Vibrational fingerprints of tungsten and cobalt based molecules adsorbed on silica surfaces

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Abstract. Tungsten and cobalt carbonyls adsorbed on a substrate are typical starting points for the electron beam induced deposition of tungsten or cobalt based metallic nanostructures. We employ first principles molecular dynamics simulations to investigate the dynamics and vibrational spectra of W(CO)\(_6\) and W(CO)\(_5\) as well as Co\(_2\)(CO)\(_8\) and Co(CO)\(_4\) precursor molecules on fully and partially hydroxylated silica (SiO\(_2\)) surfaces. Such surfaces resemble the initial conditions of electron beam induced growth processes. We find that both W(CO)\(_6\) and Co\(_2\)(CO)\(_8\) are stable at room temperature and quite mobile on a silica surface saturated with hydroxyl groups (OH), moving up to half an Angstrom per picosecond. In contrast, chemisorbed W(CO)\(_5\) or Co(CO)\(_4\) ions at room temperature do not change their binding site. These results contribute to gaining fundamental insight into how the molecules behave in the simulated time window of 20 ps and our determined vibrational spectra of all species provide signatures for experimentally distinguishing the form in which precursors cover a substrate.

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1. Introduction

Electron beam induced deposition (EBID) of organometallic precursor molecules on a substrate is a widely used method to grow size- and shape-controlled nanometer-sized structures. The obtained EBID deposits nevertheless possess a significant percentage of organic contaminants mainly from carbon and oxygen, lowering the conductivity of these deposits and thus limiting the possible applications of EBID. Several pre- and post-fabrication approaches have been employed to remove these contaminants. Recently, the authors of Ref. [10] reported that the surface residence time of an organometallic precursor should be sufficiently long (lasting from microseconds to milliseconds) to have an efficient deposition yield. In order to understand these observations, it is useful to study the behavior of the precursor molecules and their fragments on the surface of the substrate theoretically.

First principles calculations can provide a detailed description of the microscopic behavior of the deposits and are often used to improve the quality of the deposition processes. Important progress has been done, for instance, on atomic layer deposition and chemical vapor deposition processes. Recently, in an attempt to understand the EBID growth process, we analyzed by means of density functional theory (DFT) calculations the interaction of precursors like W(CO)$_6$, Co$_2$(CO)$_8$ and CH$_3$(C$_5$H$_5$)Pt[CH$_3$]$_3$ on different SiO$_2$ surfaces so as to represent the untreated and pretreated EBID surfaces. These studies illustrate the preferred orientation of the adsorbate and the nature of the interaction between the precursor molecules and the SiO$_2$ substrates. Further, interesting phenomena such as the spontaneous fragmentation of the carbonyl precursors (W(CO)$_6$ to W(CO)$_5$ and Co$_2$(CO)$_8$ to two Co(CO)$_4$ molecules) on the POH-SiO$_2$ surfaces that correspond to pre-treated surfaces were observed.

A next step towards understanding the EBID growth process is the investigation of the dynamics of the adsorbed EBID precursors on surfaces. Many theoretical and experimental studies on the adsorption process of free CO on various surfaces and several molecules on different SiO$_2$ substrates have been reported. However, little is known on the dynamics of W(CO)$_6$ and Co$_2$(CO)$_8$ precursors and their fragments on SiO$_2$ surfaces. In this work we use first principles molecular dynamics simulations to investigate the nature of adsorption of W(CO)$_6$ and Co$_2$(CO)$_8$ on fully and partially hydroxylated SiO$_2$ surfaces and provide quantitative microscopic insight into the stability of these fragmented precursors on SiO$_2$ surfaces and on their vibrational spectra.

2. Computational details

Ab initio molecular dynamics (MD) simulations were performed in the framework of density functional theory (DFT). We employed the projector augmented wave (PAW) basis as implemented in VASP with an energy cut off of 400 eV. In
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Refs. [23] and [24] we found the most stable configurations of W(CO)$_6$ and Co$_2$(CO)$_8$ on SiO$_2$ substrates by placing the molecules in different conformations on several bonding sites in FOH-SiO$_2$ and POH-SiO$_2$ surfaces and subsequently relaxing them using the conjugate gradient scheme until forces on the atoms were reduced to $\lesssim$ 0.01 eV/Å. In the present work, we considered these structures as initial configurations for the MD simulations (see in Fig. 1 and Fig. 5 the $t = 0$ ps snapshot).

Due to the large system size, the Brillouin zone was sampled at the gamma point only, and MD simulations were performed for 20 ps on a canonical ensemble at a finite temperature of $T = 298$ K using the Nose-Hoover thermostat.[34] The temperature was chosen in accordance with the reported experimental results where the largest temperature rise during W(CO)$_6$ deposition was 1 °C when a 1.42 nA electron beam was used for depositing tungsten nanostructures.[35, 36] The Verlet algorithm in its velocity form with a time step of $\Delta t = 1$ fs was used to integrate the equations of motion.

Vibrations of the gas phase precursor molecules were studied by (i) the finite displacement method and (ii) a Fourier transformation of the velocity autocorrelation function obtained from the MD trajectory (power spectrum). Vibrations through the finite displacement method were computed for the precursor molecules W(CO)$_6$ and Co$_2$(CO)$_8$ in the gas phase using Turbomole 6.0.[37, 38, 39] The geometries were optimized using triple $\zeta$ basis sets for all elements and we used an effective core potential (60 core electrons) for W in the case of W(CO)$_6$.[40] We also performed MD simulations for the precursor molecules in the gas phase by placing the molecules in a cubic box of $a = b = c = 30$ Å. Here the length of the simulation was limited to 10 ps and the trajectory was then used to analyze the power spectrum, as explained below.

The power spectrum $I(\omega)$ provides information about the distribution of the vibrational energy of the system and can be computed from the velocities $\mathbf{v}_i(t)$ of all atoms in the course of the trajectory. The method we use is described in the Appendix.

The vibrations computed for the precursor molecules in the gas phase by methods (i) and (ii) agree with each other and are explained in Section 3.3. Therefore, vibrations for the substrate and the complex precursor molecule-substrate have been evaluated only from the power spectrum so as to reduce the computational effort in computing the Hessian matrix.

3. Results

3.1. Dynamics of W(CO)$_6$ on SiO$_2$ surfaces

Previous DFT calculations [23] indicate that W(CO)$_6$ interacts through weak physisorption with surface hydroxyls on the FOH-SiO$_2$ surface and by strong chemisorption on the Si sites available on POH-SiO$_2$ surfaces with substantial changes in the structure and electronic properties. The most stable configuration of W(CO)$_6$ on FOH-SiO$_2$ has an adsorption energy of -0.498 eV while the fragment W(CO)$_5$ together
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with a free CO ligand stabilize with an energy -1.262 eV on a POH-SiO$_2$ surface. In Fig. 1, we show five snapshots in 5 ps intervals of the MD simulations of W(CO)$_6$ on a FOH-SiO$_2$ surface (upper panel) and of the fragment W(CO)$_5$ together with a free CO ligand on a POH-SiO$_2$ surface (lower panel).

Analysis of the trajectory in the FOH-SiO$_2$ case indicates that the W(CO)$_6$ molecule exhibits a considerable drift and moves around the initial binding sites in a FOH-SiO$_2$ surface. In order to visualize this drifting, Fig. 2 shows a schematic depiction of the W(CO)$_6$ displacement together with the center-of-mass (COM) analysis. The calculated drifting distance on the surface after 20 ps is ca. 5 Å. These simulations illustrate that the undissociated W(CO)$_6$ molecule changes the orientation on a FOH-SiO$_2$ surface considerably but does not desorb away from the surface.

However, a chemisorbed W(CO)$_5$ molecule which is formed by the release of a CO ligand from W(CO)$_6$ (Fig. 1 lower panel) remains localized on its binding site on a POH-SiO$_2$ surface. The dissociated CO ligand doesn’t recombine with the parent moiety and the vacant site on W remains empty and is not filled by surface hydroxyls as has been suggested as a possibility for Mo(CO)$_5$. It should be noted that W(CO)$_5$ in the gas phase is stable on a square pyramidal structure and different conformations are possible through the pathway shown in Fig. 3 involving a trigonal bipyramidal transition state.

Analysis of the adsorbed W(CO)$_5$ structure (compare the transition state on Fig. 3 with the configuration at 0 ps in Fig. 1 lower panel) indicates that the W(CO)$_5$ molecule...
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Figure 2. (Color online) Schematic illustration of the movement of $\text{W(CO)}_6$ on a FOH-SiO$_2$ surface. In the top panel, the polygon of the oxygen atoms of $\text{W(CO)}_6$ is shown, with one facet always shown in red in order to visualize the rotations of the molecule. In the lower panel the time evolution of the three center-of-mass coordinates of $\text{W(CO)}_6$ is shown.
Figure 3. (Color online) DFT optimized structure of W(CO)$_5$. In the gas phase it possess a C$_{4v}$ symmetric structure. The trigonal bipyramidal structure (middle panel) is 0.643 eV less stable than the square pyramidal structure (left and right panels) but it is stabilized by surface-molecule interaction on POH-SiO$_2$.

Figure 4. (Color online) Variations in the structural features of W(CO)$_6$ on SiO$_2$ surfaces on FOH-SiO$_2$ (left panel) and POH-SiO$_2$ (right panel). Bold (red) letters correspond to WC and normal letters (blue) for CO bond. The values shown in this figure are the standard deviation of the respective values in the initial structure.

is stabilized in a trigonal bipyramidal structure on POH-SiO$_2$ surfaces. The stabilization of such a transient intermediate has been proposed for Cr(CO)$_5$ and the present work supports such a proposal also for W(CO)$_5$. Evaluation of the changes in the WC and CO bond lengths of the adsorbates
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Figure 5. (Color online) Adsorption of Co$_2$(CO)$_8$ on FOH-SiO$_2$ (top) and POH-SiO$_2$ (POH) substrates. The illustrated snapshots are the configurations taken at every 5ps interval. S1 and S2 in POH-SiO$_2$ case denotes the two bonding sites on the surface where Co(CO)$_4$ fragments are bonded. Color code: Blue - Co, throughout this manuscript

W(CO)$_6$ and W(CO)$_5$ (see Fig. 4) during the first 20 ps of the trajectory show deviations from the initial configuration of the order of 1-2% and might be due to thermal fluctuations. We will analyze these deviations in more detail in Section 3.3. The electronic structure of the final configurations of the complex molecule-substrate on both FOH-SiO$_2$ and POH-SiO$_2$ cases shows only minor variations with respect to the initial configurations (results not shown).

3.2. Dynamics of Co$_2$(CO)$_8$ on SiO$_2$ surfaces

We now proceed with the adsorption scenario of Co$_2$(CO)$_8$ interacting with SiO$_2$ surfaces. In Ref. [24] a weak bonding of Co$_2$(CO)$_8$ on FOH-SiO$_2$ surfaces was observed, similar to the case of W(CO)$_6$, with an adsorption energy of -0.76 eV. In contrast, Co$_2$(CO)$_8$ molecules on a POH-SiO$_2$ surface fragment into two Co(CO)$_4$ moieties rather than having a CO ligand elimination as in the case of W(CO)$_6$. The fragmented Co(CO)$_4$ moieties exhibit a strong chemisorption on POH-SiO$_2$ surfaces with an adsorption energy of -1.77 eV. [24] Considering the above configurations as the initial setting for our MD simulations, Fig. 5 shows five snapshots in 5 ps intervals of Co$_2$(CO)$_8$ adsorbed on a FOH-SiO$_2$ surface (upper panel) and of Co(CO)$_4$ fragments adsorbed on a POH-SiO$_2$ surface (lower panel).

We observe a significant drift of Co$_2$(CO)$_8$ on the FOH-SiO$_2$ surface but as this is a larger molecule than W(CO)$_6$, the displacement is less pronounced than in W(CO)$_6$. This can be seen by comparing Fig. 6 where the COM movement of Co$_2$(CO)$_8$ on a
FOH-SiO$_2$ surface is depicted, with Fig. 2 (b) which is analogous to W(CO)$_6$. The calculated drifting radius of Co$_2$(CO)$_8$ within 20 ps is about 4 Å.

We now investigate the adsorption of the Co(CO)$_4$ species on POH-SiO$_2$ surfaces (Fig. 5 lower panel). We would like to note that, unlike in the case of W(CO)$_5$, the Co(CO)$_4$ species in the gas phase possesses a tetrahedral structure which remains stable with a slight distortion on the POH-SiO$_2$ surfaces (see $t = 0$ ps in Fig. 5 lower panel). During the MD simulations, the fragmented Co(CO)$_4$ species are localized on the surface but we observe severe changes in the orientation of CO ligands. In particular, we find that the Co(CO)$_4$ fragment bonded to the S2 site on the POH-SiO$_2$ surface as shown in Fig. 5 (lower panel) shows bonding of the Co atom to surface oxygen as time evolves (compare $t = 0$ ps and $t = 5$ ps snapshots). A similar situation was suggested by Rao et al. [45] during the adsorption of Co$_2$(CO)$_8$ on dehydroxylated MgO and on SiO$_2$ surfaces. However, within our simulation window, we only observe this effect for the Co(CO)$_4$ fragment bonded to the S2 site but not for the fragment bonded to the S1 site (see Fig. 5 (lower panel)) of the dehydroxylated SiO$_2$ surfaces. Such a metal-substrate bond might be due to activation of the substrate surface by dehydroxylation.
3.3. Vibrations of W(CO)$_6$ and Co$_2$(CO)$_8$ on a SiO$_2$ surface

3.3.1. W(CO)$_6$ adsorbed on SiO$_2$ surface

We first start with the analysis of the vibrational spectrum of W(CO)$_6$ in the gas phase and the modes arising due to SiO$_2$ surfaces. In Fig. 7 we show that the results obtained by the two methods discussed in Section 2 agree well in this simple case. We observe WC stretching modes and WCW bending modes at 300-600 cm$^{-1}$, and CO stretching modes at 1900-2150 cm$^{-1}$. The bending vibrations that involve WCO are seen at 60-100 cm$^{-1}$. These modes are seen with both methods.

In Fig. 8 we compare the power spectrum calculated for W(CO)$_6$ adsorbed on a FOH-SiO$_2$ surface with experimental infrared and Raman spectra [46, 47] measured for SiO$_2$ substrates. We observe a good overall agreement between our assignment to SiO$_2$ modes (Infrared and Raman active peaks at 100-200, 400-450, 700-800 and 1000-1100 cm$^{-1}$) and the experimental observations. [48, 49] The additional modes appearing in the calculated power spectrum originate from the adsorbed W(CO)$_6$ molecule (compare with Fig. 7). In this case only minor changes between the adsorbed W(CO)$_6$ molecule modes and W(CO)$_6$ in the gas phase are observed since the molecule
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Figure 8. (Color online) Comparison of the calculated power spectrum for W(CO)$_6$ adsorbed on FOH-SiO$_2$ with the experimentally measured infrared and Raman spectrum [46, 47] for the SiO$_2$ substrate. In the lower panel, the vibrational frequencies of β cristobalite at Γ and M points in the Brillouin zone as calculated in Ref. [49] are shown.

only physisorbs on the FOH-SiO$_2$ surface. In Fig. 9 (b) we show the direct comparison of the power spectrum of the physisorbed molecule W(CO)$_6$ with the vibrational modes of W(CO)$_6$ in the gas phase. In particular, the CO frequencies in the gas phase of W(CO)$_6$ between 1900 and 2110 cm$^{-1}$ (two of which are Raman active) are observed in the complex W(CO)$_6$ on FOH-SiO$_2$ without being perturbed. The molecule retains its gas-phase characteristics. These features are indeed similar to W(CO)$_6$ adsorbed on hydroxylated alumina (γ–Al$_2$O$_3$) surfaces where all the molecular vibrations are retained [50, 51] indicating the weak interaction between W(CO)$_6$ and the substrate.

We proceed with the analysis of the chemisorbed W(CO)$_6$ fragments on POH-SiO$_2$ surfaces. In Fig. 9 (a) we show the power spectrum for W(CO)$_5$ adsorbed on
POH-SiO\textsubscript{2} in comparison with that for W(CO)\textsubscript{6} adsorbed on FOH-SiO\textsubscript{2}. In addition to the shifts of several peaks, we observe two new modes occurring at 700-800 cm\textsuperscript{-1} and 1400-1600 cm\textsuperscript{-1}. In order to understand the origin of these new peaks Fig. 9 (c) depicts the power spectrum of the chemisorbed molecule W(CO)\textsubscript{5} compared to the vibrational modes of W(CO)\textsubscript{6} in the gas phase. Peaks at 700-800 cm\textsuperscript{-1} which correspond to the Raman vibrations of \(\beta\)-cristobalite \cite{48}, are now seen, due to the bonding, in the vibrations of the molecule. Also, the peaks at 1400-1600 cm\textsuperscript{-1} are a result of oxygen (of CO) interaction with substrate Si atoms.\cite{51, 52} Due to this interaction the bonding between tungsten and the carbonyl gets affected leading to a considerable split of peaks in the 1900-2100 cm\textsuperscript{-1} and 300-600 cm\textsuperscript{-1} regions that correspond to the vibrations of CO and WC bonds respectively.

3.3.2. Co\textsubscript{2}(CO)\textsubscript{8} adsorbed on SiO\textsubscript{2} surface

There are some studies aimed at understanding the vibrations of SiO\textsubscript{2} adsorbed Co\textsubscript{2}(CO)\textsubscript{8}. However they are either limited to the carbonyl region of the spectrum \cite{45, 53} or they observe immediate conversion of Co(CO)\textsubscript{4} to subcarbonyl species.\cite{54, 55} We first show in Fig. 10 the analysis of the vibrational spectrum of Co\textsubscript{2}(CO)\textsubscript{8} in the gas phase computed by two different methods as explained in \cite{2} and we find a very nice agreement also for the case of Co\textsubscript{2}(CO)\textsubscript{8} and in accordance with the existing reports.\cite{56} The two sets of vibrations in the region 1850-1900 and 2100-2000 cm\textsuperscript{-1} are assigned to the stretching modes of the bridging and terminal CO ligands and the Co-Co stretching mode in Co\textsubscript{2}(CO)\textsubscript{8} is observed between 200-250 cm\textsuperscript{-1}.

We now investigate the vibrations of Co\textsubscript{2}(CO)\textsubscript{8} adsorbed on SiO\textsubscript{2} by analysing the power spectrum. In Fig. 11 (a) we show the power spectrum of Co\textsubscript{2}(CO)\textsubscript{8} on a FOH-SiO\textsubscript{2} surface superimposed to the power spectrum of Co(CO)\textsubscript{4} fragments on a POH-SiO\textsubscript{2} surface. Similar to the case of the W(CO)\textsubscript{6} adsorption on SiO\textsubscript{2} we observe that the vibrational modes corresponding to the SiO\textsubscript{2} substrate agree well with the experimental measurements (Fig. 8). Also the power spectrum of Co\textsubscript{2}(CO)\textsubscript{8} on FOH-SiO\textsubscript{2} preserves the gas-phase molecule characteristics (cf. Fig. 10 and Fig. 11 (b)).

A comparison of the chemisorbed Co(CO)\textsubscript{4} modes with the vibrational spectrum of Co(CO)\textsubscript{4} in the gas phase is shown in Fig. 11 (c). The overall agreement of the power spectrum with that of the gas phase Co(CO)\textsubscript{4} moiety is relatively poor because the Co(CO)\textsubscript{4} moieties exhibit strong structural distortions upon bonding to the SiO\textsubscript{2} substrate which is absent in the gas phase computations. In the power spectrum, we find that the modes in the region 220-250 cm\textsuperscript{-1} (corresponding to the Co-Co stretching) and the mode at approx. 1850 cm\textsuperscript{-1} (corresponds to the bridging carbonyls) disappear owing to the fact that the Co\textsubscript{2}(CO)\textsubscript{8} molecule fragments on POH-SiO\textsubscript{2} surfaces. Further, two new modes in the 600-800 cm\textsuperscript{-1} and 1400-1600 cm\textsuperscript{-1} regions appear in the case of POH-SiO\textsubscript{2} surfaces (Fig. 11 (a) Fig. 11 (c)) illustrating the interaction of surface Si atoms with the carbonyls through the oxygen atom of the CO. However, this situation is only observed for one of the Co(CO)\textsubscript{4} moieties indicating that the fragmented species behave differently. This is a consequence of the interaction of surface oxygen atoms with
the Co atom observed for the fragment bonded to the S2 site (see Fig. 5).

3.4. Discussion

Investigation of surface adsorption and residence-time of the precursors on the surface is necessary for improving the understanding of deposition processes. The present study elucidates the vibrational footprints of precursors which interact through weak physisorption with FOH-SiO$_2$ and by strong chemisorption with POH-SiO$_2$ surfaces.

The authors of Ref. [57] found that physisorbed W(CO)$_6$ molecules on TiO$_2$ surfaces completely desorb when the system is cooled down to room temperature. Our study finds no desorption of W(CO)$_6$ molecules on FOH-SiO$_2$ surfaces in the considered length of simulation. Also, Co$_2$(CO)$_8$ molecules on FOH-SiO$_2$ surfaces were found to fragment spontaneously. [54, 58] In our calculations on FOH-SiO$_2$ surfaces we didn’t observe any tendency to fragmentation or an indication of chemisorption. Other effects (probably extrinsic) may be responsible for the experimental observations.

The bond variations of W(CO)$_6$ and Co$_2$(CO)$_8$ adsorbed on FOH-SiO$_2$ surfaces indicate uniform fluctuations (WC and CO bonds) all over the molecule. On the contrary, the relative bond values of W(CO)$_5$ on POH-SiO$_2$ surfaces show that the WC and CO bonds oriented toward the vacuum experience larger changes than the ligands oriented toward the surface. Thus, for favorable conditions, the bond between C and O for the CO bonded to the surface might cleave leaving the surface Si atoms terminated with oxygens. This situation is not observed in the present MD simulations but the higher ratio of carbon contamination with respect to oxygen (before atmospheric air exposure) in the EBID-obtained samples might provide an evidence for such a fact. [10, 11, 12, 13, 14] Similarly, we found in the case of Co$_2$(CO)$_8$ on POH-SiO$_2$ surfaces, that surface oxygen atoms are involved in bonding to the dissociated surface species. This suggests that the removal of oxygen components from the deposits might not be an easy task to achieve. Presence of oxygen contamination is also expected to occur as a result of exposure of EBID deposits to the air. Thus the composition of the EBID deposits are determined to a large extent by the number of available active Si sites (alternatively the degree of hydroxylation), the frequency of these precursor molecules approaching such a site and the exposure time to the environments.

On POH-SiO$_2$ surfaces our results for both W(CO)$_6$ and Co$_2$(CO)$_8$ show that the fragmented species remain localized, thus blocking active sites on the surface. Therefore, further deposition should occur on the deposited layers and this may be likely the reason for the increase in height of the deposits as the irradiation time increases during EBID experiments. [59]

4. Conclusions

The purpose of this work was to model by means of ab initio molecular dynamics simulations the dynamics of two precursor molecules adsorbed on several SiO$_2$ surfaces...
in order to achieve a better understanding of the microscopics of electron-beam induced deposition of nanostructures. Our results reveal that W(CO)\textsubscript{6} and Co\textsubscript{2}(CO)\textsubscript{8} molecules preserve their gas-phase bonding characteristics on FOH-SiO\textsubscript{2} surfaces. Apart from a considerable drift, only minor variations in the structure and vibrations is observed. Therefore spontaneous dissociation of these precursor molecules will not be possible on FOH-SiO\textsubscript{2} unless some surface active sites are created by external forces.

For the case of W(CO)\textsubscript{6} and Co\textsubscript{2}(CO)\textsubscript{8} on POH-SiO\textsubscript{2} surfaces, the fragmented species retain the chemisorbed character on the surface and we do not observe any reformation of the parent precursor moiety, but instead a slight tendency towards fragmentation. We also observe a smaller weakening of the surface-oriented CO bonds compared to vacuum-oriented CO bonds in W(CO)\textsubscript{6} and Co\textsubscript{2}(CO)\textsubscript{8} on POH-SiO\textsubscript{2} surfaces. Therefore, conditions that favor the formation of active sites (in this case surface Si atoms) are needed in order to have high efficiency in fragmentation and improve the metal content of the deposit.

The calculated vibrational spectra of the various molecule/substrate systems show clear fingerprints to be detected experimentally. We propose therefore the consideration of such simulations as a route to experimentally distinguish the form in which precursors cover a substrate.

Finally, while the present simulations provide insights on the surface-precursor interaction, the investigation of other processes like surface-electron, precursor-electron and deposit-molecule interaction remains a challenge for future work.

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Appendix A. Estimation of the power spectrum

We use the power spectrum for analysing the vibrational characteristics of precursor molecules in the gas phase and for the entire system of precursors chemi- or physisorbed on a silica substrate \[60\]. The power spectrum is defined as \[61, 62\]

\[
I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} C(\tau)e^{-i\omega\tau}d\tau, \tag{A.1}
\]

where \(C(\tau)\) is the velocity autocorrelation function

\[
C(\tau) = \langle v(0)v(\tau) \rangle = \lim_{T \to \infty} \left[ \frac{1}{TN} \int_0^T \sum_{l=1}^N v^l(t)v^l(t+\tau)dt \right]. \tag{A.2}
\]

\(v^l(t)\) represents the velocity of atom \(l\) at time \(t\) for all \(N\) atoms of the system. As the calculation of the time averages \(\langle \ldots \rangle\) of Eq. (A.2) is quite inefficient computationally,
we use the Wiener-Khinchin theorem which guarantees that the power spectrum can also be calculated by individually Fourier-transforming the velocities $v^l(t)$ and summing the squares of the result:

$$I(\omega) = \frac{1}{N} \sum_{l=1}^{N} \left| \int_{-\infty}^{\infty} v^l(t) e^{-i\omega t} dt \right|^2.$$  \hspace{1cm} (A.3)

Finite trajectories, calculated with a finite time step $\Delta t$, only yield estimates to the power spectrum. Instead of the Fourier integral in Eq. (A.3), discrete Fourier sums have to be calculated according to

$$V^l_{\mu} = \sum_{j=0}^{J-1} v^l_{j\mu} e^{2\pi i jk/J},$$  \hspace{1cm} (A.4)

where the $v^l_{j\mu}$ stand for the $\mu$ component ($\mu \in \{x,y,z\}$) of the velocity of atom $l$ at time step $j$, and $J$ is the number of time steps of the trajectory. The so-called periodogram estimate for the power spectrum is then defined for $J/2 + 1$ frequencies [63]:

$$P^l_{\mu}(0) = P^l_{\mu}(f_0) = \frac{1}{J^2} |V^l_{0\mu}|^2,$$

$$P^l_{\mu}(f_k) = \frac{1}{J^2} \left[ |V^l_k\mu|^2 + |V^l_{J-k}\mu|^2 \right],$$

$$P^l_{\mu}(f_{c}) = P^l_{\mu}(f_{J/2}) = \frac{1}{J^2} |V^l_{J/2\mu}|^2.$$  \hspace{1cm} (A.5)

The highest frequency $f_c = \frac{1}{2\Delta t}$ is called Nyquist frequency and is determined by the time step $\Delta t$ of the MD calculation. Thus, the finite time estimate of the power spectrum can finally be written as

$$I^J(\omega) = \frac{1}{N} \sum_{l=1}^{N} \sum_{\mu=1}^{3} P^l_{\mu}(\omega).$$  \hspace{1cm} (A.6)

The function $I^J(\omega)$ will approach the true power spectrum $I(\omega)$ of the system in the limit $J \to \infty$, i.e. in the limit of infinitely long trajectories. The power spectrum estimates now provide us with information about the distribution of the vibrational energy of a molecule or a solid over the frequencies. Power spectra at different temperatures may be used to investigate the differences in the population of vibrational modes. The integral over the power spectrum corresponds to the kinetic energy of the system.

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Figure 9. (Color online) (a) Comparison of the total power spectrum for (i) W(CO)$_6$ on a FOH-SiO$_2$ surface and (ii) W(CO)$_5$ on a POH-SiO$_2$ surface. (b) Power spectrum of the physisorbed molecule W(CO)$_6$ only in case (i) compared to the vibrational modes of W(CO)$_6$ in the gas phase. The modes are classified in Raman, infrared and other. (c) Power spectrum of the chemisorbed molecule W(CO)$_5$ only in case (ii) compared to the vibrational modes of W(CO)$_5$ in the gas phase.
Figure 10. (Color online) Calculated vibrational spectrum of the gas phase of Co$_2$(CO)$_8$ molecules by fourier transforming the velocities obtained from the MD trajectory (upper panel) and by the finite displacement method (lower panel).
Figure 11. (Color online) (a) Comparison of the total power spectrum for (i) Co$_2$(CO)$_8$ on a FOH-SiO$_2$ surface and (ii) the two Co(CO)$_4$ fragments on a POH-SiO$_2$ surface. (b) Power spectrum of the physisorbed molecule Co$_2$(CO)$_8$ in case (i) compared to the vibrational modes of Co$_2$(CO)$_8$ in the gas phase. (c) Power spectrum of the chemisorbed Co(CO)$_4$ fragments in case (ii) compared to the vibrational modes of Co(CO)$_4$ in the gas phase.