

Phonon-mode-specific modulation of electronic states in molybdenum dioxide

Florence Burri ^{*}, Marko Hollm , Erik W. de Vos , Lukas Gallmann , Ursula Keller , and Sergej Neb 

Department of Physics, *ETH Zurich*, Zurich, Switzerland



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Near-infrared pump and extreme ultraviolet probe transient absorption spectroscopy is employed to unravel the phonon-mode-specific modifications of electronic states near the Fermi energy in molybdenum dioxide. We observe distinct fingerprints of two coherent phonon modes at a frequency of 6 and 11 THz which differ vastly in their energy-dependent modulations of the electronic response. By combining our measurements with density functional theory calculations, we show that the measured energy-dependent contrast between the phonon modes is primarily governed by the modification of the projected density of states. These findings highlight the pivotal role of lattice dynamics in the ultrafast electronic response.

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I. INTRODUCTION

Near-infrared (NIR) pump and extreme ultraviolet (XUV) probe transient absorption spectroscopy has been widely used to investigate dynamical processes in molecules and solids on subfemtosecond timescales [1–5]. Beyond capturing purely electronic dynamics, it has proven to be a powerful tool for accessing lattice dynamics in solids on timescales ranging from a few hundred femtoseconds to a few picoseconds [6–8]. Its broad energy probing range provides unique access to the interplay between phonon modes and electronic states, offering deep insight into the fundamental interactions governing lattice and electronic dynamics.

Here, we study thin-film molybdenum dioxide (MoO_2), a transition metal oxide that crystallizes in the monoclinic space group $P2_1/c$, giving rise to 36 symmetry-allowed phonon modes [9]. To the best of our knowledge, molybdenum dioxide has not yet been studied on the femtosecond to picosecond timescales. In related molybdenum-based compounds, time-resolved studies have revealed, among other observations, an energy-dependent electron-phonon coupling effect [10]. Previous NIR-XUV transient absorption spectroscopy studies on transition metals [11,12] and transition metal dichalcogenides [13] have primarily explored how pump-induced modifications to the localized character of d orbitals shape the transient absorption response. Given the strong electron-phonon coupling anticipated in MoO_2 [14], we shift our focus toward the interplay of the electronic and phononic subsystem. This interplay gives rise to a wide range of solid-state phenomena governed by the electron-phonon coupling described in the Fröhlich Hamiltonian [15]. In this work, we focus on a

different aspect of electron-phonon interactions. We specifically study how coherent phonons perturb the d -orbital projected density of states, revealing a direct link between phononic motion and electronic structure modification.

In the analysis of NIR-XUV transient absorption spectroscopy measurements, theoretical modeling of pump-driven absorbance changes typically relies on computationally demanding methods such as time-dependent density functional theory (TDDFT) [16], or even more advanced approaches like the Bethe-Salpeter equation (BSE) [17–19]. These techniques are able to accurately describe band-gap dynamics in semiconductors [20,21], the dynamical Franz-Keldysh effect [22], or the effect of localization in the d states [11,13]. To investigate the interplay between charge carriers and phonons, we adopt a comparatively simple approach based on a finite-displacement supercell approach and static density functional theory (DFT). This model accounts for the phonon-mode-specific modification of the electronic structure. Although dynamically driven many-body effects are neglected, the approach qualitatively captures the defining characteristics of the phonon-induced modulation depth in the transient absorbance signal.

In this work, we resolve a phonon-mode-specific and energy-dependent modification of the d -orbital states in MoO_2 . By comparing the phononic fingerprint in transient absorption with the phonon-induced changes in the projected density of states, we establish a direct link between lattice motion and electronic structure. This connection offers an intuitive framework for interpreting the experimental data and opens a pathway to tailoring the ultrafast absorption properties of materials through selective phonon excitation.

II. EXPERIMENTAL AND THEORETICAL METHODS

NIR pump and XUV probe transient absorption spectroscopy. In this experiment, thin-film MoO_2 deposited on a silicon nitride substrate is excited by NIR pulses with a spectral range of 610 to 840 nm, a peak intensity of 1.7 TW/cm^2 , and a repetition rate of 1 kHz. To probe the

^{*}Contact author: flburri@ethz.ch

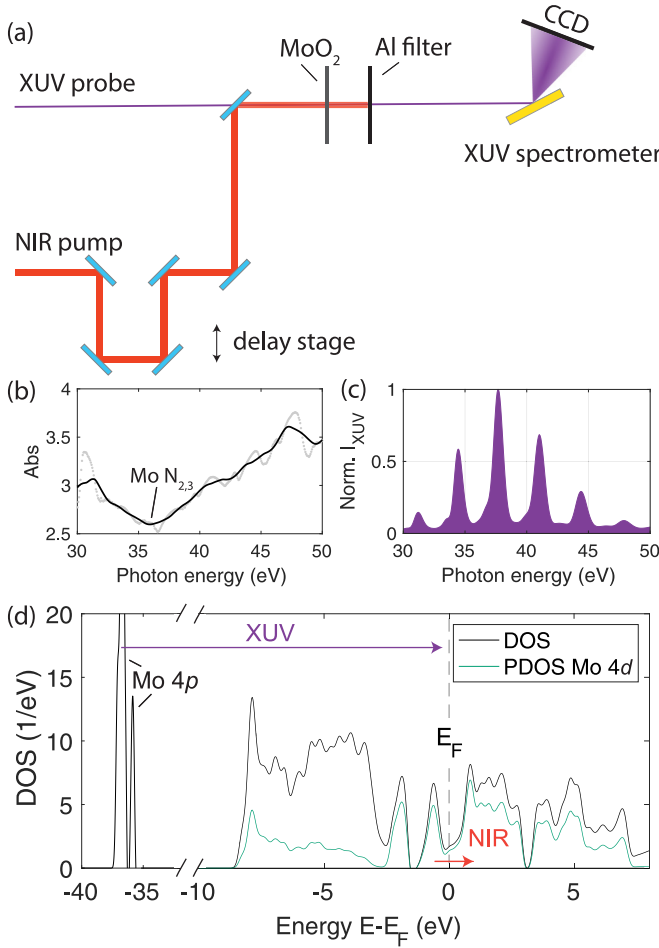


FIG. 1. (a) Schematic of the ultrafast transient absorption spectroscopy setup. The XUV probe and NIR pump pulses, delayed in time, impinge on the molybdenum dioxide sample. A thin aluminium filter blocks the NIR radiation, allowing only the transmitted XUV radiation to reach the spectrometer. (b) Static absorbance of MoO₂ at Mo N_{2,3} absorption edge (gray dots), the black line is an interpolation as guide to the eye. (c) XUV probe spectrum used in the experiment. (d) Calculated total density of states of MoO₂ (black line), along with projected density of states onto Mo 4d orbitals (green line). Red and violet arrows indicate the pump- and probe-induced transitions.

change in absorbance (ΔAbs) we use a XUV pulse train generated via high-harmonic generation (HHG) spanning an energy range from 30 to 50 eV [see Fig. 1(b)]. The instrumental time resolution, determined by the cross correlation between the NIR pump and the XUV probe pulses, is 9 ± 1 fs (see Appendix B). The probed energy range is dominated by transitions from the shallow core-level state Mo 4p to the Mo 4d conduction band states below and above the Fermi energy, as highlighted in Fig. 1(c). The change in absorbance is defined as

$$\Delta\text{Abs}(t) = \ln\left(\frac{I_{\text{XUV}}}{I_{\text{XUV+NIR}}(t)}\right), \quad (1)$$

where $I_{\text{XUV+NIR}}(t)$ and I_{XUV} are the transmitted intensities with and without the near-infrared pulse present and t denotes the delay time between NIR and XUV pulse. Positive time delays denote that the NIR pump arrives before the XUV

probe. A schematic of the experimental setup is shown in Fig. 1(a) and more details can be found in [23]. To confirm the oxidation state of the studied molybdenum oxide MoO_x, we perform a Raman spectroscopy measurement with a 532-nm laser source.

Density functional theory and phonon mode calculation. We use a density functional theory approach using a Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [24] to model the density of states (DOS) and projected density of states (PDOS) [25–27]. To account for the localized Mo *d* electrons we include a Hubbard *U* parameter in the functional [28]. Its numerical value of 4.0 eV is computationally determined using a density functional perturbation (DFPT) approach [29–31]. Convergence of the self-consistent field calculations was found at a wave-function energy cutoff of 80 Ry and a grid of 8^3 points in *k* space. Furthermore, we retrieve the molybdenum dioxide phonon modes using a finite-displacement supercell approach [32,33]. To study the effect of phonon modes on molybdenum dioxide, we elongated the atomic position of the atoms in equilibrium along several *A_g* modes and retrieved the corresponding projected density of states by DFT calculations.

III. RESULTS

In Fig. 2, the NIR pump-induced transient change in absorbance of molybdenum dioxide is shown as a function of pump-probe delay. Typically, a transition from positive to negative change in absorbance is expected along the energy axis in the vicinity of the absorption edge, here the Mo N_{2,3} located at 37 eV. This effect is referred to as band filling, as it arises from electrons promoted by the NIR pump above the Fermi energy. According to the Pauli exclusion principle, this produces an increase in XUV probe absorption below the Fermi energy and a reduction above it, resulting in a derivative-like signature in the absorbance change. In our case, however, we observe an overall positive change in absorbance from 34 to 47 eV, which is most likely driven by local field effects, as previously demonstrated for molybdenum diselenide [13]. In that material, local field effects mediated by electron localizations onto the Mo 4d orbitals result in a characteristic positive change in absorbance. A similar mechanism is also plausible for MoO₂, given the well-established role of electron localization in Mo 4d orbitals [11–13]. We observe an increase in ΔAbs for photon energies ranging from 36 to 42 eV with a rise time $\tau_r = 20 \pm 5$ fs and a decrease in change of absorbance with a decay time of $\tau_d = 90 \pm 10$ fs, derived from the fit with Eq. (C1) presented in Fig. 2(b). For higher energies ranging from 44 to 45 eV the rise time of the positive ΔAbs is $\tau_r = 130 \pm 20$ fs, derived from the fit with Eq. (C2) presented in Fig. 2(b).

The transient absorption spectrogram is modulated by oscillations attributed to the 6-THz and 11-THz phonon modes, as shown by the Fourier transform of the spectral line outs thereof, depicted in Fig. 3(a). Note that a rise and decay function [Eq. (C3) respectively (C4)] are subtracted from the line outs before taking the Fourier transform. By comparing the Fourier transform of the transient absorption spectroscopy measurement [Fig. 3(a)] with the Raman spectrum [Fig. 3(b)], we identify the symmetries of the phonon modes. Both modes,

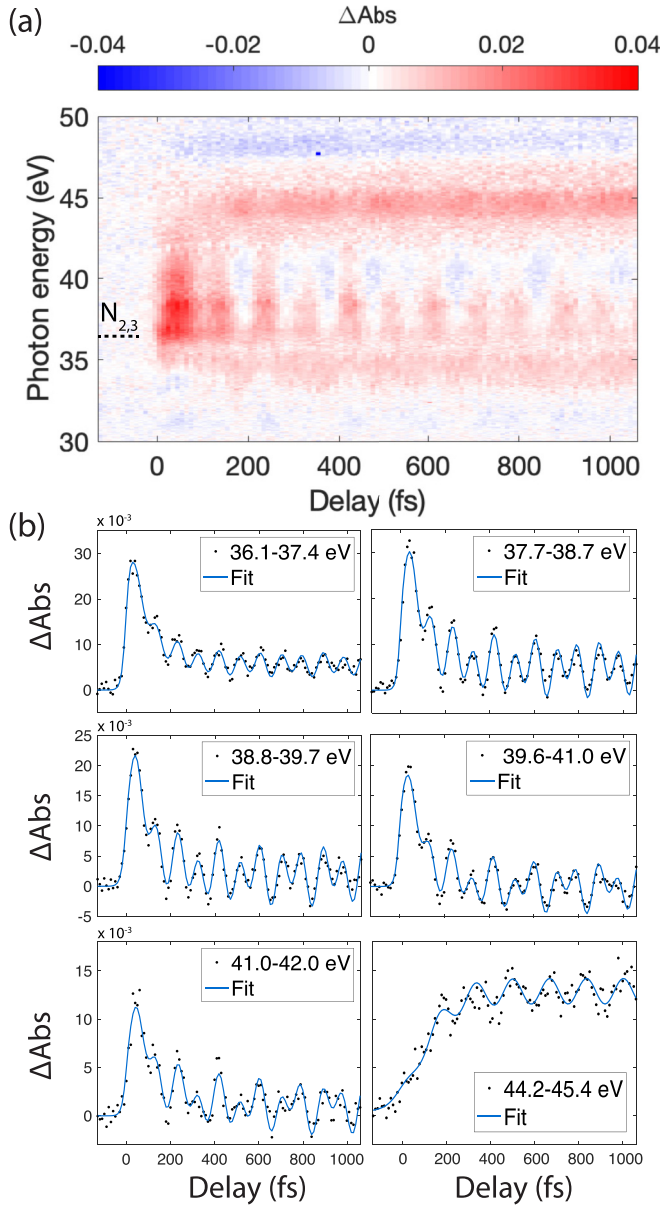


FIG. 2. (a) NIR pump and XUV probe transient absorption spectrogram as function of pump-probe delay time. The black dashed line indicates the $\text{Mo } N_{2,3}$ absorption edge. (b) Time traces of ΔAbs at selected photon energies compared to fit with Eq. (C1) for 36.1 to 42.0 eV and Eq. (C2) for 44.2 to 45.4 eV. The fitting parameters can be found in Tables I and II.

the 6 THz as well as the 11 THz, can be assigned to phonon modes with A_g symmetry. The A_g symmetry of the Raman peaks is determined by comparison with Ref. [34], which also confirms the oxidation state MoO_2 . Notably, the oscillation amplitude varies for different probing photon energies. This can also be observed by fitting the line outs to an oscillatory function [see Fig. 2(b)]. For energies close to the Fermi energy we choose a function oscillating at two distinct frequencies accompanied by an overall rise and decay [Eq. (C1)]. This suggests a dispersive excitation mechanism for the coherent phonons, as the oscillation has a cosine phase (see Table I). This can either be explained in the framework of dispersive

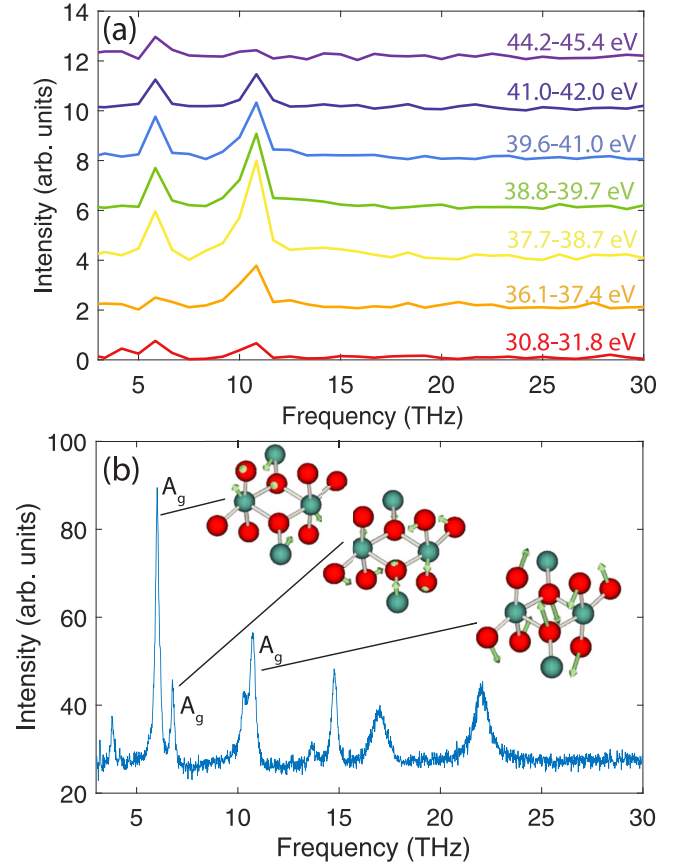


FIG. 3. (a) Fourier transform of the residual signal after removing the rise and decay dynamics from spectral line outs of the transient absorption (Fig. 2) plotted with a constant offset, for better readability. (b) Raman spectrum at 532-nm excitation wavelength. The symmetries (A_g) of the relevant modes are identified by comparing with Ref. [34]. In the inset the relevant modes are visualized. The green arrows indicate the direction of displacement, blue and red spheres represent the Mo and O atoms in the unit cell of MoO_2 .

excitation of coherent phonons or stimulated Raman scattering [35,36]. For higher-lying energy ranges, we use a function that oscillates at a single frequency accompanied by an overall rise [Eq. (C2)]. The fitting parameters can be found in Tables I and II. The oscillation amplitudes are shown in Fig. 4, the vertical error bars represent the confidence interval (95%). We compare the extracted amplitudes to the convolution of the $\text{Mo } 4p$ states and the phonon-altered $\text{Mo } 4d$ states, defined as follows:

$$\Delta S(E) = \sum_{j=\{\frac{1}{2}, \frac{3}{2}\}} \frac{A_j}{1 + (E - E_{4pj})^2/\Gamma^2} * |\text{PDOS}^+ - \text{PDOS}^-|. \quad (2)$$

Here, PDOS^+ and PDOS^- represent the projected density of states on the $\text{Mo } 4d$ states for positive and negative atomic displacement along the respective phonon mode. The spin-orbit split $4p_{1/2}$ and $4p_{3/2}$ states are modeled by the sum of two Lorentz functions centered at $E_{4p_{1/2}} = 36.7$ eV and $E_{4p_{3/2}} = 35.9$ eV with a spectral linewidth of $\Gamma = 0.55$ eV and an amplitude ratio of $\frac{A_{1/2}}{A_{3/2}} = 5$. The energy and the relative

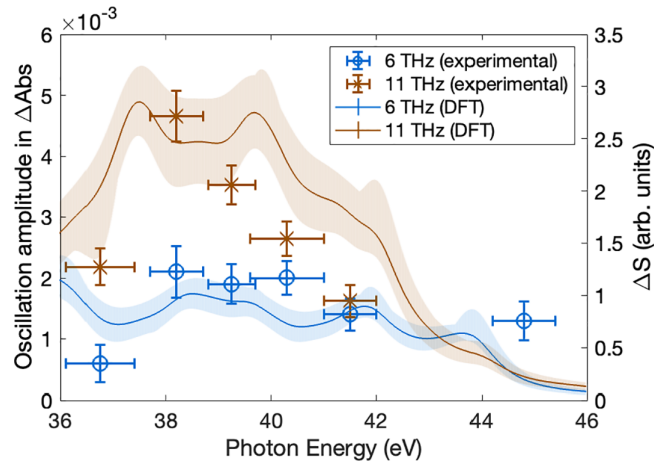


FIG. 4. Oscillation amplitudes of 6- and 11-THz modes retrieved from an oscillatory fit function accounting for the rise and decay of ΔAbs present in the transient absorption spectrum. The vertical brackets depict the confidence interval (95%) of the fit, whereas the horizontal ones indicate the XUV energy range over which the fit was done. The amplitudes are compared to the phonon induced $\Delta S(E)$, defined in Eq. (2). The shaded error bars represent the variation of $\Delta S(E)$ if the core level energy is shifted ± 0.5 eV and their spectral linewidth ± 0.2 eV.

amplitude of the two shallow core levels are chosen to match approximately with Fig. 1(c). The calculated $\Delta S(E)$ is shown (Fig. 4); the colored bands represent the uncertainty with respect to variations of the core level energy by ± 0.5 eV, as well as the spectral linewidth by ± 0.2 eV. The oscillation amplitude at 11 THz peaks around 38 eV, while the oscillation amplitude at 6 THz remains nearly constant throughout the observed energy range. A similar qualitative behavior can be observed for the aforementioned $\Delta S(E)$.

The unit cell of MoO_2 contains of four formula units, comprising a total of 12 atoms in total. The molybdenum atoms are symmetry equivalent, whereas the oxygen atoms split up into two symmetry nonequivalent positions denoted as O(1) and O(2). In our model, we displace the atoms along the 6-THz phonon mode at a certain amplitude. This leads to the following atomic displacements. The Mo atom is displaced by $0.0057 \text{ \AA}$, the O(1) atom by $0.0019 \text{ \AA}$, and the O(2) atom by $0.0001 \text{ \AA}$. Analogously, we displace the atoms along the 11-THz phonon mode at a certain amplitude. The Mo atom is displaced by $0.0035 \text{ \AA}$, the O(1) atom by $0.0058 \text{ \AA}$, and the O(2) atom by $0.0073 \text{ \AA}$. We note that the 6-THz modes mostly displace the molybdenum atom, whereas the 11-THz mode mostly displaces the two oxygen atoms. Note that we cannot make a statement about the absolute value of the phonon amplitude, but the chosen amplitudes lead to a reasonable order of magnitude in lattice displacements within the Lindemann limit [37], making them a reasonable parameter in our model.

IV. DISCUSSION

We observe a fast rise time of $\tau_r = 20 \pm 5$ fs in change in absorbance close to the absorption edge and a slower one of $\tau_r = 130 \pm 20$ fs at higher probing energies. Regarding the timescale, we attribute the response close to the

absorption edge to the hot charge carriers excited by the NIR pump, which may also involve associated localization effects [11–13]. The response observed at higher probing energies approximately 10 eV above the absorption edge is likely not originating from charge carriers directly excited by the NIR pump at a center energy of around 1.5 eV. We exclude multiphoton excitation as a cause since the feature remains over varying NIR pump peak intensities. Instead, we attribute this response to incoherent lattice vibrations. Specifically, we compare the rise time at higher energies with the decay time near the absorption edge of $\tau_d = 90 \pm 8$ fs. Their temporal overlap suggests that hot charge carriers dissipate their energy into incoherent lattice vibrations, leading to the increased absorbance change observed at higher probing energies. A similar effect has been reported in graphite, although in that case the rise of an oscillatory component was observed, attributed to additional coherent phonon excitation [38]. The observed relaxation of the hot charge carriers is one order of magnitude faster compared to prior work on a semiconductor [8]. This suggests either that electron-electron scattering present in metals is more efficient than electron-hole scattering and impact ionization present in semiconductors or that a strong electron-phonon coupling is dominant in molybdenum dioxide. It is worth noting that the decoherence time of the observed coherent phonon modes is longer than the measurement time of 1 ps. This is a key ingredient in robustly extracting a phonon-mode-specific and energy-dependent modulation amplitude in the change of absorbance. This is remarkable as the polycrystalline nature of the sample can reduce the lifetime of coherent phonons.

The phonon modes at 6 and 11 THz present in this study have a different effect on the Mo $4d$ states of MoO_2 . Experimentally, we observe a stronger maximum amplitude of the transient absorption spectrum's modulation by the 11-THz mode. This differs from the Raman spectroscopy measurement, where the peak intensity is lower for the 11-THz mode than for the 6-THz modes. This is to be expected as our measurement scheme involves resonances with electronic transitions, which can modify the relative amplitude of Raman scattering probabilities [39]. Furthermore, the aforementioned amplitude varies over the observed energy range for the 11-THz mode, while it remains approximately constant for the 6-THz modes. This qualitative behavior remains for peak intensities of the NIR pump at 1.3, 1.4, and 1.8 TW/cm^2 , as shown in Fig. 5. In comparison with theory, we can explain this difference from the effect of the phonon modes on the Mo $4d$ states. The phonon modes at 6 and 11 THz share the same symmetry A_g , but act with different magnitudes on the atomic species. The 11-THz phonon mode mostly displaces the oxygen atoms. Therefore, we conclude that the displacement of the oxygen atoms has a stronger effect on the valence electrons of molybdenum dioxide and that the effect is very sensitive to the electron's energy. The 6-THz phonon mode, on the other hand, mainly displaces the molybdenum atoms. This has an overall lower impact on the Mo $4d$ states and the impact remains constant over the energy range where Mo $4d$ states have a major contribution to the density of states. We observe that although we do not probe the oxygen states of MoO_2 directly with the XUV probe, we are highly sensitive to displacements of the oxygen atoms, even more than to

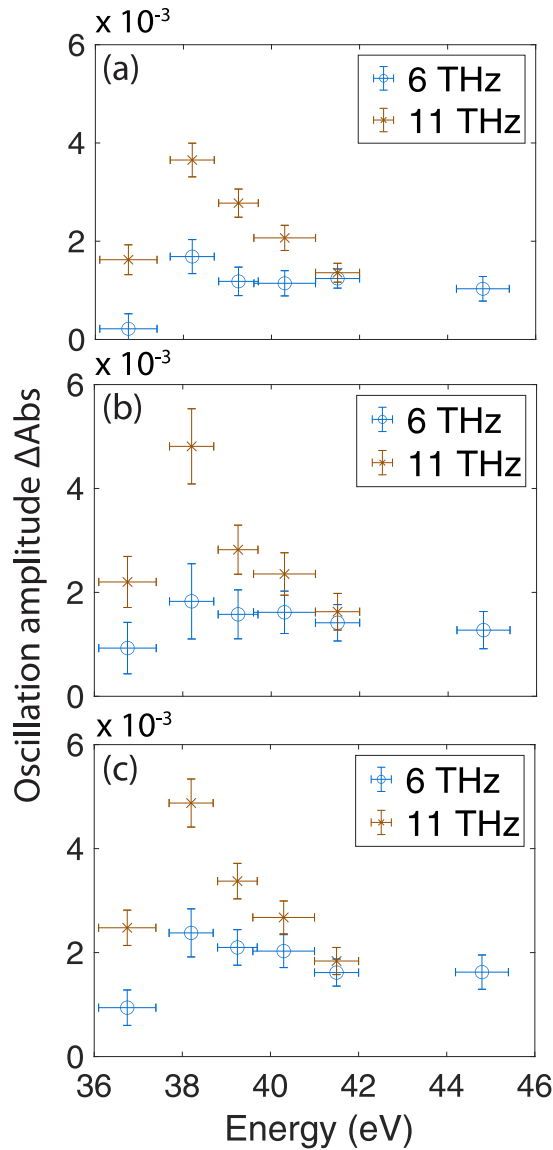


FIG. 5. Oscillation amplitude as a function of probe photon energy, retrieved from fitting procedure described in main text at NIR pump peak intensity (a) 1.3 TW/cm^2 , (b) 1.4 TW/cm^2 , and (c) 1.8 TW/cm^2 .

displacements of molybdenum atoms. This emphasizes the sensitivity of electronic states to displacements of neighboring atoms, especially in materials where hybridization effects are present.

XUV absorption can be modulated by the variation in the number of unoccupied electronic states. In our work, we considered the modulation of the PDOS to the Mo $4d$ states by two distinct phonon modes. We find agreement with the experimentally observed variation of the oscillation amplitude across the probed XUV photon energy range from 36.1 to 41.0 eV and the convolution of Mo $4p$ states with the phonon-altered Mo $4d$ states. For the oscillation amplitude around 45 eV the model's validity is limited as at 7 eV above Fermi energy almost no Mo $4d$ states are available [see Fig. 1(c)].

Given that previous studies [11,13] have emphasized the significant role of local field effects in shaping the transient

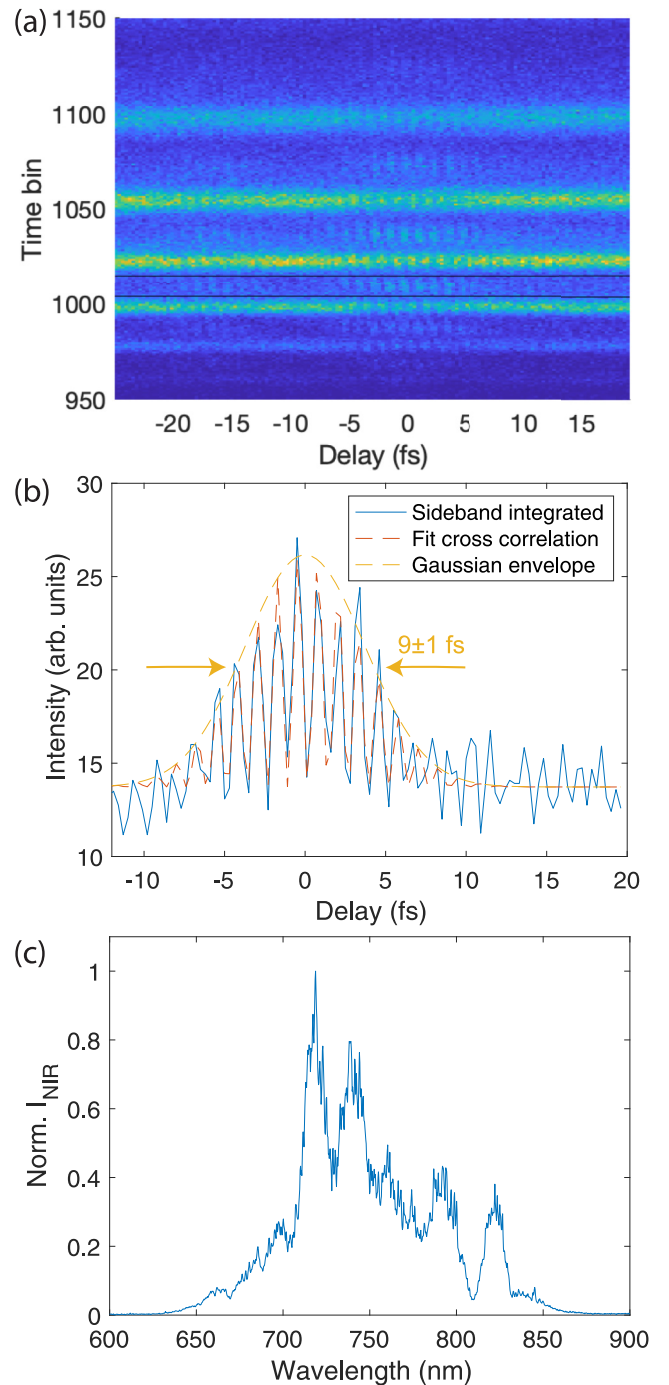


FIG. 6. (a) Time-of-flight measurement of electrons escaping from argon gas by irradiation of XUV beam and NIR beam. Black lines indicate a sideband which is displayed in (b). (b) Integrated sideband as indicated in (a) and fit with Eq. (B1). The arrows indicate the FWHM of the cross correlation between NIR and XUV of $9 \pm 1 \text{ fs}$. (c) Normalized spectrum of the NIR pulse after hollow-core fiber compression.

absorption spectrum, it may seem surprising that such a simple model is sufficient. However, a key distinction is that we do not model the full pump-induced transient absorption spectrum but rather its modulation by comparing two extrema of the phonon displacement, which decreases the requirements for a model. These are fulfilled by our simple and intuitive

model how coherent phonons perturb the d -orbital projected density of states. This qualitatively captures the observed variation in oscillation amplitude. We note that the remaining small discrepancies may stem from neglecting local field effects, which could introduce subtle energy-dependent variations. Nevertheless, we find that the dominant contribution to the variation in oscillation amplitudes across the probed energy range arises from phonon-induced modifications of the Mo $4d$ projected density of states, with other contributions playing a minor role.

V. CONCLUSION

In this NIR pump and XUV probe transient absorption spectroscopy study, we reveal a phonon-mode-specific and energy-dependent variation of the electronic structure, driven by coherent lattice vibrations. This effect manifests as a distinct modulation in the amplitude of the absorbance change, which strongly depends on both the phonon mode and probing photon energy. Using a model based on density functional theory and a finite-displacement supercell approach, we can identify the variation of available Mo $4d$ states to be responsible for the characteristic variation of this modulation amplitude through the probed energy range. This methodology can be further refined by projecting the density of states onto specific orbitals, particularly in materials where orbital contributions are energetically well separated. Moreover, this analysis is expected to be even more effective in materials with weaker or negligible electron localization effects, where the response is more directly governed by band-structure modulations.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [40].

APPENDIX A: SAMPLE PREPARATION

To prepare the MoO₂ samples, 14 nm of molybdenum is evaporated on a 10-nm silicon nitride substrate (Agar Scientific) by electron beam evaporation and subsequently annealed in atmospheric, oxidation-enabling conditions at a temperature of 550 °C for 45 min. To evaluate oxygen concentration and structure of the sample, we perform a Raman spectroscopy measurement [see Fig. 3(b)] and compare it with the literature [34]. The broad peaks for frequencies above 14 THz indicate the polycrystalline nature of the sample.

APPENDIX B: PULSE CHARACTERIZATION

To determine the temporal overlap between pump and probe beam, we perform a reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) [41] measurement. By fitting a sideband indicated by black lines (Fig. 6) to a 2ω oscillatory function of the form

$$I(t) = ae^{\frac{(t-t_0)^2}{2\tau^2}} [\cos(2\omega t + \pi\phi) + 1] + d, \quad (\text{B1})$$

we find delay zero t_0 and a full-width at half-maximum (FWHM) of 9 ± 1 fs of the cross correlation between the electric fields of the NIR and XUV pulses. All pump-probe data appearing in the main paper are calibrated with this delay zero t_0 . Note that ω is the center frequency of the NIR beam.

APPENDIX C: FITTING OF PHONON OSCILLATION

In the main paper, we show the amplitude and rise time obtained by fitting the spectral averages of the transient absorption spectroscopy measurement to Eq. (C1) for energies ranging from 36.1 to 42.0 eV and to Eq. (C2) for energies ranging from 44.2 to 45.4 eV:

$$\Delta\text{Abs}(t) = \frac{1}{1 + e^{\frac{-t}{\tau_r}}} [A_1 \cos(2\pi f_1 t + \phi) + A_2 \cos(2\pi f_2 t + \phi) + B e^{\frac{-t}{\tau_d}} + C], \quad (\text{C1})$$

$$\Delta\text{Abs}(t) = \frac{1}{1 + e^{\frac{-2(t-t_1)}{\tau_r}}} [A_2 \cos(2\pi f_2 t + \phi) + C], \quad (\text{C2})$$

where the oscillation amplitudes A_1 , A_2 , the decay amplitude B , the oscillation frequencies f_1 , f_2 , the rise time τ_r , the decay time τ_d , time t_1 , and the phase ϕ are fit parameters. The averaged change in absorbance compared with the fit can be seen in Fig. 2(b). In Tables I and II, we present all the fit parameters, including their confidence interval (95%).

TABLE I. Fit parameters of Eq. (C1) at NIR pump peak intensity of 1.7 TW/cm².

Energy range (eV)	[36.1,37.4]	[37.7,38.7]	[38.8,39.7]	[39.6,41.0]	[41.0,42.0]
$10^3 A_1$	2 ± 0.3	5 ± 0.4	4 ± 0.3	3 ± 0.3	2 ± 0.3
$10^3 A_2$	0.6 ± 0.3	2 ± 0.4	2 ± 0.3	2 ± 0.3	1 ± 0.3
$10^3 B$	30 ± 2	30 ± 2	30 ± 2	20 ± 2	10 ± 2
f_1 (THz)	10.6 ± 0.07	10.7 ± 0.05	10.7 ± 0.05	10.7 ± 0.05	10.7 ± 0.07
f_2 (THz)	6.0 ± 0.1	5.9 ± 0.06	6.0 ± 0.06	6.0 ± 0.05	5.9 ± 0.08
$\pi^{-1}\phi$	1.1 ± 0.09	1.0 ± 0.06	1.1 ± 0.06	1.1 ± 0.06	1.0 ± 0.09
τ_r (fs)	20 ± 3	20 ± 4	20 ± 4	20 ± 4	20 ± 7
τ_d (fs)	90 ± 1	90 ± 8	90 ± 8	90 ± 8	100 ± 20

TABLE II. Fit parameters of Eq. (C2) at NIR pump peak intensity of 1.7 TW/cm².

Energy range (eV)	[44.2,45.4]
$10^3 A_2$	1 ± 0.3
f_2 (THz)	6 ± 0.1
$\pi^{-1}\phi$	2 ± 0.1
τ_r (fs)	130 ± 20
t_1 (fs)	100 ± 10

In Fig. 3(a) we take the Fourier transform of the averaged ΔAbs 's residual after subtraction of rise and/or decay of the signal. For energies ranging from 30.8 to 31.8 eV the original averaged ΔAbs is taken for the Fourier transform. For energies ranging from 36.1 to 42.0 eV the following rise and decay

function is subtracted:

$$\Delta\text{Abs}(t) = \frac{1}{1 + e^{-\frac{2t}{\tau_r}}} [B e^{\frac{-t}{\tau_d}} + C]. \quad (\text{C3})$$

The parameters are the same as in Eq. (C1). For energies ranging from 44.2 to 45.4 eV the following rise function is subtracted:

$$\Delta\text{Abs}(t) = \frac{C}{1 + e^{-\frac{2(t-t_1)}{\tau_r}}}. \quad (\text{C4})$$

The parameters are the same as in Eq. (C2). In the main paper all the analysis is done for a transient absorption spectroscopy measurement at a NIR pump peak intensity of 1.7 TW/cm². Here, we present the oscillation amplitude for three additional transient absorption spectroscopy measurements at 1.3, 1.4, and 1.8 TW/cm². We observe that the energy-dependent variation of the oscillation amplitude is qualitatively the same over the observed NIR pump peak intensity range.

- [1] E. Goulielmakis, Z.-H. Loh, A. Wirth, R. Santra, N. Rohringer, V. S. Yakovlev, S. Zherebtsov, T. Pfeifer, A. M. Azzeer, M. F. Kling, S. R. Leone, and F. Krausz, Real-time observation of valence electron motion, *Nature (London)* **466**, 739 (2010).
- [2] M. Holler, F. Schapper, L. Gallmann, and U. Keller, Attosecond electron wave-packet interference observed by transient absorption, *Phys. Rev. Lett.* **106**, 123601 (2011).
- [3] M. Chini, X. Wang, Y. Cheng, Y. Wu, D. Zhao, D. A. Telnov, S.-I. Chu, and Z. Chang, Sub-cycle oscillations in virtual states brought to light, *Sci. Rep.* **3**, 1105 (2013).
- [4] M. Lucchini, J. Herrmann, A. Ludwig, R. Locher, M. Sabbar, L. Gallmann, and U. Keller, Role of electron wavepacket interference in the optical response of helium atoms, *New J. Phys.* **15**, 103010 (2013).
- [5] M. Schultze, E. M. Bothschafter, A. Sommer, S. Holzner, W. Schweinberger, M. Fiess, M. Hofstetter, R. Kienberger, V. Apalkov, V. S. Yakovlev, M. I. Stockman, and F. Krausz, Controlling dielectrics with the electric field of light, *Nature (London)* **493**, 75 (2013).
- [6] A. R. Attar, H.-T. Chang, A. Britz, X. Zhang, M.-F. Lin, A. Krishnamoorthy, T. Linker, D. Fritz, D. M. Neumark, R. K. Kalia, A. Nakano, P. Ajayan, P. Vashishta, U. Bergmann, and S. R. Leone, Simultaneous observation of carrier-specific redistribution and coherent lattice dynamics in 2h-MoTe₂ with femtosecond core-level spectroscopy, *ACS Nano* **14**, 15829 (2020).
- [7] J. Oh, H.-T. Chang, C. T. Chen, S. Aloni, A. Schwartzberg, and S. R. Leone, Carrier and phonon dynamics in multilayer WSe₂ captured by extreme ultraviolet transient absorption spectroscopy, *J. Phys. Chem. C* **127**, 5004 (2023).
- [8] J. R. Adelman, H. Laurell, L. B. Drescher, H. K. D. Le, P. Yang, and S. R. Leone, Coherently coupled carrier and phonon dynamics in elemental tellurium probed by extreme ultraviolet transient absorption, *Phys. Rev. B* **111**, 184315 (2025).
- [9] V. Eyert, R. Horny, K.-H. Höck, and S. Horn, Embedded peierls instability and the electronic structure of MoO₂, *J. Phys.: Condens. Matter* **12**, 4923 (2000).
- [10] T. Fukuda, K. Makino, Y. Saito, P. Fons, A. Ando, T. Mori, R. Ishikawa, K. Ueno, J. Afalla, and M. Hase, Coherent optical response driven by non-equilibrium electron-phonon dynamics in a layered transition-metal dichalcogenide, *APL Mater.* **12**, 021102 (2024).
- [11] M. Volkov, S. A. Sato, F. Schlaepfer, L. Kasmi, N. Hartmann, M. Lucchini, L. Gallmann, A. Rubio, and U. Keller, Attosecond screening dynamics mediated by electron localization in transition metals, *Nat. Phys.* **15**, 1145 (2019).
- [12] E. W. de Vos, S. Neb, A. Niedermayr, F. Burri, M. Hollm, L. Gallmann, and U. Keller, Ultrafast transition from state-blocking dynamics to electron localization in transition metal beta-tungsten, *Phys. Rev. Lett.* **131**, 226901 (2023).
- [13] Z. Schumacher, S. Sato, S. Neb, A. Niedermayr, L. Gallmann, A. Rubio, and U. Keller, Ultrafast electron localization and screening in a transition metal dichalcogenide, *Proc. Natl. Acad. Sci. USA* **120**, e2221725120 (2023).
- [14] L. R. Baker, U. Diebold, J. Y. Park, and A. Selloni, Oxide chemistry and catalysis, *J. Chem. Phys.* **153**, 050401 (2020).
- [15] H. Fröhlich, Theory of the superconducting state. I. The ground state at the absolute zero of temperature, *Phys. Rev.* **79**, 845 (1950).
- [16] S. A. Sato, K. Yabana, Y. Shinohara, T. Otake, and G. F. Bertsch, Numerical pump-probe experiments of laser-excited silicon in nonequilibrium phase, *Phys. Rev. B* **89**, 064304 (2014).
- [17] G. Strinati, Application of the Green's functions method to the study of the optical properties of semiconductors, *Riv. Nuovo Cimento* **11**, 1 (1988).
- [18] C. Attaccalite, M. Grüning, and A. Marini, Real-time approach to the optical properties of solids and nanostructures: Time-dependent Bethe-Salpeter equation, *Phys. Rev. B* **84**, 245110 (2011).
- [19] E. Perfetto, D. Sangalli, A. Marini, and G. Stefanucci, Nonequilibrium Bethe-Salpeter equation for transient photoabsorption spectroscopy, *Phys. Rev. B* **92**, 205304 (2015).
- [20] M. Schultze, K. Ramasesha, C. Pemmaraju, S. Sato, D. Whitmore, A. Gandman, J. S. Prell, L. J. Borja, D. Prendergast, K. Yabana, D. M. Neumark, and S. R. Leone, Attosecond band-gap dynamics in silicon, *Science* **346**, 1348 (2014).

- [21] F. Schlaepfer, M. Lucchini, S. A. Sato, M. Volkov, L. Kasmi, N. Hartmann, A. Rubio, L. Gallmann, and U. Keller, Attosecond optical-field-enhanced carrier injection into the GaAs conduction band, *Nat. Phys.* **14**, 560 (2018).
- [22] M. Lucchini, S. A. Sato, A. Ludwig, J. Herrmann, M. Volkov, L. Kasmi, Y. Shinohara, K. Yabana, L. Gallmann, and U. Keller, Attosecond dynamical Franz-Keldysh effect in polycrystalline diamond, *Science* **353**, 916 (2016).
- [23] R. Locher, M. Lucchini, J. Herrmann, M. Sabbar, M. Weger, A. Ludwig, L. Castiglioni, M. Greif, M. Hengsberger, L. Gallmann, and U. Keller, Versatile attosecond beamline in a two-foci configuration for simultaneous time-resolved measurements, *Rev. Sci. Instrum.* **85**, 013113 (2014).
- [24] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Restoring the density-gradient expansion for exchange in solids and surfaces, *Phys. Rev. Lett.* **100**, 136406 (2008).
- [25] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. De Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos *et al.*, QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- [26] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. Buongiorno Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. Dal Corso, S. De Gironcoli, P. Delugas, R. A. DiStasio, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo *et al.*, Advanced capabilities for materials modeling with Quantum ESPRESSO, *J. Phys.: Condens. Matter* **29**, 465901 (2017).
- [27] P. Giannozzi, O. Baseggio, P. Bonfà, D. Brunato, R. Car, I. Carnimeo, C. Cavazzoni, S. De Gironcoli, P. Delugas, F. Ferrari Ruffino, A. Ferretti, N. Marzari, I. Timrov, A. Urru, and S. Baroni, Quantum ESPRESSO toward the exascale, *J. Chem. Phys.* **152**, 154105 (2020).
- [28] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study, *Phys. Rev. B* **57**, 1505 (1998).
- [29] I. Timrov, N. Marzari, and M. Cococcioni, Hubbard parameters from density-functional perturbation theory, *Phys. Rev. B* **98**, 085127 (2018).
- [30] I. Timrov, N. Marzari, and M. Cococcioni, Self-consistent Hubbard parameters from density-functional perturbation theory in the ultrasoft and projector-augmented wave formulations, *Phys. Rev. B* **103**, 045141 (2021).
- [31] I. Timrov, N. Marzari, and M. Cococcioni, HP – A code for the calculation of Hubbard parameters using density-functional perturbation theory, *Comput. Phys. Commun.* **279**, 108455 (2022).
- [32] A. Togo, First-principles phonon calculations with phonopy and phono3py, *J. Phys. Soc. Jpn.* **92**, 012001 (2023).
- [33] A. Togo, L. Chaput, T. Tadano, and I. Tanaka, Implementation strategies in phonopy and phono3py, *J. Phys.: Condens. Matter* **35**, 353001 (2023).
- [34] O. de Melo, Y. González, A. Climent-Font, P. Galán, A. Ruediger, M. Sánchez, C. Calvo-Mola, G. Santana, and V. Torres-Costa, Optical and electrical properties of MoO₂ and MoO₃ thin films prepared from the chemically driven isothermal close space vapor transport technique, *J. Phys.: Condens. Matter* **31**, 295703 (2019).
- [35] H. J. Zeiger, J. Vidal, T. K. Cheng, E. P. Ippen, G. Dresselhaus, and M. S. Dresselhaus, Theory for dispersive excitation of coherent phonons, *Phys. Rev. B* **45**, 768 (1992).
- [36] T. E. Stevens, J. Kuhl, and R. Merlin, Coherent phonon generation and the two stimulated Raman tensors, *Phys. Rev. B* **65**, 144304 (2002).
- [37] F. A. Lindemann, The calculation of molecular vibration frequencies, *Physikalische Zeitschrift* **11**, 609 (1910).
- [38] T. P. H. Sidiropoulos, N. Di Palo, D. E. Rivas, S. Severino, M. Reduzzi, B. Nandy, B. Bauerhenne, S. Krylow, T. Vasileiadis, T. Danz, P. Elliott, S. Sharma, K. Dewhurst, C. Ropers, Y. Joly, M. E. Garcia, M. Wolf, R. Ernstorfer, and J. Biegert, Probing the energy conversion pathways between light, carriers, and lattice in real time with attosecond core-level spectroscopy, *Phys. Rev. X* **11**, 041060 (2021).
- [39] R. M. Martin and L. M. Falicov, Resonant Raman scattering, in *Light Scattering in Solids*, edited by M. Cardona (Springer, Berlin, 1975), pp. 79–145.
- [40] See <https://doi.org/10.3929/ethz-c-000782787> for access.
- [41] P. M. Paul, E. S. Toma, P. Breger, G. Mullot, F. Augé, P. Balcou, H. G. Muller, and P. Agostini, Observation of a train of attosecond pulses from high harmonic generation, *Science* **292**, 1689 (2001).