

Spatially Resolved Vibronic Excitations of an Isolated Adsorbed Organometallic Complex via Multiple Tunneling Channels

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Vibronic excitations of molecules at nanoscale interfaces are important for molecular electronics and spintronics and have therefore attracted considerable attention. For single molecules in mechanically controlled break junctions or in a scanning tunneling microscope (STM), vibronic excitations are typically described by a double-barrier tunneling junction model. In this model, a homogeneous electric field is considered and the atomic structure of the metal contacts is neglected. Here, we report experimental STM data of a new nonplanar organometallic complex, $[\text{Mo}(\text{CO})_3(\text{Pyridine}_3\text{S}_3)]$, on $\text{Ag}(111)$. Spatially resolved maps of the vibronic excitations show several features related to the reordering of the occupied molecular orbitals due to the rapidly decaying potential of the tip apex. Such rearrangement leads to a significant shift in the vibronic levels as the tip position is changed. These observations, together with our modelling results, demonstrate that the molecular orbitals can be controlled by the field of the STM tip, whose atomic-scale variation deserves more attention in studies of nonplanar molecules.

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Vibronic coupling, i.e., the interaction of electronic and vibrational motion, is typically described within a Franck-Condon picture [1,2], where the molecule undergoes an instantaneous electronic excitation and the unchanged nuclear coordinates then correspond to a vibrational excited state. This effect has important implications for charge transport across single-molecule junctions, and scanning tunneling microscopy is an ideal technique for studying this excitation [3–8]. In scanning tunneling spectroscopy (STS), vibronic excitations manifest themselves as sidebands of the transient charge resonances [9–19]. In most studies, the molecules were placed on a decoupling layer to increase the lifetime of the charged state and the vibronic coupling.

A double barrier tunneling junction (DBTJ) model [9–22] has been used to describe the evolution of vibronic resonances in STS. In this model, the scanning tunneling microscope (STM) tip is planar on the scale of the molecule, and shifts the electrostatic potential of the whole molecule relative to the surface. Although this model neglects the key property of a STM tip, namely, its

sharpness, agreement with experimental data is achieved by treating the relative voltage drops across the tip-molecule and molecule-sample parts of the junction as an adjustable parameter.

A notable exception is Ref. [23], where a spatially resolved voltage drop was calculated and shown to cause two-level conductance fluctuations [24]. The electrostatic potential of an atomically sharp tip apex has also been investigated in the context of STM manipulation [25,26]. In addition, the electromagnetic modes of atomic scale structures are being intensively studied [27–31]. With respect to the transient charging of molecules, Krane *et al.* reported that vibronic excitations of an oligothiophene on a MoS_2 layer depend on the tip position on a submolecular scale [32].

Here, we report the vibronic excitations of a nonplanar complex $[\text{Mo}(\text{CO})_3(\text{Py}_3\text{S}_3)]$ (Py_3S_3 = thiacalixpyridine) on $\text{Ag}(111)$ surface using a low-temperature (4.6 K) STM. Detailed methods are provided in Supplemental Material [33]. In the spectra, the vibronic levels exhibit a pronounced dependence on the tip position (both vertical and horizontal). The vibronic resonances are resolved as multiple features in dI/dV images. According to our calculations, the resonances are governed by the original occupied molecular orbitals near the Fermi level of $[\text{Mo}(\text{CO})_3(\text{Py}_3\text{S}_3)]$ and the confined potential of the tip apex. Rather than rigidly shifting the entire molecular states [9,10], the electric field of the tip modifies these frontier

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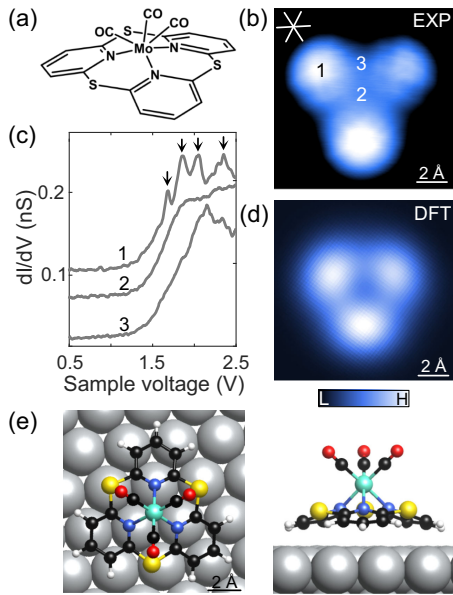


FIG. 1. (a) Chemical structure of $[\text{Mo}(\text{CO})_3(\text{Py}_3\text{S}_3)]$. (b) STM topograph of an isolated $[\text{Mo}(\text{CO})_3(\text{Py}_3\text{S}_3)]$ on Ag(111). Set point: 1.6 V, 10 pA. The white lines denote the close-packed direction of the substrate. (c) dI/dV spectra obtained with the tip positioned at the CO lobe (1), the molecule center (2), and the gap between two COs (3). The tip positions are depicted by 1–3 in (b). To clarify, the spectra are vertically shifted. (d) Simulated STM image by DFT with bias set at 1.5 V (e) Relaxed molecule structure on Ag(111) surface shown from top view (left panel) and side view (right panel). The cyan, black, red, blue, yellow, white, and gray spheres represent Mo, C, O, N, S, H, and Ag atoms, respectively.

orbitals, leading to diverse shifts of the vibronic levels over a wide bias range.

$[\text{Mo}(\text{CO})_3(\text{Py}_3\text{S}_3)]$ [Fig. 1(a)] was prepared according to Ref. [40] and sublimated onto Ag(111) kept at room temperature (see Supplemental Material [33]). After deposition, we find isolated, clover-shaped molecules [Fig. 1(b)]. Comparison with a topograph calculated with density functional theory (DFT) [Fig. 1(d)] reveals that the protruding lobes originate from the CO groups of the molecule. The relaxed adsorption structure is shown in Fig. 1(e). Spatially resolved differential conductance spectra [Fig. 1(c), see also Supplemental Material [33]] reveal a broad feature and several resonance peaks (black arrows) above the CO lobes (1). The peaks are less pronounced above the molecular center (2) and between CO groups (3).

The evolution of the resonances with the tip position was measured on the molecule shown in Fig. 2(a). The resonance at ≈ -250 mV is hardly affected by the lateral tip position [Fig. 2(b)]. However, the resonances at positive V [Figs. 2(c)–2(f)] shift significantly. Similar observations from other complexes [10,19] have been interpreted using the DBTJ model as being due to vibrations coupled to a frontier orbital of the molecule. In this model, a fraction η of the bias voltage drops between the molecule and the

surface, shifting the molecular levels by ηV with respect to the surface Fermi level (E_F) [11,12,22]. At the onset voltage V_0 , a molecular state aligns with the surface E_F , allowing current to flow through the molecule. As η is tip-height dependent [9,10,12,14,22,41], a higher V_0 is required at a larger tip-molecule distance (smaller η). During the electron transport, an electron or a hole is attached to the molecule, resulting in a transiently charged state. The associated vibrational modes can be detected at larger $|V|$. In particular, Wu *et al.* observed that the vibrational peaks associated with the positively (negatively) charged state shift strongly at positive (negative) V with the shift being proportional to the tip-molecule distance [10]. At the opposite polarity, the shift was small and inversely proportional to this distance. We therefore assign the observed vibrational resonances to the transient ionization state, i.e., the discharging of the highest occupied molecular orbital (HOMO). The peak positions derived from Fig. 2(c) are shown in Fig. 2(d). They vary linearly with the tip height with slopes of 3.1, 3.1, 3.6, 3.3, and 3.8 meV/pm for peaks 1–5, respectively.

Within the harmonic approximation, a single vibrational mode produces evenly spaced resonances [9,10]. However, the separations of nearest peaks in Figs. 2(c) and 2(d) vary drastically: 260 (5–4), 100 (4–3), 200 (3–2), and 220 meV (2–1). At a lower tip height, small peaks (red arrows) appear on the right shoulders of 2 and 5, separated by 30 and 50 meV from the respective main peaks. Unevenly spaced features have also been observed from tetrabromo-tetraaza-pyrene [19], which was ascribed to anharmonic effects and the atomic rearrangements caused by a charge redistribution [42]. Here, we propose a different mechanism, namely, vibrational excitations that proceed via distinct tunneling channels, as will be discussed below.

Figure 2(e) presents dI/dV spectra recorded from lateral tip positions along the dotted line in Fig. 2(a), with an open feedback loop. The resonance peaks of dI/dV versus lateral position form intersecting parabola. At shorter tip-molecule distance, the same features are observed [Fig. 2(f)], albeit at lower voltages. Owing to weaker signal variation, however, d^2I/dV^2 is displayed for contrast enhancement. The vibronic levels form two sets of parabola with minima located on the left (A) and right (B) side of CO [Fig. 2(f)]. The voltages leading to resonances vary substantially on a subnanometer scale, i.e., on the lateral scale of the complex itself. Dashed curves indicate the parabola that are due to the transient ionization levels of the molecule. The parabolic contours at higher energies (black arrows) correspond to the vibronic excitations. The minima at A and B indicate the presence of two centers on either side of the CO subunit, where the transient charging and vibronic excitations proceed at particularly low voltages. Given the molecular threefold symmetry, six centers are anticipated and also discernible in the constant-height

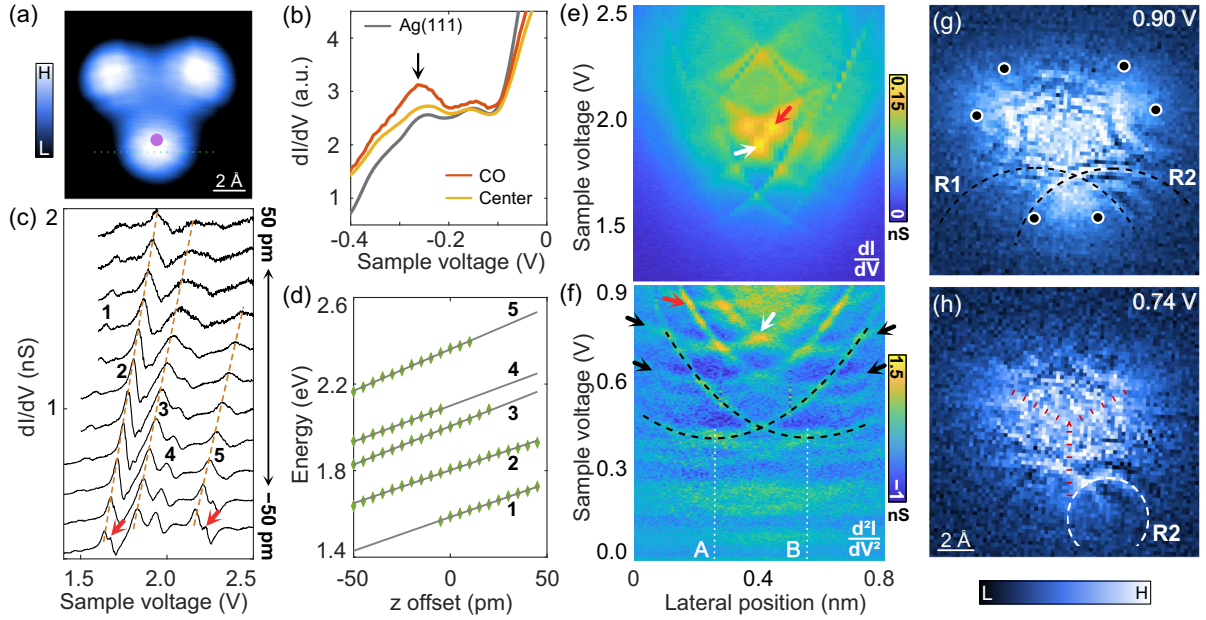


FIG. 2. (a) STM topograph of a [Mo(CO)₃(Py₃S₃)] molecule. Set point: 1.6 V, 10 pA (b) dI/dV spectra obtained above the molecule with the tip height set at -2.5 V and 100 pA. The peak denoted by the black arrow is assigned to the HOMO. The spectra of a wide bias range are shown in Fig. S2. (c) dI/dV spectra recorded at tip heights (z) from -50 to 50 pm. 0 pm corresponds to the tip height at 1.6 V and 10 pA. The lateral tip position is marked by a purple dot in (a). Brown dashed lines guide the eye to the evolution of a few vibronic peaks. The main peaks are denoted by 1–5. (d) The energies (green diamonds) of the vibronic peaks in (c) as a function of vertical tip offset, fitted by straight lines. (e),(f) Spatially resolved maps of dI/dV (e) and d^2I/dV^2 (f) recorded while the tip was moved along the dashed line in (a) at fixed height. The tip heights in (e) and (f) were set with the tip positioned over CO at 1.6 V, 10 pA, and 0.9 V, 200 pA, respectively. Contours of the ionization levels are highlighted with dashed parabolae. The respective minima are located at tip positions A and B. Black arrows mark some contours that are due to vibrational excitations. White and red arrows indicate positions where two vibronic excitations coincide and the signal amplitude is enhanced. (g),(h) High-pass filtered constant-height dI/dV images measured at $V = 0.9$ (g) and 0.74 V (h). Black dashed arcs (R1 and R2) show the vibrational modes arising from two different centers (black dots) of the same CO (g). The white dashed circle in (h) denotes the same vibrational mode (R2) in (g). The red dashed lines represent the orientations of the CO subunits.

dI/dV images [black dots in Fig. 2(g)]. Interestingly, an enhanced signal is present at the intersections between the two sets of vibronic levels [white and red arrows in Figs. 2(e) and 2(f)].

In dI/dV maps, charging and vibronic excitations appear as concentric rings around atomic-scale quantum dots [19,21,22,41,43,44]. In the present case, however, we find multiple centers close to the edges of a molecule. As a consequence, arcs are observed instead of complete rings; for example, R1 and R2 above the same CO subunit in Fig. 2(g). When varying V at fixed tip height [Fig. 2(h) and Movie 1] or the tip height at fixed V [Fig. S3(a)–S3(c)], the arc diameters change.

The electric field in the junction is comprised of two components: (1) E_0 , resulting from the spherical tip body and the planar surface; and (2) E_p , due to the polarized atomic-scale tip apex [25,26]. Considering the small size of the molecule, E_0 can be approximated as homogeneous field [10], which implies a rigid shift of the molecular levels when the tip height is varied. E_p is more localized and exhibits a large gradient [25,26]. This potential can be approximated as $V'(r) \propto r^{-\tau}$, with $\tau = 2$ estimated from

Refs. [25,26,45]. Details are presented in Supplemental Material [33].

We consider the occupied states near E_F , namely, the twofold degenerate HOMO (HOMO₁ and HOMO₂) and the HOMO-1 [Fig. 3(a)], and treat the atomic-scale potential as a perturbation. Other orbitals are neglected because they are separated by > 2 eV while the gap between the HOMOs and the HOMO-1 is only 0.264 eV (Fig. S4). Moreover, they are hardly affected by the perturbation (Fig. S5). Taking the HOMO-1 into account is crucial because the position dependent matrix elements $[\langle \psi_{1(2)} | V' | \psi_3 \rangle]$ describing mixing between HOMO₁₍₂₎ and HOMO-1 are of similar magnitude to $\langle \psi_1 | V' | \psi_2 \rangle$. Depending on the tip position the three orbitals mix differently resulting in three new eigenstates, denoted α , β , and γ , whose energies are displayed in Fig. 3(b). The projection of the eigenstates onto HOMO₁ is represented with colors. As the tip moves across the CO group [dashed line in Fig. 3(c)], the energy of state $\alpha(\beta)$, $E^{\alpha(\beta)}$, initially increases and then decreases, and the energy maximum dwells on the left (right) side of the CO group [blue (brown) arrows in Fig. 3(b)]. A two-dimensional map of the energy

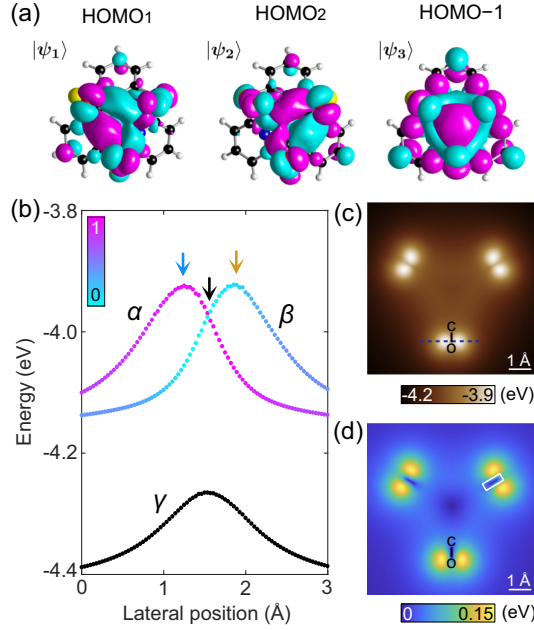


FIG. 3. (a) Isodensity plots of the two degenerate HOMOs ($|\psi_1\rangle, |\psi_2\rangle$) and the HOMO-1 ($|\psi_3\rangle$) of $[\text{Mo}(\text{CO})_3(\text{Py}_3\text{S}_3)]$ as calculated in the gas phase without external potential. (b) Energy of new eigenstates α , β , and γ vs the lateral position of the tip at fixed height. The colors denote the projection of eigenstates onto HOMO₁, i.e., $\langle\psi_1|S\rangle^2$, where S represents state α and β . The projection of state γ is not shown. The dashed line in (c) indicates the trajectory of the tip apex. (c) Lateral distribution of the maximum energy of states α and β . (d) $|E^\alpha - E^\beta|$ obtained simultaneously as (c).

[Fig. 3(c)] reveals six maxima with the symmetry observed in the experimental dI/dV maps [Fig. 2(g)]. Moreover, states α and β intersect [black arrow in Fig. 3(b)] at specific tip positions, which collectively outline a narrow strip along the CO groups [white rectangle in Fig. 3(d)]. In the experimental data, the intersection of the ionization contours occurs in similar areas.

The modeling results lead to the interpretation illustrated in Fig. 4. State $\alpha(\beta)$ is aligned with the surface Fermi level at the voltage

$$V_0 = E_0^{\alpha(\beta)} / (\eta e) \quad (1)$$

where $E_0^{\alpha(\beta)} = E_F - E^{\alpha(\beta)}$ and E_F is the Fermi level of the unbiased junction [10]. At higher voltages, states α and β are shifted above the surface Fermi level, and vibronic excitations occur via both states. Figure 3 implies that $E_0^{\alpha(\beta)}$ is controlled by the position of the tip apex. When the tip is positioned on the left side of the CO [Fig. 4(a)], the state α lies higher than β and the excitations of α appear at lower V in dI/dV spectra [e.g., position A in Fig. 2(f)]. The sequence of the states α and β is reversed on the right side of CO [Fig. 4(c) and position B in Fig. 2(f)].

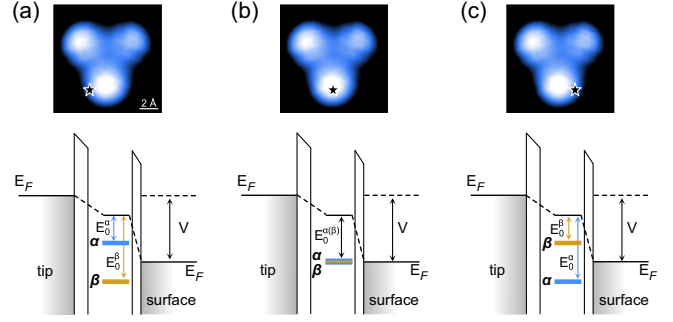


FIG. 4. (a)–(c) Top panel: tip positions (asterisks) with respect to the molecule; bottom panel: corresponding energy schematics. The molecule is insulated from the tip and the sample by tunneling barriers. The states α and β are indicated by blue and brown lines, respectively. Colored arrows show the energy differences of these states and the Fermi level of the unbiased junction.

When the tip is centered above CO, the states α and β are degenerate [Fig. 4(b) and black arrow in Fig. 3(b)], resulting in identical ionization and vibronic levels in the spectrum. The peak intensities of the states add up to a stronger resonance as seen in Figs. 2(e) and 2(f) (white arrows). An enhancement also occurs when any vibronic levels of the two states are aligned [red arrows in Figs. 2(e) and 2(f)].

According to Eq. (1), the variation of V_0 of each state is opposite to its energy. Therefore, the trend in the variation of the ionization levels as a function of lateral tip position [Fig. 2(f)] appears inverted with respect to those in Fig. 3(b).

The vibronic resonances in a dI/dV spectrum can be divided into two groups that originate from states α and β , respectively. Their energies are affected by the position of the tip relative to the centers shown in Fig. 2(g). These two groups of resonances may shift differently when the tip position is changed laterally or vertically. This can lead to unevenly spaced resonances or different slopes for the resonance energies as a function of the tip height. Such effects may also be observed at symmetric tip positions [Figs. 2(c) and 2(d)] when the tip apex is not highly symmetric.

Using the approach of Refs. [19,22,41], the tip position-dependent η is estimated as $\eta = 1/(1 - V_{\text{ion}}/V_{\text{HOMO}})$, where V_{HOMO} and V_{ion} are the voltages of the HOMO and ionization peaks, respectively. For the tip height in Fig. 2(f), $\eta = 0.22$ – 0.38 . This value is comparable to previously reported data from molecules on insulating layers (0.2 [9], 0.25 [14]) or in direct contact with a metal surface (0.12–0.35 [19]). It should be noted, however, that this estimate neglects the field induced orbital mixing.

In our model, the inclusion of all three orbitals [HOMO_{1(2)}} and HOMO-1] and the rapid decay of the potential are essential to reproduce the experimental features. Reduced models with only two degenerate HOMOs or a weaker potential decay ($\tau < 2$) (Fig. S6)

do not match the data, in particular the intersection of the vibronic levels.

In summary, the atomic-scale electrostatic potential of a STM tip has been shown to induce position-dependent shifts of the molecular orbitals of $[\text{Mo}(\text{CO})_3(\text{Py}_3\text{S}_3)]$ on Ag(111). Although the molecule is in direct contact with the metal, these shifts are as large as ~ 200 meV. Conductance maps exhibit complex patterns because the tunneling current flows simultaneously through several molecular states, which are differently affected by the potential. The observations show that the electrostatic potential of the STM tip deserves further attention, especially when studying nonplanar molecules.

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Data availability—The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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