

## Vibrational Frequency Used as Internal Clock Reference to Access Molecule-Metal Charge-Transfer Times

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Dynamical charge transfer processes at molecule-metal interfaces proceed in the few fs timescale that renders them highly relevant to electronic excitations in optoelectronic devices. Yet, knowledge thereof is limited when electronic ground state situations are considered that implicate charge transfer directly at the Fermi energy. Here we show that such processes can be accessed by means of vibrational excitations, with nonadiabatic electron-vibron coupling leading to distinct asymmetric line shapes. Thereby the characteristic timescale of this interfacial dynamical charge transfer can be derived by using the vibrational oscillation period as an internal clock reference.

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In modern material sciences, molecule-metal interfaces play a decisive role in the functionality of molecular electronic devices. Despite their importance in technological applications our microscopic understanding is lagging behind, probably due to the experimental difficulties to detect and single out the weak interface signatures. Acquiring comprehensive and conclusive evidence to expand our knowledge base regarding charge transfer processes at the molecule-metal interface remains challenging, though, especially defining the dynamics at ultrafast timescales [1].

Electron transfer processes across an interface connecting two weakly coupled electronic systems can be accessed in various ways, e.g., by means of breaking junctions [2], scanning tunneling microscopy [3], or by using photoemission spectroscopy, often in combination with pump-probe techniques [4–6]. While the former provide a precise map of the charge transport through well-defined single molecule junctions, the dynamics and time frame of the very process is revealed by the latter only. In photoemission experiments excitation typically involves electronic states far above  $\epsilon_F$ ; adoption of the derived dynamical properties to the neutral ground state (or the like) might then be problematic. Even more so, it is the charge transport at (or close to) zero energy, i.e., right at the Fermi energy, that is most relevant to the functioning of molecular electronic circuitry.

To assess the role of the molecule-metal interface in charge transport within devices it is thus indispensable to focus on charge transfer processes at or close to  $\epsilon_F$ .

In this Letter we will explore the electron dynamics for ground-state configurations of molecular adsorbates by means of vibrational mode excitation, provoking charge oscillations between the molecule and the metal substrate. Strictly speaking, this approach comprises a nonground state situation as well (vibrational excitation); however,

deviation thereof is only minor, representing a key advantage with respect to the mentioned electron spectroscopies. In our analysis we will take advantage of the fact that the degree of nonadiabaticity in the electron-vibron coupling is directly reflected in the vibrational line shape. As a key ingredient we will be using the vibrational frequency of specific modes of the molecular constituents to serve as an intrinsic and precise clock to extract the relevant timescale. The usage of an internal clocking scheme is both compelling and effective and has been used in a different context in core level photoemission studies (core hole clock) to derive charge transfer times down to the sub fs range for adsorbed rare gas atoms and diatomic molecules [7,8].

We will be examining vibrational line shapes to address the topic of electron-phonon and electron-vibron coupling in general, as well as questions regarding adiabaticity in particular. Electron-vibron coupling describes the oscillatory motion of atoms within (adsorbed) molecules in view of their coupling to electronic levels of the molecule and the metal substrate; given that the Born-Oppenheimer approximation is satisfied, the coupling between these two entities will proceed adiabatically. As vibrational excitations represent a nonequilibrium situation, e.g., in view of the electronic response of the surroundings, nonadiabaticity, to some extent, is commonly expected.

Historically, nonadiabatic electron-vibron coupling, in combination with electron-hole pair excitation, has been introduced to explain short lifetimes of vibrational modes associated with (small) molecules (CO, NO) adsorbed on metal substrates [9]. This irreversible process must be distinguished from the reversible charge oscillations across the molecule-metal interface (interfacial dynamical charge transfer, IDCT). Essentially, the former process primarily accounts for the homogeneous line broadening, studied in various instances in the past, while the latter produces

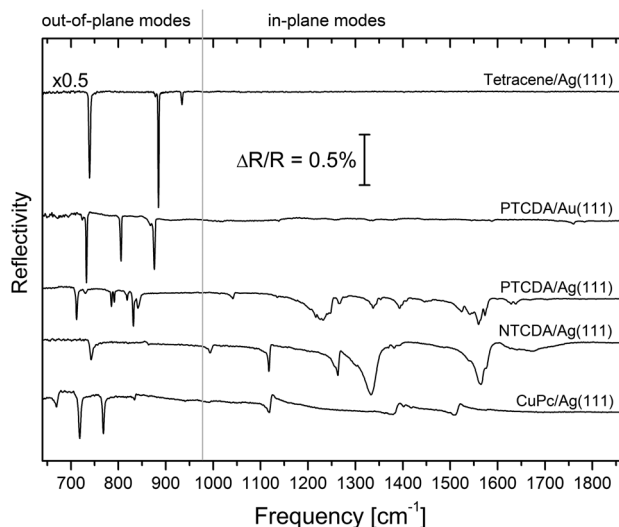


FIG. 1. Collection of infrared absorption spectra, obtained from CuPc/Ag(111), NTCDA/Ag(111), PTCDA/Ag(111), PTCDA/Au(111), and Tetracene/Ag(111) monolayers. The spectra were obtained at 80 K using a spectral resolution of  $2 \text{ cm}^{-1}$ ; individual curves are vertically offset for better display. The spectral region of C-H stretching modes has been omitted as the respective absorptions are negligibly small.

asymmetric line shapes of the respective vibrational bands; these can be accessed experimentally and have been described theoretically by Persson and Persson [9,10], as well as Langreth [11], who have derived expressions for the associated Fano-type line shapes. The model system at that time, adsorbed CO, however, did not show a noteworthy asymmetry, pointing at a negligible deviation from adiabaticity in the electron-vibron coupling. For quite some time, H(D) on W(100) was the only system displaying pronounced asymmetric vibrational line shapes [12,13].

Molecular layers studied in the present work are more promising as they come with a well-defined interface separating the two electronic systems, molecule and metal substrate; moreover, they display a characteristic set of vibrational modes with specific symmetry properties and displacement patterns. Infrared absorption spectroscopy (IRAS), used in this work, represents a versatile method to study such systems; due to its high spectral resolution and strict symmetry selection rules identification and characterization of molecular species is straightforward, based on their vibrational signatures (see Supplemental Material for a detailed description [14]). This is essential insofar as molecule-metal charge-transfer processes can be uniquely correlated with a particular molecular species.

In Fig. 1, a compilation of IR spectra associated with various molecular species adsorbed on noble metal substrates is presented. Specifically, Tetracene, PTCDA, NTCDA and CuPc, all of them planar molecules, have been deposited on Ag(111) or Au(111) surfaces. According to the literature, all molecular species are adsorbed with

their molecular plane oriented parallel to the surface [17–20]; deviations from planarity due to interactions with the substrate are only moderate or weak [18,20]. This weak molecule-metal coupling strength is reflected in insignificant frequency shifts of vibrational modes with respect to the values of the respective isolated or bulk species. Noteworthy exceptions are the C = O stretch modes of the acyl groups at the corners of NTCDA and PTCDA which are subject to a bold redshift by about  $150 \text{ cm}^{-1}$  when adsorbed on Ag(111), due to chemical interactions with substrate Ag atoms [20,21]. The key observation when comparing individual spectra in Fig. 1 is that the intensities of in-plane modes ( $\nu > 1000 \text{ cm}^{-1}$ ) vary distinctly, while the IR absorptions of out-of-plane modes (prevailing at  $\nu < 1000 \text{ cm}^{-1}$ ) display about similar dipolar strength. This marked variation of in-plane mode intensities is ascribed to IDCT being active for the bottom three spectra, while it is absent for the two uppermost spectra.

Apparently, the strength or weakness of in-plane vibrational modes is neither a specific property of the substrate, nor of a particular molecular species, as IDCT is absent for PTCDA on Au(111) while it is quite prominent when adsorbed on Ag(111). On Ag(111), IDCT is likewise observed for adsorbed NTCDA and CuPc, besides PTCDA, but not for Tetracene. A prerequisite for IDCT to be operative is that molecular electronic states at or close to the Fermi energy  $\epsilon_F$  exist [9,22,23]. In accordance with this hypothesis, studies of the electronic structure have identified features at or slightly below  $\epsilon_F$  ascribed to the former lowest unoccupied molecular orbital (f-LUMO) for PTCDA, NTCDA, and CuPc on Ag(111) [24–27]; for Tetracene/Ag(111) and PTCDA/Au(111) the weaker adsorbate-substrate interaction renders the respective LUMO empty [28,29].

Partially filled molecular orbitals may form as a result of hybridization with electronic levels of the substrate, leading to a static charge transfer between molecule and substrate; more importantly, such a constellation of electronic states enables charge oscillations across the molecule-metal interface induced by vibrational mode excitations (details in the Supplemental Material [14]).

To refine our understanding of IDCT we will take a closer look at the various contributions to a vibrational mode's dynamic dipole moment  $\mu_{\text{dyn}}$ . For adsorbed species these essentially comprise two components: (i)  $\mu_{\text{mol}}$  coming from nuclear motion of atoms within a molecule carrying (static) charges, in addition to contributions connected with charge redistribution within the molecule, and (ii)  $\mu_{\text{IDCT}}$  associated with dynamic charge transfer across the adsorbate-substrate interface. Electron-vibron coupling and dynamical charge flow within the molecule is expected to proceed adiabatically.  $\mu_{\text{mol}}$  must then be discriminated from  $\mu_{\text{IDCT}}$ , as coupling to the substrate, in general, is much weaker; this means that it is more difficult to maintain the charge equilibrium between metal and molecule at short

timescales, leading to a delayed response of  $\mu_{\text{IDCT}}$  with respect to  $\mu_{\text{mol}}$ .

The effect of such a delay in the buildup of the dynamic dipole moment and its interaction with incoming IR radiation has been described by Langreth by defining  $\mu_{\text{IDCT}}$  and accordingly  $\mu_{\text{dyn}} = \mu_{\text{mol}} + \mu_{\text{IDCT}}$  as a complex quantity [11].  $\mu_{\text{dyn}}$  can then be split in a purely real  $\mu_{\text{mol}}$  and a complex term  $\mu_{\text{IDCT}} = \mu_{1,\text{IDCT}} + i\mu_{2,\text{IDCT}}$ , so that  $\mu_{\text{dyn}} = (\mu_{\text{mol}} + \mu_{1,\text{IDCT}}) + i\mu_{2,\text{IDCT}}$ . Here, the real part refers to the instantaneous response of the dynamical dipole moment. The complex nature of  $\mu_{\text{IDCT}}$  or  $\mu_{\text{dyn}}$  then accounts for the delayed response of the interfacial charge flow with respect to vibrational motion. The molecular layers presented in Fig. 1 are ideal model systems as their weak adsorbate-substrate interaction leads to a significant phase lag between  $\mu_{\text{mol}}$  and  $\mu_{\text{IDCT}}$ , resulting in vibrational line shapes with pronounced asymmetry.

To quantify the degree of nonadiabaticity, Langreth [11] has introduced a parameter  $y = \omega\tau$  describing the ratio of the imaginary and the real part of the complex quantity  $\mu_{\text{dyn}}$ , that is,  $\omega\tau = [\mu_{2,\text{IDCT}}/(\mu_{\text{mol}} + \mu_{1,\text{IDCT}})]$ . A related quantity  $\omega\tau_{\text{IDCT}}$  refers to  $\mu_{\text{IDCT}}$  alone instead of  $\mu_{\text{dyn}}$  so that  $\omega\tau_{\text{IDCT}} = \mu_{2,\text{IDCT}}/\mu_{1,\text{IDCT}}$ . For a particular vibrational mode at  $\omega_0$  with narrow linewidth  $\gamma \ll \omega_0$ , absorption is non-negligible in the region of the resonance only and we can take  $y = \omega\tau \simeq \omega_0\tau$ . We then obtain an expression that combines the charge transfer time  $\tau_{\text{IDCT}}$  with the asymmetry parameter  $\omega_0\tau$  of the resulting Fano-type line shapes through  $\tau_{\text{IDCT}} = 1/\omega_0(\mu_{\text{mol}}/\mu_{1,\text{IDCT}} + 1) \cdot \omega_0\tau$ .

In fact, the sign of  $\mu_{\text{IDCT}}$  need not be identical to  $\mu_{\text{mol}}$  when considering different types of vibrational modes. This leads to a partial compensation of  $\mu_{\text{IDCT}}$  and  $\mu_{\text{mol}}$  and gives rise to negative values of  $\omega_0\tau$  even though  $\tau_{\text{IDCT}}$ , as a rule, will always be positive (details in Supplemental Material [14]).

In Fig. 2 enlarged sections of the IR spectra of CuPc/Ag(111) and of NTCDA/Ag(111) are shown. The displayed frequency regions contain various in-plane as well as out-of-plane vibrational modes (see also the spectra supplied in Supplemental Material [14]). We find that the respective asymmetry parameter values differ notably for the two types of modes; in fact, they consistently show a reversal of their asymmetry. Specifically, CuPc in-plane modes ( $a_{1g}$ ) at 671 and 835  $\text{cm}^{-1}$  display positive asymmetry parameters, while out-of-plane modes ( $a_{2u}$ ) at 719 and 768  $\text{cm}^{-1}$  yield negative  $\omega_0\tau$ . Similarly, the asymmetry changes its sign for the NTCDA modes located at 742 and 862  $\text{cm}^{-1}$ , both representing out-of-plane modes ( $b_{3u}$ ), as compared to those at 995 and 1118  $\text{cm}^{-1}$ , which have been identified as in-plane modes ( $a_g$ ). We conclude that rather than the particular vibrational frequency, it is the specific character of a vibrational mode that decides on the sign of the respective asymmetry parameter.

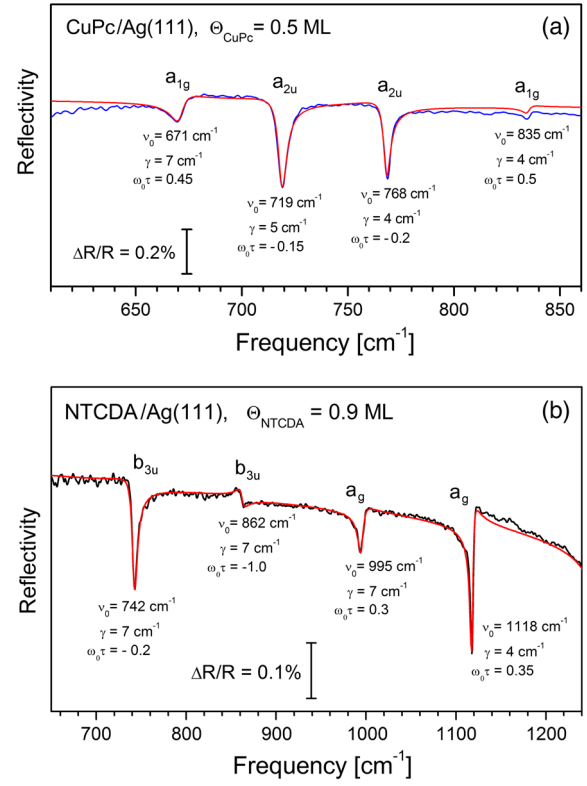


FIG. 2. Infrared absorption spectra of (a) CuPc/Ag(111), and (b) the relaxed NTCDA/Ag(111) monolayers. The asymmetric lines have been fitted using Fano-type line shapes according to Langreth [11]. The derived parameters are indicated in the respective panels. The indicated irreducible representations refer to the  $D_{4h}$  and the  $D_{2h}$  symmetry groups of CuPc and NTCDA, respectively.

By applying the Langreth expression [11], the asymmetry parameter  $\omega_0\tau$  is readily retrieved by means of curve fitting. We have analyzed various in-plane vibrational modes of NTCDA, CuPc, and PTCDA adsorbed on Ag(111) that display pronounced asymmetric or even dispersive line shapes [19,30]; the derived values are summarized in Table I. For NTCDA/Ag(111) and PTCDA/Ag(111) the asymmetry parameters amount to  $\omega_0\tau = 0.3\text{--}0.4$ , while notably higher values up to 1.0 are found for CuPc/Ag(111).

We stress that  $\omega_0\tau$  must not be used directly to derive the molecule-metal charge transfer time  $\tau_{\text{IDCT}}$ , as  $\tau_{\text{IDCT}} \neq \tau$  and only for  $|\mu_{\text{mol}}| \ll |\mu_{\text{IDCT}}|$  can we expect  $\tau_{\text{IDCT}} \simeq \tau$ . This condition is actually favorably fulfilled for in-plane vibrational modes of parallel oriented planar molecules adsorbed on noble metal surfaces, used throughout in our study [31]. We can thus conclude that  $\mu_{\text{dyn}} = \mu_{\text{mol}} + \mu_{\text{IDCT}} \approx \mu_{\text{IDCT}}$ , so that  $\omega_0\tau_{\text{IDCT}} \simeq \omega_0\tau$ , i.e., the derived asymmetry parameter  $\omega_0\tau$  represents a realistic measure of the phase delay  $\omega_0\tau_{\text{IDCT}}$  associated with the electron transfer between molecule and Ag(111) substrate.

Using the above expression for  $\tau_{\text{IDCT}}$ , the asymmetry values in Table I can now be used to extract the

TABLE I. Asymmetry parameters  $\omega_0\tau$  and charge transfer times  $\tau_{\text{IDCT}}$  derived from a line shape analysis of various in-plane vibrational modes of CuPc, NTCDA, and PTCDA<sup>a</sup> adsorbed on Ag(111).

Molecule	Line position [cm <sup>-1</sup> ] <sup>b</sup>	$\omega_0\tau$	$\tau_{\text{IDCT}}$ [fs]
CuPc	671	0.45	3.6
	835	0.5	3.2
	1121	0.75	3.5
	1388	1.0	3.8
	1516	0.9	3.1
NTCDA	995	0.3	1.6
	1118	0.35	1.7
	1257	0.3	1.3
	1264	0.3	1.3
	1338	0.35	1.4
PTCDA	1042	0.3	1.5

<sup>a</sup>For PTCDA the number of suitable modes is limited as the majority of vibrational bands display a complex internal structure, impeding their proper evaluation.

<sup>b</sup> $\omega_0$  is derived from vibrational mode line positions  $\nu_0$  according to  $\omega_0$  [1/s] =  $2\pi c\nu_0$  [cm<sup>-1</sup>].

characteristic charge transfer time  $\tau_{\text{IDCT}}$ , with  $\omega_0$  acting as an internal clock reference. We find that the effective charge transfer times  $\tau_{\text{IDCT}}$  varies notably for individual molecular species, reflecting the respective molecule-metal interaction strength. Specifically, values of about 1.5 fs are derived for NTCDA and PTCDA on Ag(111) and around 3.5 fs for CuPc/Ag(111), signaling a distinctly higher degree of nonadiabaticity in the latter case.

This marked difference in charge transfer time  $\tau_{\text{IDCT}}$  is in accordance with the quite strong distortion of the initially planar structure of NTCDA and PTCDA adsorbed on Ag(111); it is primarily caused by the chemical bonding of O atoms located at both ends of the molecules to surface Ag atoms [18,32]. This chemical interaction is in line with the strong shift of carboxyl stretching frequencies in our IR spectra. Warping of CuPc/Ag(111), on the other hand, is rather weak [27]. The derived notably weaker molecule-substrate interaction for CuPc is in perfect agreement with the larger bonding distance of CuPc/Ag(111) (3.08 Å) [27], as compared to the values reported for the carbon backbone of NTCDA (2.997 Å) [32] and of PTCDA (2.86 Å) [18,33].

For NTCDA on Ag(111) a correlation of the *f*-LUMO energy position and the respective oscillatory motion,  $dE_{\text{LUMO}}/d\xi_i$ , with  $\xi_i$  denoting a generalized NTCDA normal mode coordinate, has been established based on DFT calculations [34]. Thereby the respective contributions to  $\mu_{\text{mol}}$  (denoted as  $\mu'_{\text{nuc}}$  in [34]) and  $\mu_{\text{IDCT}}$  have been quantified.

In fact, and in accordance with our observations, out-of-plane modes ( $b_{3u}$ ) yielded non-negligible  $\mu_{\text{mol}}$ , as well as opposite signs of  $\mu_{\text{mol}}$  and  $\mu_{\text{IDCT}}$ . As a consequence,

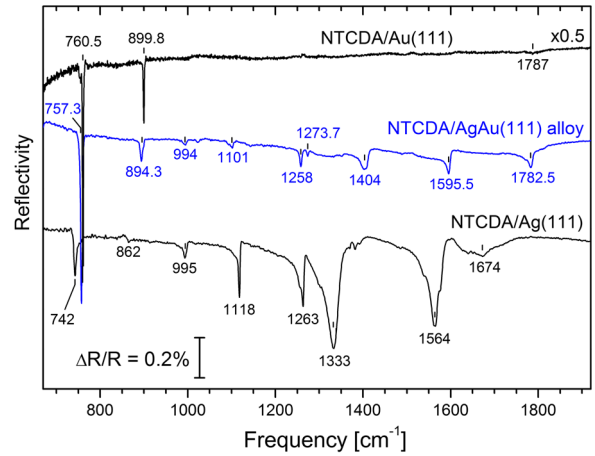


FIG. 3. Infrared absorption spectra of NTCDA adsorbed on Au(111) (top), Ag(111) (bottom), and an AgAu(111) surface alloy created by annealing an Ag/Au(111) monolayer to 580 K (center). Spectral resolution was 0.5 cm<sup>-1</sup> for NTCDA/Au(111), while 2 cm<sup>-1</sup> was used otherwise.

out-of-plane modes show a rather broad distribution of asymmetry parameters, consistent with the spectra in Fig. 2. If we take the values for  $\mu_{\text{mol}}$  and  $\mu_{\text{IDCT}}$  reported in [34] for the 742 cm<sup>-1</sup> mode to calculate  $\tau_{\text{IDCT}}$  by means of the expression above and using  $\omega_0\tau = -0.2$ , we obtain a value of  $\tau_{\text{IDCT}} = 1.6$  fs [35]. This close match with the values derived from our analysis of in-plane modes (Table I) is actually not surprising, as the molecular orbital associated with IDCT ought to be the same for all vibrational modes, independent of their character.

In Fig. 3 we have modified the substrate electronic structure by deposition of Ag atoms on Au(111) to create an AgAu(111) surface alloy [36] after annealing to 580 K (see Supplemental Material for the complete annealing series [14]). The idea is to adjust the dynamics of vibrationally induced charge transfer processes across the molecule-metal interface. As a probe molecule NTCDA has been deposited at 80 K on Au(111), the Ag/Au alloy, and Ag(111); all layers have been annealed to 400 K to induce lateral ordering and to desorb surplus second-layer species.

It is apparent that IDCT is entirely absent for NTCDA on Au(111), in contrast to NTCDA adsorbed on Ag(111), and on the AgAu(111) alloy surface. This means that IDCT can effectively be switched on by adding Ag atoms to the Au(111) surface. The reason for the activation of IDCT is ascribed to the enhanced chemical interaction of NTCDA with Ag atoms of the substrate surface layer. The adsorption-induced vibrational frequency shifts for NTCDA on AgAu(111) with respect to the gas phase or bulk values are relatively small, though, and we conclude that the molecule-metal interaction, while stronger than on Au(111), is notably weaker for the alloy surface as compared to Ag(111).

Most relevant in the current context, the in-plane modes of NTCDA on the Ag/Au alloy substrate display characteristic dispersive line shapes, indicating substantially larger asymmetry parameters as compared to NTCDA/Ag(111). Accordingly, the timescale  $\tau_{\text{IDCT}}$  of molecule-metal charge transfer increases to about 2 fs, which is significantly slower than found for NTCDA on Ag(111). Functionalizing the metal substrate surface thus represents an effective way to tune  $\tau_{\text{IDCT}}$ .

In conclusion, we have investigated the charge transfer dynamics across the molecule-metal interface for various molecular contact layers. By means of vibrational excitations and evaluation of asymmetric line shapes induced by nonadiabatic electron-vibron coupling, the dynamic charge transport right at  $\epsilon_F$  has been probed. This is advantageous insofar as it avoids electronically excited states far above  $\epsilon_F$  that are commonly encountered in various electron spectroscopies and in this way is much more relevant to charge transport in molecular electronic devices. In our analysis the vibrational mode frequency has been used as an internal clock reference to derive the charge-transfer time  $\tau_{\text{IDCT}}$ , representing an intrinsic property of the molecule-metal interface. Typically,  $\tau_{\text{IDCT}}$  is in the few fs range, corresponding to a notable fraction of the oscillation period. Our approach to explore the dynamics of charge transfer processes across molecule-metal interfaces is both accurate and generally applicable, and represents a powerful method to characterize this technologically highly relevant material class.

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