The basis for a quantum-mechanical description of matter is the many-electron wave function. At various levels of approximation, up to the exact configuration interaction wave function, this can be written in terms of single-electron wave functions: the orbitals. The advantage is that orbitals provide a link between spectral properties and spatial electron distributions, which is of obvious benefit in chemistry (1, 2). Consequently, there has been a lot of interest in measuring orbitals (3–6), despite considerable subtleties (7, 8). With photoemission tomography, a powerful technique has recently been introduced by which the electron distribution in orbitals of molecules adsorbed at surfaces can be imaged in momentum space (9–12). Addressing molecular orbitals of excited states in pump-probe experiments would bring photoemission tomography to its culmination, because it would empower it to provide access to molecular excitation and electron transfer processes at surfaces not only in time but also in space: Instead of just recording the photoemission intensity from the corresponding energy level, the evolution of the electron wave function after excitation could be traced by monitoring the orbitals in momentum space. Photoemission by conventional lasers with photon energies of a few electron volts can access only small electron momenta parallel to the surface. The prominent features in frontier orbital photoemission from organic molecules, as determined by the periodicity of the molecular C–C bond network, are therefore out of reach (9). Recently, however, probe photon energies that are high enough have become available through laser high-harmonic generation (HHG) and have enabled time-resolved photoemission experiments to record band structure movies of solids, i.e., to trace the temporal evolution of the electron system over the complete Brillouin zone (13–16). In their investigation of the laser-induced phase transition of In nanowires on Si(111), Nicholson et al. (15) related this information to real-space chemical bond formation in a lattice. However, photoemission tomography of unoccupied states of molecules, the missing element to following molecular electron dynamics in time and space, has not yet been accomplished. In gas-phase photochemistry, it has long been recognized that femtosecond time-resolved photoelectron spectroscopy is a powerful method to investigate the coupled electron and nuclear dynamics (17–19). There, it is difficult to align molecules in all three dimensions to record momentum maps in the molecular frame (19–21). At metal surfaces, molecules are readily fixed in space (9–12). The spectroscopy of unoccupied states, however, requires sufficient electronic decoupling from the substrate at the same time.

The present experiments were performed on 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) molecules that were decoupled from the Cu(001) substrate by an ultrathin oxide layer (22). The submonolayer oxygen coverage also provides a \((\sqrt{2} \times \sqrt{2})R45^\circ\) 20 surface corrugation that imposes two clearly defined azimuthal orientations of PTCDA, labeled \(0^\circ\) and \(90^\circ\) with respect to the laboratory frame of reference [Fig. 1A and (23)]. We used tunable visible pump pulses for resonant excitation of the molecules, combined it with a HHG light source (24) for photoemission, and detected the photoelectron distribution at high parallel momenta (up to \(-2 \text{ Å}^{-1}\)) with a momentum microscope (23, 25).

Figure 1A displays the scheme of our experiment. We excited the molecules with 2.3-eV pump pulses and used 21.7-eV probe pulses at variable delay times \(t_p\) for photoemission. The parallel photoelectron momenta \(k_{xx}\) and \(k_{yy}\) were mapped onto the detector, and the energy \(E\) was retrieved simultaneously by a time-of-flight measurement. The recorded four-dimensional data cube \(I(E, k_{xx}, k_{yy}, t_p)\), where \(I\) denotes the photoemission intensity, enables one to deduce the spatial electron distribution in terms of orbitals in momentum space, their energy position, and their time evolution.

Figure 1B shows a cut through a data cube, displaying \(I(E, k_{xx})\) at zero delay time. As expected for \(\pi\)-orbitals of flat lying PTCDA molecules, photoemission occurred at parallel momenta of \(-1.4\) to \(1.6\) Å\(^{-1}\), the pronounced intensity at \(1.3\) to \(2.3\) eV below the Fermi energy \(E_F\) (defined as \(E = 0\)) derived from standard one-photon photoemission from the highest occupied molecular orbital (HOMO) sitting on top of the Cu d-band onset and \(0\)–\(2\) states of the oxide (23), whereas the weaker intensity at \(0.25\) eV above \(E_F\) originated from two-photon photoemission of the lowest unoccupied molecular orbital (LUMO), populated by the pump pulse before photoionization. These assignments are unambiguous, because constant energy intensity maps, evaluated at orbital energies \(E\) as a function of \(k_{xx}\) and \(k_{yy}\), are fingerprints of individual orbitals. If the final state of the photoemission process is approximated as a plane wave, these so-called momentum maps are closely related to the Fourier transform of the orbitals (9, 23). Theoretical momentum maps that have been generated by Fourier transforming the calculated Kohn-Sham HOMO and LUMO of PTCDA are displayed in the excitation scheme (Fig. 1A).

In Fig. 2, A and B, we present measured momentum maps at the energies of the LUMO and HOMO for three different delay times. Each orbital shows a distinct momentum distribution that can be traced on the ultrafast time scale of the experiment. The detailed structure of the patterns can be explained from the two orthogonal molecular orientations that coexist on the surface. We expect to observe a superposition of the two corresponding momentum maps, as shown for the theoretical ones in Fig. 2, C and D. The agreement between the theoretical and measured momentum maps is indeed excellent, both for the LUMO around temporal overlap \(t_p = 0\) (Fig. 2, A and C) and for the HOMO (Fig. 2, B and D). The direction of the incident light broke the symmetry of the generic momentum maps. That the LUMO was not populated for negative delay time (Fig. 2A; −46 fs) confirms that there is no static charge transfer from the Cu(001)-20 surface to the molecules (22). It is also important to note that the maximum LUMO intensity was about three orders of magnitude lower than the HOMO intensity.
Saturation effects due to optical pumping as well as cross-talk between excited molecules can thus be neglected for the data analysis.

The measured Dyson orbital (23, 26) in Fig. 2A resembles the Kohn-Sham LUMO of PTCDA (Fig. 2C), a finding that is confirmed by a calculation of the Dyson orbital (23). This indicates that, to a good approximation, the excited N electron wave function contains the LUMO as a single-electron orbital and that the subsequent photoemission removed the excited electron from the LUMO. We stress that this intuitive picture of the excitation process in terms of frontier orbitals in the independent electron approximation requires photoemission tomography, and, in particular, the observation of a good agreement between measured Dyson orbitals and calculated Kohn-Sham orbitals, for its confirmation. In conventional femtosecond spectroscopy without momentum-space information, we would be following the evolution of a peak in the energy distribution curve but would not be able to identify the underlying state as an approximate single-particle orbital.

An obvious question addresses the lifetime of the excited state. The single-photon pattern for the HOMO in Fig. 2B shows no dependence on the delay time. Obviously, only a small fraction of the molecules were excited by the pump pulse. By contrast, integrated intensities revealed that after about 100 fs, the LUMO population suffered a single-exponential decay with a lifetime of $T_1 \approx 250$ fs (23). Importantly, no changes in the excited orbital as such took place during this lifetime, as revealed by its constant pattern in momentum space (Fig. 2A). For an excited molecule at a metal surface, this longevity is quite notable (27, 28). It not only confirms the potency of the atomically thin oxide as a decoupling layer but also makes future time-resolved investigations of chemical bond breaking highly promising, because a lifetime of 250 fs exceeds the time scale of typical vibrational motion.

Next, we used the tomographic information to investigate real-space excitation pathways. To this end, we broke the symmetry between the two differently oriented PTCDA molecules, aligning the plane of light incidence with the long axis of the 0° molecule (Fig. 3), and followed, through their momentum-space patterns, both molecules separately. We found that s-polarized light only excited the 90° molecule [Fig. 3A; in agreement with a group theory analysis (23)], and p-polarized light was able to excite both molecules, albeit with surprisingly different excitation dynamics (Fig. 3B): The LUMO pattern of the 0° molecule lit up much earlier and much brighter than that of the 90° molecule. A plot of integrated intensities over the relevant regions of parallel momentum confirmed the mark- edly different behavior (Fig. 3C): Whereas for the 90° molecule the LUMO signal gradually built up over the duration of the pump pulse and subsequently decayed with the time constant of $T_1 \approx 250$ fs, it rose quickly for the 0° molecule and reached a pronounced maximum after 15 fs, before exhibiting at later times ($t_p > \sim 75$ fs) the same slow decay as for the 90° molecule. Upon excitation with s-polarized light, the 90° molecule behaved similar to the 0° molecule under p-polarized excitation (Fig. 3C).

A possible explanation for the occurrence of the pronounced maximum near $t_p = 0$ would be the presence of a very fast decaying intermediate state that is excited under certain excitation conditions. The analysis of the momentum maps, however, excludes this possibility. Not only are the momentum maps of Fig. 3 characteristic of that of the LUMO for all delay times, patterns at higher energies also do not indicate the excitation of another state in our experiment (23). Instead, we suggest that the differences in the excitation dynamics are due to two distinct real-space excitation pathways of the electron in the sample before it is photoemitted. Our model describes the experiment by a four-level system consisting of the HOMO ($|\phi_1\rangle$) and an occupied substrate state ($|\phi_s\rangle$) as initial states, the LUMO as intermediate state ($|\phi_i\rangle$), and the photoemission final state ($|\phi_f\rangle$) (Fig. 3D). In a perturbative description of light-matter interaction, the pump pulse creates a coherent polarization $|\Psi, t\rangle$ between the ground state ($|\phi_1\rangle$) or ($|\phi_s\rangle$) and excited state ($|\phi_i\rangle$) in the first order of the electric field. The conversion of this polarization in the second order of the electric field into an excited-state population $n_f$ is governed by phase-destroying elastic scattering processes. In one limit, if this dephasing is fast and the inelastic decay of $|\phi_1\rangle$ is slow, the build-up of $n_f$ follows the time-integrated intensity of the pump pulse. This was the situation for the 90° molecule excited with p-polarized light (Fig. 3C). The field component $E\parallel$ drives a perpendicular electron motion between substrate and molecule, involving the initial state ($|\phi_1\rangle$) that is coupled to a bath, which resulted in fast dephasing. In this limit, the emitted photoelectron could be traced back to the metal. Although this mechanism applies to both the 0° and 90° molecules (Fig. 3C), in the case of the 0° molecule, a competing process takes place (see below), such that the signature of the fast dephasing was only seen in the data for the 90° molecule.

In the opposite limit, if dephasing is slow, the oscillating polarization between ground and excited states decays slowly. In this coherent regime, the interaction of the electric field of the probe pulse with $|\Psi, t\rangle$ can contribute to the two-photon photoemission process for short delay times. In addition, if the driving pump laser is slightly detuned from the transition energy, the excited state can be populated and depopulated by the pump pulse. Both effects give rise to a pronounced peak in the photoemission signal, as observed in
Fig. 3C for the 90° molecule excited with s-polarized light as well as for the 0° molecule excited with p-polarized light.

For a quantitative evaluation of the data, we applied a density matrix approach and solved the optical Bloch equation for the four-level system (Fig. 3D). We found that the experimental data are described well with an extremely short dephasing time $T_2^* \approx 3$ fs of the substrate state $|\phi_i\rangle$ and a surprisingly long decoherence time $T_2$ in excess of 150 fs for the polarization between $|\phi_1\rangle$ and $|\phi_2\rangle$ (23). The existence of such a long-lived coherence in an electronic excitation at a metal surface is unexpected (28, 29). It has previously only been observed for image-potential states with high quantum numbers where the electron is mainly located in the vacuum, tens of angstroms above the surface (28). In the present experiment, this long coherence time can be rationalized by the fact that the pump pulse induced an in-plane oscillatory electron motion that is confined to the molecule: For both combinations, s-polarization–90° molecule and p-polarization–0° molecule, there is an $E$ field component along the long axis of the respective molecule (Fig. 3C), i.e., parallel to the HOMO-LUMO transition dipole, thus permitting an excitation directly from the HOMO $|\phi_1\rangle$ into the LUMO $|\phi_2\rangle$. If the hybridization of the molecule with the metal beneath the oxide is negligible, which is also revealed by the long inelastic lifetime $T_1$ measured for the LUMO, this spatial confinement of electron motion in $(\mathbf{r}, t)$ to the molecule explains the long coherence. Our modeling thus suggests that for this excitation pathway, the emitted photoelectron can be traced back to the HOMO (30).

We have shown that photoemission tomography, in combination with laser pump-probe techniques, makes it possible to image orbital momentum maps of excited electronic states. This allows the identification of excitation mechanisms by tracing electrons not only in time but also in space. We expect that future experiments of this type will enable studies of molecular electron transfer processes at surfaces and interfaces with unprecedented detail. With progress in laser alignment, one may envision that the field of gas-phase photochemistry will also benefit from time-resolved photoemission tomography (19–21). Moreover, an extension to attosecond time resolution seems feasible. The availability of momentum-space information relaxes pertinent requirements on energy resolution, allowing in turn for an increase in time resolution. In this way, the temporal and spatial evolution of electronically excited states should become resolvable by photoemission tomography even before the nuclei start to move.

**Fig. 2. Momentum maps of the frontier orbitals.** (A) Experimental momentum maps obtained at selected delay times $t_p$ and $E = +0.45$ eV. Both pump and probe beams are p-polarized. The two dotted circles indicate the momentum integration range (23). (B) Same as for (A) but at $E = -2.18$ eV (intensity reduced by a factor 1850). (C) Two-dimensional cuts through the Kohn-Sham LUMO of gas-phase PTCDA (left) and corresponding theoretical momentum maps with polarization factor $P(k)$ plotted for two orientations 0° and 90° (middle) and their sum (right). (D) Same as for (C) but for the HOMO. Both orbitals have been calculated for neutral, closed-shell PTCDA. However, an open-shell calculation of the highest occupied orbital for the PTCDA anion yields almost indistinguishable results from the LUMO of neutral PTCDA (23). The colored arrows indicate projected light incidence (45°). hv, photon energy.

**Fig. 3. Momentum-resolved LUMO dynamics for different excitation pathways.** (A) Momentum map integrated over all delay times $t_p$ for an s-polarized pump pulse. The momentum map is overlaid by theoretical constant-intensity contours as expected for the 0° (white) and 90° (middle) and their sum (right). (B) Momentum maps for a p-polarized pump pulse at selected delay times. (C) Temporal evolution of the photoelectron intensity of the two LUMOs (0°, black circles; 90°, orange squares) for s- and p-polarized pump pulses. Intensities are integrated within circular regions with a radius of 0.2 Å centered within the main lobes of each molecular orientation. The experimental geometries are illustrated schematically. Solid lines indicate the best fit solution to the optical Bloch equations for the four-level system discussed in the text. The dashed orange line illustrates a completely incoherent excitation. It is obtained within the same model by setting the decoherence time to zero. Gray triangles show the cross-correlation (cc) of the pump and probe pulses. (D) Schematic representation of the four-level model used to fit the data in (C). $E_{\text{vac}}$, vacuum level.
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SUPPLEMENTARY MATERIALS

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