Electron-Vibron Coupling at Metal-Organic Interfaces

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We study the significance and characteristics of interfacial dynamical charge transfer at metal-organic interfaces for the model system of organic semiconductor NTCDA on Ag(111). We combine infrared absorption spectroscopy and dispersion-corrected density functional theory calculations to analyze dynamic dipole moments and electron-vibron coupling at the interface. We demonstrate that interfacial dynamical charge transfer is the dominant cause of infrared activity in these systems and that it correlates with results from partial charge and density of states analysis. Nuclear motion generates an additional dynamic dipole moment but represents a minor effect except for modes with significant out-of-plane amplitudes.

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Metal organic interfaces are essential elements influencing the performance of molecular electronics applications like light-emitting devices or field-effect transistors. Here, electronic excitations via charge-transfer excitons often play a key role. The formation mechanisms of these excitons via electron-hole pair (EHP) formation at the interface thus need to be understood. The coupling of EHP to adsorbate vibrations (electron-vibron coupling) is one way to induce a interfacial dynamical charge transfer (IDCT) which delivers key information about the electronic structure at the interface. The IDCT by an orbital dipping in and out of the Fermi sea is well-known and was previously described for small molecules on metal surfaces\textsuperscript{[1, 2, 3]}. It has been found for larger organic adsorbates on metal surfaces more recently\textsuperscript{[4, 5, 6, 7, 8, 9, 10, 11]}. The underlying basic mechanisms were analyzed by Langreth\textsuperscript{[10]}. Currently lacking is a combined theoretical and experimental proof for IDCT at a relevant metal-organic interface, a quantification of the nuclear and electronic contributions\textsuperscript{[10]}, and a rationalization of the amount of IDCT for specific vibrational modes at the interface.

Prerequisites for the occurrence of IDCT are (i) partial occupation of an adsorbate molecular orbital upon adsorption and (ii) strong electron-vibron coupling to the substrate\textsuperscript{[11, 12]}. This was met in early studies for CO on Cu(100)\textsuperscript{[1]} and O$_2$ on Pt(111)\textsuperscript{[2]}. Later, IDCT was observed in studies on fullerene C$_{60}$\textsuperscript{[12, 13]}. The IDCT is also relevant for the strong damping of high frequency vibrations of adsorbates via energy dissipation, which was one of the driving forces for its analysis\textsuperscript{[1, 10, 14]}. Line width analysis for IR measurements then leads to an estimate of vibrational lifetimes\textsuperscript{[10]}. The occurrence of electron-vibron coupling is essentially a breakdown of the Born-Oppenheimer approximation. For systems with strong non-adiabaticity, IDCT thus leads to asymmetric line shapes in vibrational spectra\textsuperscript{[10, 11]}. While a theoretical treatment of this asymmetry requires a time-dependent analysis\textsuperscript{[15]}, which is not feasible for the system investigated here, an empirical evaluation for NTCDA on Ag(111) has been presented recently by Braatz et al.\textsuperscript{[13]}. In this Letter, we will present a microscopic view on the vibrational modes of NTCDA on Ag(111) based on experiment and computation focusing on the quantitative analysis of IDCT on the observed infrared (IR) intensity distribution. We correlate this to results of charge-transfer analysis associated with the electron-vibron coupling. We demonstrate that IDCT is the dominating effect for electron-vibron coupling in this system, quantify the charge-transfer associated with IDCT and verify that IDCT is crucial for symmetric $a_g$ modes to become IR-active, in stark contrast to the free molecule. The system chosen here constitutes a model system for a more general class of metal-organic interfaces with noble metal substrates and planar $\pi$-conjugated organic semiconductor species and we expect the results to be transferable to systems with similar energy level matching. Quantification of electron-vibron coupling has been identified as a major challenge for these interfaces\textsuperscript{[19]}. Experimentally, infrared absorption spectroscopy (IRAS) is the method of choice to extract information regarding IDCT since it provides accurate vibrational energy and intensity measurements for modes of species located at the interface. Furthermore, IRAS implies strict selection rules and probes molecular layers in a non-destructive way. The IR intensity of a vibrational mode is proportional to the square of the dynamic dipole moment of this vibration: $I_{IR} \propto \mu_{\text{dyn}}^2$. Contributions to this dynamic dipole moment stem from nuclear motion ($\mu_{\text{nuc}}$) and dynamic charge transfer across the adsorbate-substrate interface (i.e. IDCT) resulting in an electronic contribution $\mu_{\text{elec}}$\textsuperscript{[10]}. For an adsorbate on a metal substrate only the $z$-component of this dipole contributes to the intensity due to dipole selection rules. Therefore, $\mu_{\text{nuc}}$ is determined by out-of-plane displacements of the adsorbate atoms.

Atomic and electronic ground state structures of metal-organic interfaces are well represented by
 dispersion-corrected density functional theory (DFT) [20, 21]. The description of vibrational spectra has also successfully been achieved in the past [22, 23].  

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTCDA) represents a model system with typical properties for an important class of organic semiconductors suitable for metal-organic interfaces: (i) highly symmetric planar atomic structure, (ii) delocalized \( \pi \)-electron system, (iii) strong binding to metal surfaces with multiple bonding mechanisms. The totally symmetric \( a_g \) modes are IR-inactive for the free molecule (\( \mu_{dyn} = 0 \)). According to IRAS the vibrational spectrum of NTCDA on Ag(111) is strongly dominated by these in-plane vibrational modes, which suggests a notable contribution to \( \mu_{dyn} \) from IDCT [18]. Near edge x-ray absorption fine structure (NEXAFS) measurements showed strong electron-vibron coupling in this system which renders it highly suitable for the quantitative determination of IDCT [24].

Computational investigations applied dispersion-corrected DFT computations at the GGA level (PBE-D3) [25, 26] in a plane wave approach using the projector augmented wave method with an energy cutoff of 350 eV and a \( \Gamma \)-centered (3 3 1) Monkhorst-Pack k-space grid within the code VASP 5.2.12 [28–31]. The adsorption structure of one NTCDA molecule on a four-layer Ag(111) slab (lattice parameter determined as \( a = 4.073 \) Å) was optimized in a \( 4 \times 4 \) supercell [22]. IR spectra for relaxed structures (without employing empirical scaling factors) were derived via finite-differences calculation of a partial Hessian matrix, displacing adsorbate atoms (a negligible influence of substrate atom displacement was found) and computing intensities based on the z-component of \( \mu_{dyn} \). IDCT has been deduced by displacing the ground state structure along the respective normal coordinates in positive and negative direction. For the displaced structures, projected density of states (pDOS) were derived together with partial charges via Atoms In Molecules (AIM) [33, 34] and Natural Population Analysis (NPA) [35, 36] approaches.

NTCDA preferentially adsorbs with the central C=C bond occupying a bridge position on the Ag(111) surface as shown in Figure 2. The detailed discussion of structural parameters which agree well with experimental data of x-ray standing wave measurements is presented elsewhere [37]. The molecule is bonded by van-der-Waals interactions together with direct oxygen-silver chemical bonds leading to a strong adsorption and thus fulfilling the first prerequisite for IDCT [8]. The partial filling of the LUMO upon adsorption is a well-known phenomenon for NTCDA [38] and thus the second requirement for IDCT is also satisfied.

In Figure 3 the experimental and computed IR spectra of NTCDA on Ag(111) are displayed. The IRAS spectrum refers to 0.15 monolayers deposited at 28 K. The low temperature ensures that isolated NTCDA molecules are present and the formation of denser islands is avoided, in accordance with the arrangement used in our theoretical analysis. In order to improve the noise level, the spectrum displayed represents the sum of several consecutive measurements. Within this series no alterations in vibrational peak positions and intensities have been found. Comparison to spectra for the relaxed monolayer of NTCDA on Ag(111) yield moderate frequency shifts and slight intensity variations most probably due to some modest structural modification as a result of the different local environment. In general, we obtain a very good agreement of experiment and theory in terms of vibrational energies and relative intensities. Thus, we can trust the computational spectrum to reproduce all the essential features of the IR spectrum for NTCDA on Ag(111) and focus on the further examination of the theoretical spectrum.

The determination of mode symmetry for the vibrations of the adsorbate has been achieved by comparison of the displacement patterns to the free NTCDA molecule. Although the molecule bends upon adsorption (Fig. 1) and point group symmetry reduces from \( D_{2h} \) to approximately \( C_{2v} \), the respective symmetry labels of modes are maintained as this way of labelling is the most helpful and intuitive one. In Figure 2 it is apparent that most of the intense IR bands belong to the totally symmetric \( a_g \) irreducible representation. Notably, these modes are IR-inactive in the free molecule since they do not exhibit dynamic dipole moments.

Next, we analyze the contribution of IDCT to the IR intensities by displacing the adsorbate atoms along the respective normal modes. For the most intense mode at 1565.6 cm\(^{-1}\) (\( a_g \)) the displacement pattern and the corresponding pDOS of the \( \pi \)-orbitals (composed of \( p_z \) atomic orbitals) of NTCDA are displayed in Figure 3 (top). Shown is the pDOS for the equilibrium structure (black line) together with the pDOS of the positively (orange line) and negatively (blue line) displaced structures. The equilibrium structure unveils the partial occupation of the bands stemming from \( \pi \)-orbitals (Fermi level crossing the pDOS line), thus reflecting the known partial LUMO occupation upon adsorption. For the displaced structures, we see a strong shift of the pDOS maximum and connected to this, a change in density at the Fermi level. Thereby, we directly observe the electron-vibron coupling in this system and we identify a strong depen-
idence of the electronic structure on the vibrational motion – a direct prove for IDCT. Analogous behavior is observed for the other \( a_g \) modes in the adsorbate.

Analyzing all modes (Table II), we find that IR-active modes exhibit a change in dynamic dipole moment perpendicular to the metal surface as expected from the selection rules discussed above. We quantified the contribution of IDCT to this intensity by analyzing the charge-transfer in the course of the vibration via partial charge schemes. We employed the density-based AIM scheme as well as the orbital/band-based NPA scheme which lead to virtually the same picture. If we have a significant change in partial charge of the adsorbate in the course of the vibration (i.e. a significant electron-vibron coupling), we see an active mode in the IR spectrum. This is a strong indication that IDCT is the leading effect in the system investigated. Furthermore, we can quantify the influence of charge-transfer on IR intensity as depicted in Fig. 2. The comparison with the dynamic dipole moment is merely a control here. We see a strong correlation of the charge-transfer for all \( a_g \) modes with the IR intensity, as indicated by both approaches (AIM, NPA).

Further support for the leading hypothesis can be found by analyzing the modes exhibiting different symmetries. The modes at 717.9 cm\(^{-1} \) (\( b_{3u} \)) and 813.0 cm\(^{-1} \) (\( b_{3u} \)) and 1628.9 cm\(^{-1} \) (\( b_{1u} \)) exhibit significant, albeit much lower intensities in the experimental as well as the computed spectrum (Figure 2). For the \( b_{3u} \)-symmetric modes, we find a significant out-of-plane bending component as expected from symmetry considerations (\( \mu_{\text{dyn}} \) perpendicular to molecular plane). This can be quantified by computing the dynamic dipole moment stemming from this nuclear motion. We determined the respective value for \( \mu_{\text{nuc}} \) from the distorted structure without the presence of the substrate (Table II). The comparison of \( \mu_{\text{dyn}} \) and \( \mu_{\text{nuc}} \) then gives a good estimate of \( \mu_{\text{elec}} \), i.e. the relative importance of IDCT and nuclear motion contribution to the dynamic dipole moment. For all \( a_g \) modes, we confirm IDCT as leading term since the \( \mu_{\text{nuc}} \) contributions are always small compared to the total dynamic dipole. A noteworthy exception is the mode at 1625.7 cm\(^{-1} \) which comprises a substantial vibrational amplitude for the downward-bent acyl-oxygen atoms at the periphery of the adsorbate. Moreover, analysis of the displacement patterns unveils a mixed nature for the two modes of adsorbed NTCDA at 1625.7 and 1628.9 cm\(^{-1} \) with a dominant \( a_g \) (\( b_{1u} \)) contribution for the former (lat-

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**Fig. 2.** Computed (top) and measured (bottom) IR spectrum for NTCDA on Ag(111). Intensity scaling (x5) was applied to signals below 1200 cm\(^{-1} \) in the computed spectrum. Flags indicate symmetry of respective modes applying free molecule nomenclature.

**Fig. 3.** Equilibrium Structure (ES) of NTCDA with positive (ES+\( \Delta Q \), orange) and negative (ES-\( \Delta Q \), light blue) distortion along the \( a_g \) mode at 1565.6 cm\(^{-1} \) (top) and along the \( b_{3u} \) mode at 1509.8 cm\(^{-1} \) (bottom) together with the corresponding pDOS (\( \pm 0.5 \) eV around the Fermi level \( E_F \)) stemming from \( p_z \) states of NTCDA. The displacement has been amplified for better illustration.
We suspect that this mixing of character is provoked by their close spectral vicinity. This also explains the surprising intensity of the mode at 1628.9 cm$^{-1}$ since the $b_{1u}$ symmetry should render it dipole forbidden on a metal surface ($\mu_{dyn}$ along NTCDa long axis). This example shows the limit of the assignments based on molecular mode-symmetries which is clear-cut for all other vibrations.

For the modes without significant intensities (i.e. 2, 4, 11, 12 in Table I), none of the two mechanisms discussed above (IDCT, nuclear motion) is active. Exemplarily, for the $b_{2u}$-symmetric mode at 1509.8 cm$^{-1}$, the pDOS is represented in Figure 3 (bottom). No dynamical change of the electron density at the Fermi level is found. The analysis of charge-transfer via partial charge analysis (Tab. II) also does not reveal significant contributions. Additionally, we conclude that for these modes nuclear motion in z-direction is missing either. Thus, although several of these vibrations are IR-active in the free molecule they do not show any intensity on the Ag(111) substrate due to screening of parallel dipoles on a metal surface.

**TABLE I. Computed properties of vibrational modes.**

| No. | $\nu$/$\text{cm}^{-1}$ | Sym. | Int. | $\mu_{dyn}$ | $\mu_{nuc}$ | $\Delta q_{AIM}$ | $\Delta q_{NPA}$ |
|-----|----------------|------|------|--------------|--------------|----------------|----------------|
| 1   | 648.1         | $a_g$| 0.004| 0.18        | 0.14         | 0.01           | 0.01           |
| 2   | 665.4         | $b_{2g}$| 0.000| 0.00        | 0.00         | 0.01           | 0.00           |
| 3   | 717.9         | $b_{1u}$| 0.058| 0.59        | 1.14         | 0.05           | 0.11           |
| 4   | 720.8         | $a_u$ | 0.000| 0.00        | 0.01         | 0.01           | 0.00           |
| 5   | 813.0         | $b_{2u}$| 0.002| 0.11        | 0.17         | 0.03           | 0.04           |
| 6   | 987.0         | $a_g$ | 0.002| 0.12        | 0.09         | 0.02           | 0.02           |
| 7   | 1104.2        | $a_g$ | 0.021| 0.37        | 0.04         | 0.05           | 0.04           |
| 8   | 1256.9        | $a_g$ | 0.038| 0.53        | 0.08         | 0.06           | 0.07           |
| 9   | 1345.5        | $a_g$ | 0.581| 1.95        | 0.10         | 0.26           | 0.42           |
| 10  | 1404.8        | $a_g$ | 0.133| 0.94        | 0.12         | 0.16           | 0.20           |
| 11  | 1435.8        | $b_{1u}$| 0.000| 0.02        | 0.00         | 0.00           | 0.00           |
| 12  | 1509.8        | $b_{2u}$| 0.000| 0.00        | 0.00         | 0.01           | 0.00           |
| 13  | 1565.6        | $a_g$ | 1.000| 2.51        | 0.21         | 0.39           | 0.55           |
| 14  | 1625.7        | $a_g$ | 0.264| 1.27        | 0.64         | 0.24           | 0.41           |
| 15  | 1628.9        | $b_{1u}$| 0.024| 0.37        | 0.18         | 0.07           | 0.12           |

a Computed IR intensity normalized to highest value.  
b Dynamical dipole moment difference between ES+ΔQ and ES-ΔQ structures in Debye.  
c Dynamical dipole moment difference between ES+ΔQ and ES-ΔQ structures in Debye (without substrate).  
d AIM partial charge difference between ES+ΔQ and ES-ΔQ structures in elementary charges.  
e NPA partial charge difference between ES+ΔQ and ES-ΔQ structures in elementary charges.

Examination of atomic displacement patterns can also explain the irregularities seen in Fig. 1 associated with the presumed linear relationship of partial charges with intensities. The largest deviations are seen for mode 14, where the contribution from the secondary mechanism (nuclear motion) is substantial. In comparison to mode 9 which shows similar charge-transfer ($\Delta q_{AIM}$, $\Delta q_{NPA}$) but much stronger IR intensity it can be concluded that the nuclear motion and the IDCT contributions obviously go in different directions. Such evidence agrees with the experimental observation regarding Fano line shapes of IR absorption bands which may display different signs of the asymmetry parameter [18]. The main factor here is whether the dynamic dipole moments due to nuclear displacement and IDCT point in the same or opposite directions. Thus we can elucidate the interdependence of both mechanisms via a detailed analysis of the intensity data.

In conclusion, we have investigated electron-vibron coupling effects associated with vibrational excitations at metal-organic interfaces for the model system NTCDa on Ag(111). Using infrared absorption spectroscopy and employing density functional theory based bonding and vibrational analysis we derived unequivocal evidence for the dominating role of interfacial dynamical charge transfer (IDCT) for dynamic dipole moments and associated infrared activities. Nuclear motion (out-of-plane bending) is found to be a secondary mechanism only. The magnitude of IDCT for totally symmetric vibrational modes can be understood by pDOS shifts and partial charge analysis. This provides a simple, quantitative measure for the complex phenomenon. Our general approach will facilitate the analysis of other relevant metal-organic interfaces with similar matching of energy levels in the future. On the basis of the thus obtained improved understanding, fine-tuning of the atomic and electronic structure for these types of interfaces becomes feasible.

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