Surface Chemistry

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Structural Identification of Conjugated Molecules on Metal Surfaces by Means of Soft Vibrations**

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Identification of molecular structures in nature remains a tremendous challenge. In heterogeneous catalysis, single-molecule vibrational spectroscopy and microscopy have progressively led to a better understanding of surface chemistry at the atomic level.[1] Inelastic electron tunneling spectroscopy and scanned energy photoelectron diffraction have exhibited great capabilities to characterize NO and CO

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adsorption and dehydrogenation products of alkenes and aromatic molecules.[2–4] However, for these latter compounds, the analysis of the spectra is rendered difficult by the large number of possibilities. In this case, theoretical simulations have recently opened exciting perspectives.[5]

Powerful techniques such as high-resolution electron energy loss spectroscopy (HREELS) and synchrotron far-infrared reflection absorption spectroscopy (IRAS) have provided complementary measurements of CO and NO vibrations on various metal surfaces.[6,7] The adsorption modes were essentially elucidated on the basis of the analogy of the high frequency modes with those of organometallic compounds. Although the analysis of low-frequency molecule–metal bands has also been achieved and recently corroborated by theory,[8,9] the assignment is rarely simple, and the customary analogy with organometallic compounds has been questioned several times.[10,11] Moreover, interpretation of the spectra becomes particularly tough for multifunctional molecules.

The identification of the adsorption structures of conjugated molecules on metal surfaces is a probative example for which IRAS investigations have provided limited conclusions.[12–14] Competitive flat adsorption forms were suggested from a similar analogy without clearly answering the question of molecular coordination to the surface with typical π or di-σ structures.[12,13] A recently proposed promising route compared experimental and theoretical HREELS results for acrolein on Pt(111).[15] However, additional references for the low-frequency modes are missing so far for identifying unambiguously the adsorption structures of such complex multifunctional molecules.

In this work soft molecule–metal vibrations were unveiled by a systematic density functional theory (DFT) study. To investigate a significant number of adsorption structures, four conjugated molecules and six metal surfaces were selected (see Figure 1). The relationships between adsorption structure and strength, molecular conjugation, and soft molecule–metal vibrations are examined hereinafter.

The edges of supported metallic particles, which are relevant to catalysis, were modeled by Au, Ag, Cu, Pt, Pd, and Ni(110)-(1 × 2) missing-row surfaces with slabs of six metal layers in thickness. All the calculations are performed with VASP under accurate conditions (see Supporting Information for details). The four unsaturated molecules are defined in Figure 2 a: a carboxylic acid (carboxy), an ester (acetoxy), an

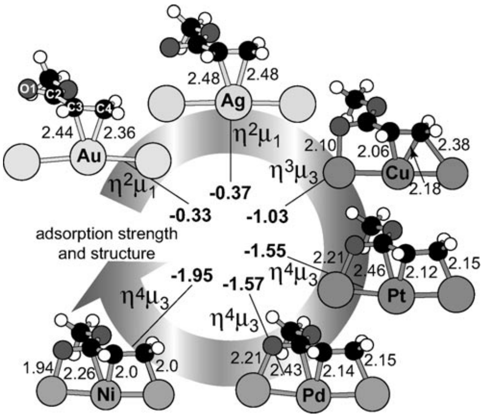

Figure 1. Mean adsorption strength [eV] and stable adsorption structures (distances in Å) of the multifunctional molecules on the ridge of the (110)-(1 × 2) metal surfaces. The *s-trans* ester (acetoxy) compound is chosen here for illustration.

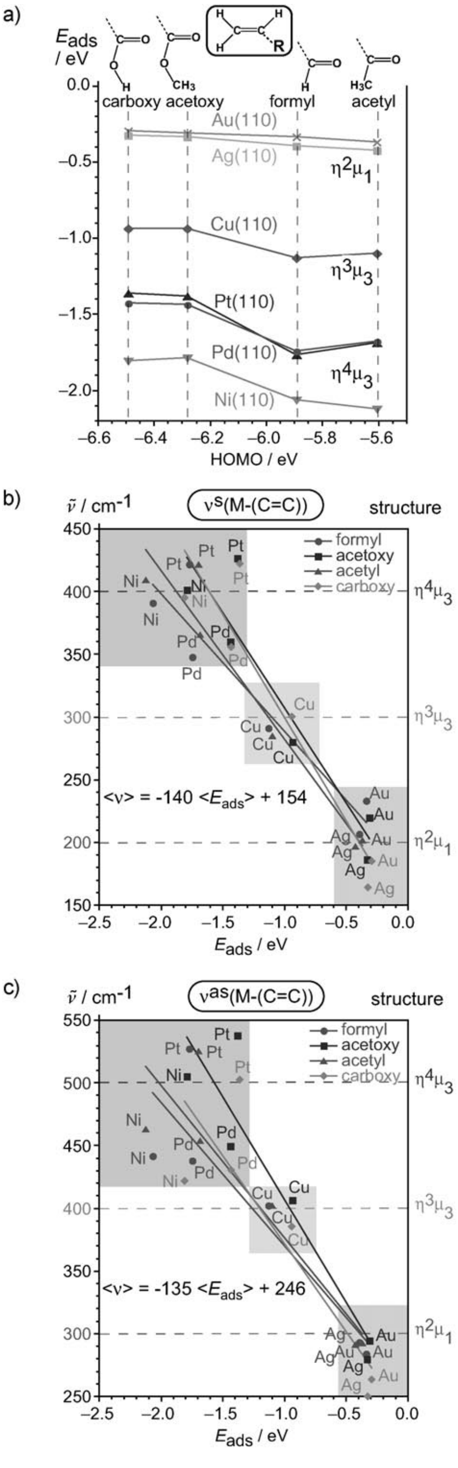

Figure 2. a) Adsorption energy E_{ads} [eV] of the *trans* conjugated molecules on six metal surfaces as a function of gas-phase HOMO energy [eV]. b) Symmetric ν^s(M–(C=C)) and c) antisymmetric ν^{as}(M–(C=C)) stretching frequency [cm^{-1}] as a function of E_{ads} [eV] and structure $\eta^i\mu_j$.

aldehyde (formyl), and a ketone (acetyl). These flat compounds, which have conjugated C=C and C=O bonds, exhibit *s-cis* and *s-trans* conformations. After adsorption, both conformations may compete, as shown previously for π(C=C) and di-σ(C=C) structures on Au(110) and Pt(110) surfaces respectively.[16] To simplify the analysis, only the results of the *s-trans* adsorbates are discussed here.

Adsorption strength and molecular structure are intimately correlated, and the evolution from sp noble metal (Au, Ag, Cu) to d transition metal (Pt, Pd, Ni) surfaces is revealed in Figure 1. For all the considered adsorbates, DFT shows that the most stable adsorption geometries are $\eta^2\mu_1$ [π(C=C)] on Au(110) and Ag(110), $\eta^3\mu_3$ on Cu(110), and $\eta^4\mu_3$ [η^4(C=C,C=O)] on Pt(110),[17] Pd(110), and Ni(110). Figure 2a shows the adsorption energy of these stable structures for the six metals. The mean adsorption strength increases from Au (−0.33 eV) to Ni surfaces (−1.95 eV). The $\eta^3\mu_3$ structure on Cu(110) is atypical, since the C4 carbon atom shares formally five bonds with the Cu surface, the H atoms, and C3. This peculiar structure is discussed below on the basis of an electronic analysis.

The loss of conjugation, which is characterized by breaking of the molecular plane and progressive opening of the CH_2 moiety, is linked to the adsorption strength (see Figure 1). As shown in Figure 2a, the DFT adsorption energy E_{ads} decreases on the six metal surfaces with increasing depth of the HOMO in the gas phase. Hence, the greater the donor ability of the substituent (acetyl), the higher the HOMO, and the more stable the adsorbate. This effect, which is rather moderate on sp metals (60–190 meV), becomes stronger on d metal surfaces (330–410 meV).

Having determined the stable structures, molecular recognition based on vibrational characterization appeared to be a natural further step. Assignment of the low-frequency vibrations requires preliminary analysis of the normal modes (see Figure 3). Beside the external vibrations (frustrated translations and rotations of the adsorbate not reported here), several metal–molecule stretching modes appear in an intermediate frequency range (170–630 cm^{-1} for all the adsorption states) between the surface metal phonons (0–250 cm^{-1}) and the high molecular frequencies. To illustrate this result, the calculated EELS spectra of one molecule (acetoxy) on the six metal surfaces are presented in Figure 4 (see Supporting Information for all the other spectra). The number of normal modes intrinsically depends on the adsorption structure. Since the C=C bond systematically interacts with the metal, the symmetric ν^s(M−(C=C)) and antisymmetric ν^{as}(M−(C=C)) stretching modes are common characteristic vibrations for all surfaces (see Figure 3). On Cu(110), the additional Cu−O bond appearing in the $\eta^3\mu_3$ form provides a third ν(Cu−O) stretching mode. Moreover, the additional M−(C=O) bonds of the $\eta^4\mu_3$ structures on Pt, Pd, and Ni(110) give two supplementary vibrations: the symmetric ν^s(M−(C=O)) and antisymmetric ν^{as}(M−(C=O)) modes.

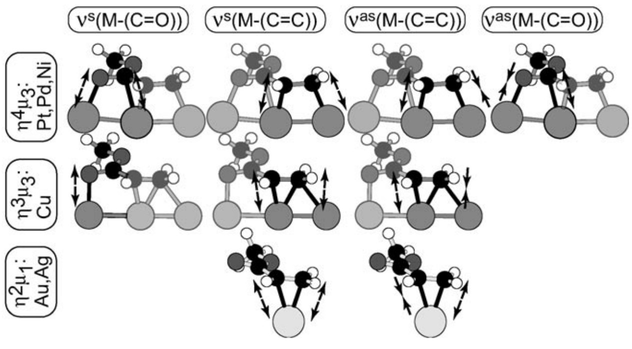

Figure 3. Molecule–metal stretching vibrations: symmetric ν^s(M−(C=O)), ν^s(M-(C=C)) and antisymmetric ν^{as}(M−(C=C)), ν^{as}(M−(C=O)).

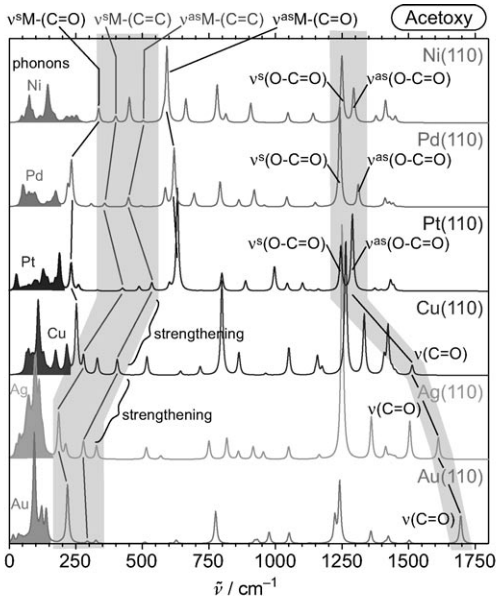

Figure 4. DFT EELS spectra of the most stable adsorption structures of the *trans* ester (acetoxy) compound on all the (110)-(1×2) surfaces.

First, the type of adsorption structure determines the range of molecule–substrate frequencies. This result is demonstrated in Figure 2b and c by focusing the analysis on the symmetric and antisymmetric M−(C=C) vibrations. On Au and Ag, the weakly coordinated adsorbates ($\eta^2\mu_1$) are associated with softer mean ν^s(M−(C=C)) vibrations (210 and 189 cm^{-1}, respectively). In contrast, on Pt, Pd, and Ni, the multicoordinated molecules ($\eta^4\mu_3$) are associated with stronger mean stretching frequencies of 423, 357, and 399 cm^{-1} respectively. The intermediate $\eta^3\mu_3$ structure on Cu(110) has a medium averaged frequency of 289 cm^{-1}.

Hence, this clear-cut separation allows the definition of specific frequency ranges for each structure: 165–234 cm^{-1} for π, 280–300 cm^{-1} for $\eta^3\mu_3$, and 348–427 cm^{-1} for η^4 (see the shaded areas in Figure 2b). This analysis is supported by the results for the ν^{as}(M−(C=C)) vibrations with a systematic mean frequency shift of +100 cm^{-1} (Figure 2c).

Second, the low molecule–metal frequencies are correlated with the adsorption strength, as shown in Figure 2b and c. A crude model averaged over the four molecules shows that the soft ν^s(M−(C=C)) and ν^{as}(M−(C=C)) vibrations are strengthened when the adsorption energy increases from noble metals (Au, Ag, Cu) to transition metals (Pd, Ni, Pt). This vibrational strengthening is indicated in the DFT EELS spectra of Figure 4. The mean slopes γ of the correlations are similar ($-140 \leq \gamma \leq -135$ cm^{-1} eV^{-1}) for both M−(C=C) vibrations, which are separated by a mean vertical frequency shift of +92 cm^{-1}. Beyond these correlations, the soft M−(C=C) vibrations are easily identifiable in the EELS spectra, since they are active and dominate the frequency range of 200–600 cm^{-1} with the M−(C=O) modes (left gray area in Figure 4). On sp metals ($\eta^2\mu_1$ and $\eta^3\mu_3$ structures), the M−(C=C) vibrations are intense at low frequencies, whereas they appear at higher frequencies for the $\eta^4\mu_3$ structures on d metals. In contrast, the C=O stretching mode can be recognized in the high-frequency region *only* if the C=O bond does not interact strongly with the metal surface (see the bands in the right gray area of Figure 4 at 1702, 1618, and 1519 cm^{-1} for Au, Ag, and Cu respectively). In fact for strong adsorption on Pt, Pd, and Ni, the ν(C=O) vibration is coupled with ν(C−O) and appears at lower frequencies (1200–1300 cm^{-1}). Such a frequency shift results in decreased coupling with the δ(CH) bending modes at 1300–1450 cm^{-1} and consequent attenuation of these latter vibrations.

The peculiar structure on Cu(110) is qualitatively explained by an electronic analysis based on the electron localization function (ELF). After adsorption on Au (see Figure 5a), the C=O and C=C bonds preserve a dominant π character, as shown by the presence of two disjointed disynaptic basins along the *z* axis (see the Supporting Information for more details). Conversely, the strong adsorption on Pt completely changes the picture in favor of a dominant σ character, as shown by the unique disynaptic basins around the bonds (Figure 5c). The pairing region with the metal is clearly revealed below the terminal C4 atom by the presence of a single disynaptic basin V_1(C,Pt). The intermediate structure on Cu is undeniably peculiar. The anomaly at C4 is explained as follows: Lateral shift of the C=C moiety results in loss of its π character. This favors the formation of an atypical pseudometallic three-centered bond between C4 and two Cu atoms characterized by one trisynaptic basin V_1(C,Cu,Cu) just below C4 (Figure 5b).

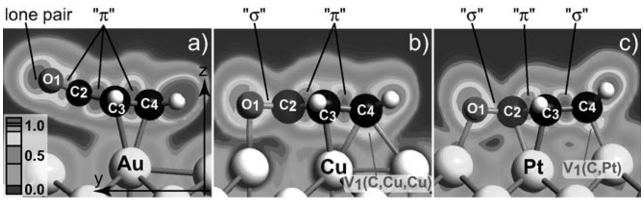

Figure 5. Two-dimensional sections in the *yz* plane of the isosurfaces of the ELF for adsorption of the *trans* aldehyde (formyl) on a) Au, b) Cu, and c) Pt.

In summary, I have reported on a systematic theoretical investigation of the EELS spectra of multifunctional molecules on metal surfaces. Density functional theory calculations demonstrate that the low-frequency molecule–metal vibrations are strongly correlated with adsorption strength and structure, in agreement with previous results for CO and NO.[8,9] Weak adsorption on noble metals (Au, Ag) is associated with weakly coordinated π structures and provides softer molecule–metal stretching modes. Conversely, strong adsorption on transition metals (Pt, Pd, Ni) is stabilized by highly coordinated η^4 forms and results in harder M−(C=C) vibrations. The structure on Cu is an intermediate case in which the C=C bond forms an atypical multicentered bond with the surface. The calculated EELS spectra support the argument for possible recognition of the molecular structure on the basis of the frequency ranges of the soft vibrations. Future comparisons between new highly resolved spectroscopic investigations extended to low frequencies and the present theoretical results open exciting and promising perspectives for the structural identification of reactants in heterogeneous catalysis.

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