EELS cross sections, \( \sigma_d^c \), cannot be determined for these isotopes. However, if we assume that the difference between the desorption cross sections for \( \text{H}_2 \) and HD in Fig. 8a is due to desorption via direct transitions to free continuum states, we can estimate \( \sigma_d^c \) for HD from the value for \( \text{H}_2 \). The difference is 0.22 \( \times 10^{-16} \text{ cm}^2 \) at 2.8 eV and \( \sigma_d^c = 0.68 \times 10^{-16} \text{ cm}^2 \) for \( \text{H}_2 \) at 3 eV which gives \( \sigma_d^c = 0.46 \times 10^{-16} \text{ cm}^2 \) for HD. Relating \( \sigma_d^c \) to the molecular mass we find a mass dependence \( \sigma_d^c \propto m^{-0.97} \). \( \text{H}_2 \) and HD data in the energy range 1 – 6.5 eV give \( \sigma_d^c \propto m^{-0.8} - m^{-1.1} \) with a mean around \( m^{-1} \). For \( \text{D}_2 \) we then obtain \( \sigma_d^c = \sigma_d^c(\text{H}_2) \cdot \frac{1}{2} = 0.34 \times 10^{-16} \text{ cm}^2 \). This estimate of the desorption cross section for \( \text{D}_2 \) via direct transitions to free continuum states is almost a factor of 3 smaller than the measured \( \sigma_d \) for \( \text{D}_2 \) at 2.8 eV in Fig. 8a. Hence we find that our present understanding of the measured EELS differential cross sections does not support a model where \( \text{D}_2 \) is assumed to desorb exclusively via such transitions.

Summarizing our discussion above, we find that electron induced desorption via the \( ^2\Sigma_u \) electron scattering resonance may proceed by two or three resonance excited channels. Both models support a picture where rotation-translational conversion is the prominent desorption channel for \( \text{H}_2 \) and HD and that direct transitions to free continuum states contribute to desorption of \( \text{H}_2 \), HD and \( \text{D}_2 \). In the first model [11] \( \text{D}_2 \) is assumed to desorb exclusively by the latter mechanism while our present analysis suggests that desorption of \( \text{D}_2 \) also occurs via rotation-translational conversion from the excited vibrational states of the molecule-surface potential well. The measured differential EELS cross sections do provide crucial spectroscopic information about the plausible desorption channels. However, a translation of our EELS data to desorption cross sections requires specific assumptions which makes it difficult to discriminate between the two models using mere EELS cross sections. Theoretical calculations may resolve the problem, e.g. by determining the probability for \( \text{D}_2 \) to desorb via rotation-translational conversion from the excited vibrational levels. From experimental point of view, an elegant way is to identify the signatures of the desorption channels by measuring the velocity distribution of the desorbing molecules. Desorption via transitions to free continuum states will result in a smooth velocity distribution while rotation-translational conversion will show up as sharp peaks at distinct velocities which depend on whether the molecules desorb from the ground state level or from excited levels of the molecule-surface potential well.

IV. CONCLUDING REMARKS

The high-resolution inelastic electron scattering spectrum from a monolayer of \( \text{H}_2 \) physisorbed on a cold Cu(100) surface shows the characteristic \( \text{H}_2\)-Cu(100) bonding mode, the internal \( \text{H}_2 \) rotation and vibration modes and the various combinations of these modes. Excitation via the \( ^2\Sigma_u \) resonance results in large differential cross sections for all the modes with a characteristic maximum around 3-4 eV electron impact energy. Excitation of the internal \( \text{H}_2 \) modes depends on the initial \( \text{H}_2 \) rotation state. \( \text{H}_2 \) physisorbed on a Cu(100) surface populates, due to ortho-para conversion at surface defects, the \( j = 0 \) rotation state and the cross section for excitation of the \( \nu = 0 \rightarrow 1 \) \( \text{H}_2 \) vibration is then expected to be 0 at 90° scattering angle. This characteristic gas phase signature is not observed for \( \text{H}_2 \) on Cu(100). The strong elastic electron reflectivity from the Cu(100) surface adds multiple scattering contributions to the observed spectrum. This effect is particularly pronounced for the \( \nu = 0 \rightarrow 1 \) \( \text{H}_2 \) vibration because of the anisotropic angular distribution. The dominant inelastic forward scattering is efficiently reflected from the substrate resulting in an intense vibrational EELS peak at 90° scattering angle. The rotation and rotation-vibration combination modes have rather isotropic angular distributions in the gas phase and the multiple scattering contributions for physisorbed \( \text{H}_2 \) are correspondingly weaker.

We have presented a scenario where the multiple scattering can be corrected for by an incoherent scattering model and found that the peak cross sections for excitation of the internal modes of physisorbed \( \text{H}_2 \) agree with the gas phase data. This observation is consistent with previous theoretical calculations for \( \text{H}_2 \) physisorbed on a free-electron metal surface. These show that the \( \text{H}_2 \ ^2\Sigma_u \) resonance is weakly perturbed by the proximity of the molecule to the metal surface and that the probability for excitation of the internal \( \text{H}_2 \) vibration is the same as for \( \text{H}_2 \) gas. The calculated resonance energy was found to be shifted to a lower electron impact energy by about 0.5 eV due to the \( \text{H}_2 \) image charge interaction at the metal surface. The differential cross sections for \( \text{H}_2 \) gas and \( \text{H}_2 \) physisorbed on Cu(100) show distinct resonance peaks around 3 – 4 eV electron energy. However, we note that a separation of direct and indirect scattering processes is required in order to establish the influence of the Cu(100) substrate on the \( ^2\Sigma_u \) resonance energy.

Our EELS measurements reveal that the \( \text{H}_2\)-Cu(100) bonding mode is excited via the \( ^2\Sigma_u \) resonance. The observed differential cross section of the fundamental transition is large, in fact similar to the value of the \( \text{H}_2 \) rotation mode. The bonding mode is excited via the attractive image force between the temporary \( \text{H}_2^+ \) ion and the metal substrate, and the cross section for this transition can be evaluated from an harmonic oscillator model. Including corrections for multiple scattering, we find that the calculated peak cross section agrees remarkably well with the experimental observation. The EELS spectrum also ex-
helic transitions to higher excited states of the bonding mode, in fact even to the continuum states and concomitantly desorption of the physisorbed molecule. This process contributes to electron-induced desorption via the $^2\Sigma_u$ resonance.

The EELS spectra include resonance excited rotation transitions from the ground state as well excited vibrational states of the molecule-surface potential well. H$_2$ and HD can desorb by rotation-translation conversion from all these states. D$_2$ can, for energetic reasons, only desorb via conversion from the excited states. The EELS cross sections, corrected for multiple scattering, support a picture where rotation-translation energy conversion is the prominent desorption mechanism. We have estimated the cross section for desorption of D$_2$ via direct transitions to free continuum states and found that this process alone can not account for the observed desorption cross section. The scenario we have discussed predicts characteristic velocity distributions of the desorbing molecules reflecting the specific desorption channels.

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[1] The internal vibrational energies of physisorbed homonuclear molecules like H$_2$, N$_2$, and O$_2$ are shifted to lower energies by $\sim 1\%$ of the gas phase value, e.g. H$_2$: 515.5 meV gas phase, 511.3 meV on Cu(100) (see this work) N$_2$: 2331 cm$^{-1}$ gas-phase, 2324 cm$^{-1}$ on Pt(111)(1 $\times$ 1)H and O$_2$: 1556 cm$^{-1}$ gas phase 1548 cm$^{-1}$ on Pt(111)(1 $\times$ 1)H (see K. Gustafsson and S. Andersson, J. Chem. Phys. 125, 044717 (2006)).


[3] The H$_2$ physisorption potential is only weakly corrugated on relatively close packed metal surfaces.


[15] Ti. H$_2$-Cu(100) bonding mode is dipole active. The EELS intensity is large and peak in a narrow angular range around the specular direction (see Ref. 24). The background in the range 500-590 meV in Fig. 1b is due to dipole excited electron-hole pair transitions (see S. Andersson and B.N.J. Persson, Phys. Rev. Lett. 50, 2028 (1983)).


[22] H$_2$ adsorption on a Cu(111) surface kept at 5K may form a dense hexagonal ordered overlayer as observed by scanning tunneling microscopy. The H$_2$-H$_2$ separation corresponds to a surface density of 0.8$\cdot$10$^{15}$ H$_2$/cm$^2$, see J. A. Gupta, C. P. Lutz, A. J. Heinrich, and D. M. Eigler, Phys. Rev B 71, 115416 (2005).


[26] The $j = 0 \rightarrow 2$ rotation energies are 44, 33 and 22 meV for H$_2$, HD and D$_2$ respectively and exceed the desorption thresholds at 25.5 and 26.2 meV for H$_2$ and HD but not the threshold at 27.1 meV for D$_2$.

[27] We note that the maximum phonon energy of Cu is 30 meV and, for D$_2$ the excited vibrational states as well as the rotational state may decay via one-phonon emission. For H$_2$ and HD the rotation energies exceed the one phonon energy range and the probability for decay via two-phonon emission is small.
