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Surface Chemistry

“Hot” Surface Activation of Molecular Complexes: Insight from Modeling Studies**

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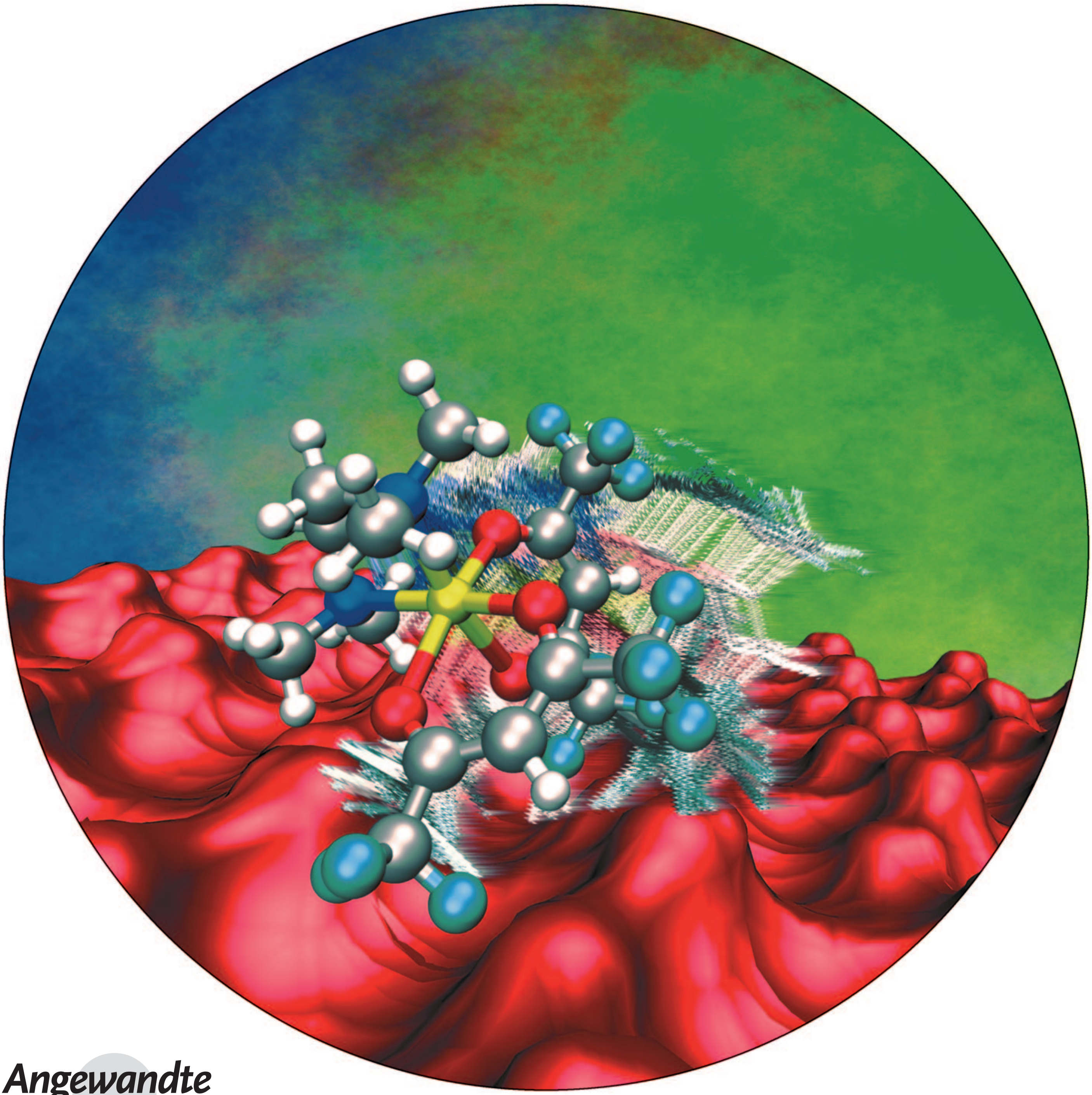

The activation of gas-phase molecules on hot solid surfaces, a major issue for both fundamental research and technological applications, plays a key role in the fabrication of advanced materials supported on suitable substrates.[1] The interest relates to the increasing requirement of attaining a deeper insight into the first molecular activation stages, a critical step in the bottom-up nucleation of functional nanostructures with specific size–structure relationships. While molecular activation is in general influenced by the surface chemical composition, in the harsh conditions typical of hot substrates, the surface–molecule energy transfer becomes crucial. As a consequence, physisorption competes with desorption, a diverse reactivity emerges, and novel activation mechanisms may be triggered, thus leading to products not attainable under mild conditions. Atomistic-level details of encounters between gas-phase molecules and hot surfaces are not easily available,[2] owing to both the fast kinetics associated with high temperatures and the difficulties of performing experimental in situ analysis on a molecular scale. In this context, first-principles modeling studies[3–5] are of significant relevance in the design and tailoring of specific molecular routes to functional nanosystems, such as chemical vapor deposition (CVD) processes, in which surface temperature is a decisive factor. Herein, we report on how the multifaceted dynamical behavior of a CVD precursor on a hot substrate, captured by simulation, disclosed a novel general activation channel for high-temperature surface processes: the fast rolling motion of vibrationally excited molecules. This surface mobility regime, never reported to date, combines fast lateral transport of an adsorbent with excitation of its internal modes, thus suggesting that energetic collision of rolling species is actually one of the ways through which molecules are activated and react at a hot surface.

Observations were collected in a computer experiment in which the Cu^{II} complex [Cu(hfa)$_2$tmeda][6] (see Figure 1, left) was put in contact with a hot model surface (750 K). [Cu(hfa)$_2$tmeda] is a successful CVD precursor[7] for the deposition of silicon-supported Cu$_x$O ($x = 1$, 2) nanostructures for H$_2$ production and gas-sensing applications.[8] On purely empirical grounds, the complex is considered a good CVD precursor thanks to its favorable mass-transport properties and, in particular, to the fact that it sublimes without side decomposition. Yet the conversion of [Cu(hfa)$_2$tmeda] into Cu$_x$O systems evidences a temperature-dependent ligand elimination through molecular activation on the hot substrate, the exact mechanism of which is unknown to date. The solid-state Cu$_x$O nucleation occurs when [Cu(hfa)$_2$tmeda] (sublimated at ca. 343 K in a cold-wall CVD reactor) in O$_2$/H$_2$O-based atmosphere interacts with oxidized Si(100) heated substrates (523–823 K). Both the system structure and composition (CuO vs. Cu$_2$O) and its spatial organization (from continuous films to anisotropic quasi-1D nanowires) can be finely tuned through controlled variation of both reaction atmosphere and surface temperature.[8a,d]

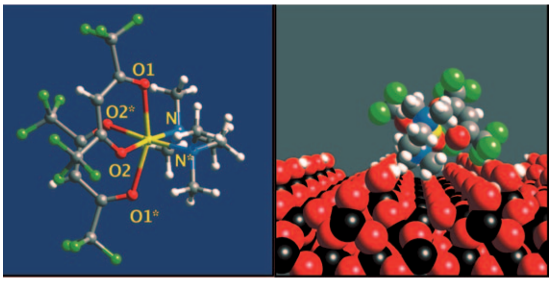

Figure 1. Left: ball-and-stick representation of [Cu(hfa)$_2$tmeda] (hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate, tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). The isolated molecule (C_2 symmetry) has a Jahn–Teller distorted octahedral CuO$_4$N$_2$ geometry and a dipole moment of 9.4 D.[7] Right: representation of the minimum-energy structure of [Cu(hfa)$_2$tmeda] on top of a hydroxylated silica layer. Cu yellow, O red, N blue, F green, C gray, H white, Si black.

Under these conditions, the exposed substrate surface is a hydroxylated silica layer.[1b,9] On this basis, the surface model used herein consists of a slab of amorphous silica approximately 1 nm thick, with a concentration of 2.8 surface silanol (Si−OH) groups per square nanometer (see Figure 1, right, and the Experimental Section). A [Cu(hfa)$_2$tmeda] molecule was positioned on top of such a surface. The system temperature was set to 750 K, and the time evolution was monitored by first-principles molecular dynamics (FPMD) for a total of approximately 30 ps. The target molecule remained close to the substrate during the whole simulation, that is, with its closest contact with the surface atoms always within 2–3 Å (see Figure 2, left). Nevertheless, the complex cannot be considered as firmly physisorbed, as the time evolution of the x and y components of the Cu coordinates (Figure 2, right) indicates a remarkable mobility on top of the surface.

Three regimes were identified along the [Cu(hfa)$_2$tmeda]/hot surface simulation. In the first part of the trajectory (0–4 ps interval, region a), the complex diffuses over the surface through a series of small back-and-forth bumps, with a rocking motion. In such a slow "bump-and-rock" diffusion regime, favorable longer-lasting molecule–surface contacts may be established. Indeed, a low-mobility behavior is observed subsequently (4–20 ps interval, region b), in which the motion is confined to an area approximately 1 × 1 Å^2 (highlighted in green in Figure 2,

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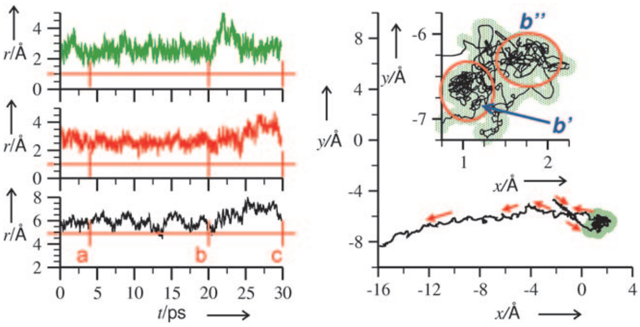

Figure 2. Left: Selected distances *r* versus time between [Cu(hfa)$_2$tmeda] and hydroxylated silica surface atoms. Black, red, and green lines correspond to the shortest distances of Cu, tmeda H, and hfa F atoms, respectively, from the closest surface atom. The a, b, and c labels refer to the different regimes described in the text. Right: Projection on the *xy* plane, parallel to the substrate surface, of the approximately 30 ps trajectory of Cu (black line). The red arrows indicate the time direction of the trajectory. A low-mobility region (regime b) of the trajectory is highlighted by a green shadow and magnified in the inset.

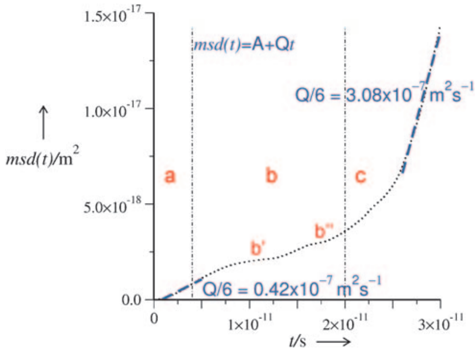

Figure 4. Mean square displacement calculated for the [Cu(hfa)$_2$tmeda] central atom (Cu) on top of the hot hydroxylated silica surface (black dotted line). *msd*(*t*) sections showing linear behavior versus time have been interpolated using a least-square fitting to *msd*(*t*) = A + Q*t*. In the linear segments in regions a and c (blue dashed lines), the values of Q/6 provide an estimation of the diffusion coefficient in these regions. The vertical dot-dashed lines mark the borderlines between the a, b, and c regimes.

right). A closer inspection of this trajectory segment allows us to identify two subregions, b′ and b″ (inset, Figure 2), in which the complex is localized in two small areas (ca. 0.25 Å^2 each). This regime can hence be associated with two physisorption events separated by a short site-to-site diffusion phase. Finally (20–30 ps interval, region c), a fast "roll-and-go" diffusion of the complex over the substrate takes place. In this high-mobility regime (see Figure 3 and movies in Supporting Information), the [Cu(hfa)$_2$tmeda] ligands change their position and orientation relative to the surface by rotating around an imaginary axis passing through the complex center (Cu atom). Moreover, although a pseudo-octahedral geometry around Cu is basically maintained, the molecule instantaneously undergoes severe conformational distortions while its motion remains confined to a layer close and almost parallel to the surface. The [Cu(hfa)$_2$tmeda] behavior, far more complex than that of a rolling hard sphere, is therefore the first observed manifestation of a novel temperature-induced surface transport mechanism.

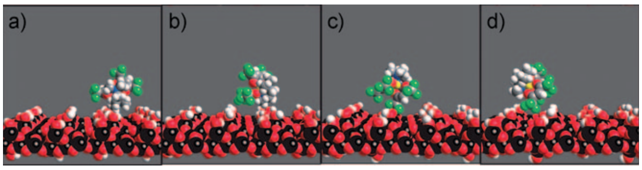

Figure 3. Snapshots taken from the last part of the trajectory (region c) highlighting the roll-and-go diffusion of [Cu(hfa)$_2$tmeda] on hydroxylated silica. Pictures are separated by 2.4 ps from (a) to (d). Atom color codes as in Figure 1.

The mean square displacement $msd(t) = \langle[\mathbf{r}(t) - \mathbf{r}(0)]^2\rangle$ calculated for the Cu atom along the trajectory (Figure 4) illustrates the differences in the aforementioned three regimes. In region a, a diffusive motion is detected, as indicated by the linear behavior of *msd*(*t*) versus *t*.[10] The diffusion coefficient of the complex on top of the hot surface is estimated to be approximately $0.4 \times 10^{-7}\,m^2s^{-1}$ for such a regime. In region b, *msd*(*t*) shows two plateaus that can be associated with the two physisorption events b′ and b″. Finally, in region c, characterized by high complex mobility, *msd*(*t*) shows a rapid increase. Correspondingly, a large diffusion coefficient (ca. $3 \times 10^{-7}\,m^2s^{-1}$) has been estimated. It is worth pointing out that the high-mobility phase follows a labile physisorption event, thus highlighting the relevance of energy transfer between the hot surface and the molecule in this context. Such a behavior is in line with the fact that *kT* (ca. 1.5 kcal mol^{-1}) is an appreciable fraction of the calculated complex physisorption energy (5.0 kcal mol^{-1}).

Besides disclosing such rich and multifaceted dynamics, the simulation reveals that interaction with the hot surface strongly perturbs the [Cu(hfa)$_2$tmeda] internal degrees of freedom, as clearly emerges from the time behavior of the Cu–ligand (Cu–L) bond lengths (Figure 5). All Cu–L distances show pronounced oscillations;[11] the largest effects are detected for the weakest contact in the gas-phase molecule,[7] Cu–O1, which elongates up to about 4 Å. In the physisorption regime b, Cu–L bond distortion correlates with separation from the surface; for example, O1*, which is closer to the surface than O1, shows larger bond oscillations (Table 1). Therefore the complex loses its C_2 symmetry as a consequence of interactions with the hot surface, and the extent of symmetry breaking is more pronounced than for a 0 K surface (see Table 1). After approximately 13 ps, the oscillation amplitudes of all the Cu–L bonds undergo a non-negligible increase, which becomes remarkable in region c. This trend, where the Cu–O2 distances transiently become even longer than the Cu–O1 ones, gives evidence of the large structural distortions experienced by the molecule in the fast diffusion regime and points to a general excitation of the molecular internal modes. Interligand interactions, which are relevant for activation, are promoted as well. In particular, close contacts between tmeda CH_3 protons and hfa O1 atoms (down to 1.73 Å; Figure 5 e) suggest a possible decomposition

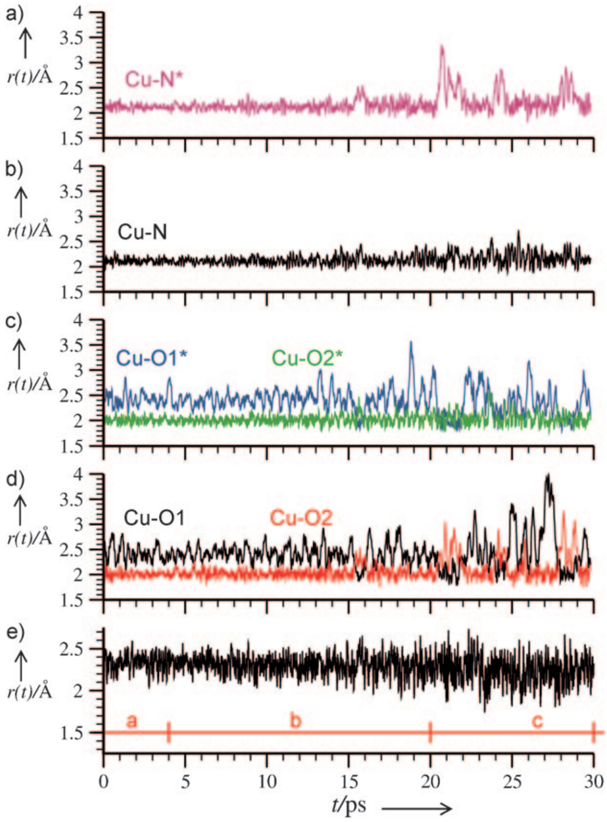

Figure 5. a–d) Time evolution of Cu–ligand distances and e) shortest tmeda H–hfa O1 distance *r*(*t*) along the simulation. The a, b, and c labels refer to the different regimes described in the text.

Table 1: Minimum ($R_{\min}$), maximum ($R_{\max}$), and average ($\langle R_{Cu}\rangle$) distances between Cu and ligand atoms and average distances of the O1, O1*, O2, O2*, N, N* atoms from the closest surface oxygen atom ($\langle D_{surf}\rangle$).[a]

Atom	$R_{\min}$	$R_{\max}$	$\langle R_{Cu}\rangle$	R_{Cu}	$\langle D_{Surf}\rangle$	D_{surf}
O1	1.882	2.963	2.41 ± 0.17	2.375	5.62 ± 0.79	5.534
O1*	1.858	3.565	2.43 ± 0.20	2.419	4.81 ± 0.63	3.898
O2	1.748	2.518	2.03 ± 0.07	2.012	4.85 ± 0.63	4.772
O2*	1.817	2.452	2.02 ± 0.07	2.007	7.40 ± 0.43	6.513
N	1.933	2.445	2.12 ± 0.07	2.096	5.86 ± 0.41	5.800
N*	1.922	2.914	2.14 ± 0.10	2.113	4.71 ± 0.29	4.700

[a] Distances in Å. Data from the trajectory part corresponding to complex physisorption (stage b, 4–20 ps) at 750 K. For the averaged parameters, the standard deviations are reported. R_{Cu} and D_{surf} values refer to an optimized (0 K) complex–surface structure. The guess configuration for geometry optimization was taken from stage b of the trajectory.

path of the complex by detachment of the hfa ligand through protonation of O1 by the tmeda H atoms.[12] These interactions are emphasized in the rolling diffusion phase.

In summary, the early activation stages of a molecular complex on a substrate at high temperature (750 K) have been unraveled by an FPMD simulation. The hot surface induces significant bond oscillations and interligand interactions on the molecule, which alternates physisorption with low or high molecular mobility. In the spanned simulation time (ca. 30 ps), a novel phenomenon emerged: fast “roll-and-go” diffusion. Such a regime greatly enhances the vibrational excitation of the molecule, increases the probability of highly energetic intermolecular collisions on top of the substrate, and configures itself as a general activation route, which may be operative in a broad variety of processes at hot surfaces.

Experimental Section

The behavior of [Cu(hfa)$_2$tmeda] on a model hydroxylated silica surface[13] was simulated within density functional theory (DFT) using periodic boundary conditions and plane waves (PW) basis sets. The surface was modeled by periodically repeating a 1 nm thick slab of stoichiometry $Si_{36}O_{72}\cdot 8H_2O$ (with water dissociatively chemisorbed) and dimensions of 1.69 × 1.69 nm^2. The simulation system, consisting of 185 atoms, was built by placing a [Cu(hfa)$_2$tmeda] molecule on the model surface in a 1.69 × 1.69 × 2.6 nm^3 simulation box. FPMD[14] simulations were performed on this system with the CPMD code (www.cpmd.org). Ultrasoft pseudo-potentials[15a] were adopted for Cu, F, O, N, C, and H atoms, while a norm-conserving pseudo-potential was adopted for Si.[15b,c] PW cut-off values were 30 and 240 Ry for the orbital expansion and electronic density, respectively. The Perdew–Burke–Ernzerhof spin density functional (multiplicity = 2)[16] was adopted. Benchmark calculations for this level of theory can be found elsewhere.[7] A time step of 0.121 fs was used for the trajectory integration. The inertia parameter for the electronic coefficients was 500 au. After 5 ps equilibration, data were collected along a ca. 30 ps production run in the canonical ensemble using a target temperature of 750 K and Nose–Hoover thermostats.[17] Geometry optimization was performed on the lowest-energy configuration sampled in the trajectory. The complex binding energy was calculated by subtracting from the energy of such an optimized configuration the sum of the energies of the optimized substrate slab and that of the isolated complex calculated in the same simulation box. Optimizations were performed using a quasi-Newton algorithm[14b] and a convergence criterion of 10^{-4} au as maximum force per atom. The calculated surface–[Cu(hfa)$_2$tmeda] binding energy was 5.0 kcal mol^{-1}.

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