**S.1. Method for extracting bond length from laser-induced electron diffraction images**

The laser-induced electron diffraction (LIED) method aims at probing the femtosecond dynamics of gaseous molecules under conformal transformation with atomic-scale spatial resolution. In a typical pump-probe scheme, a pump pulse creates a dynamic system and then the LIED probe would map the time-dependent positions of atoms. In such experiment, the duration of the probe pulse defines the temporal resolution, while the spatial resolution is retrieved from the electron diffraction image accumulated during this time. In this Letter, we report on an approach that allows the application of a single laser pulse to interrogate the bond length change of simple homonuclear diatomic molecules. Our results show that sub-Angstrom spatial resolution (5 pm) is facilitated by using intense long wavelength sources (> 1 µm). In addition, variation of the wavelength is equivalent to changing the delay between pump and probe. In our case, the clock is initialized by tunnel ionization (pump) and the probe is a field-driven wave packet that rescatters (diffracts) with the parent molecular core at a later time, i.e. approximately one optical cycle. The LIED method bridges a number of concepts from strong-field rescattering physics and conventional electron diffraction (CED). This document summarizes the practical steps and theoretical tools used in LIED, the data analysis method and error assessment.

**S.1.A. Summary of practical steps for retrieving bond length in LIED**

Figure S1 presents the LIED procedure in four pragmatic steps. In the LIED method a field-driven electron wave packet rescattering with its parent ionic core forms a conceptual analogy to CED where an external high-energy electron beam scatters from a molecular target gas. The following section discusses how these two different methods are made equivalent based on fundamental principles.

Panel 1: Measure the electron momentum angular distribution produced by tunnel ionization by a mid-infrared laser. The relevant electrons in the distribution are those created by high-energy rescattering events (> 100 eV).

Panel 2: *Field-free* electron-ion differential cross sections (DCS) are extracted from the momentum distribution using the principles of the quantitative rescattering theory (QRS). The theory formalizes the LIED process as a field-driven wave packet (electron beam) scattering from a molecular ion (core), see Eqn. (S1). The well-known imaging technique of conventional electron diffraction (CED) is conceptually similar: a beam from an electron gun impinges on gas-phase molecules and the elastic DCS is recorded.

**Figure S1:** The progression for extracting time-resolved bond lengths from the LIED method. Panel 1: an electron momentum distribution of a molecule is measured using an intense mid-infrared field. The long wavelengths promote tunnel ionization and penetrating hard collisions with the core. Panel 2: the quantitative rescattering (QRS) theory provides the fundamental principles for extracting *field-free* differential cross-sections (DCS) from the backscattered electrons in the momentum distribution. Procedurally, the next two panels are similar to the analysis of a conventional electron diffraction (CED) experiment. Panel 3: the molecular contrast factor (fringe pattern) is constructed within the independent atom model (IAM) and in Panel 4, the bond length, R(t), is extracted. The LIED method differs from the CED experiment since the extracted bond length is time resolved with femtosecond timing.
Panel 3: At this point, the LIED analysis proceeds in an analogous manner to the established methods of CED. The independent atom model (IAM) is used to analyze the extracted DCS. The elastic electron-atom scattering amplitudes for all the neutral atoms in the molecule at the selected recollision energies are calculated and the tunnel ionization rates of molecules by the laser at different alignment angles evaluated using Eqn. (S3).

Panel 4: The molecular bond length is determined at specific collision energies and different wavelengths. Using the parameters discussed in Panel 3, the theoretical DCS for different interatomic separations are calculated using IAM and compared to the experimental DCS extracted in Panel 2. The best-fit bond length is extracted using a genetic algorithm (GA). The GA’s fitness function is the variance of the difference between calculated and experimental DCS, as defined by Eqn. (S4). The time dependence of the bond length change is determined using the classical correspondence between wavelength and wave packet propagation time, as shown in Fig. S2b.

**S.1.B. Tunnel ionization, electron dynamics and rescattering**

In conventional electron diffraction (CED) experiments, the diffraction image (or DCS) is directly obtained from a laboratory-prepared multi-kilovolt electron beam\(^1\). In LIED, the electron “beam” is generated via tunnel ionization occurring when a molecule is exposed to a sufficiently intense low frequency laser field, as illustrated in Fig. 1a in the main text. In the tunneling regime the ionization rate is exponential with the field amplitude. According to Keldysh theory\(^3\), tunneling occurs when the Keldysh parameter, \( \gamma = (I_P/2U_P)\)\(^{0.5} \), is less than unity. Here \( I_P \) is the ionization energy and \( U_P \) is the average quiver energy of a free electron in the laser field. It is given by \( U_P (eV) = 9.33 \times 10^4 W/cm^2 \times \lambda^2 \) (\( \mu \)m), where \( I \) is the peak intensity of the laser and \( \lambda \) is the wavelength. A critical component of our technique is the use of a mid-infrared laser that provides access to \( \gamma < 0.5 \) (or equivalently, large return energies compared to the Coulomb potential of the ion) for all the experiments reported here. Fig. S2a shows a typical photoelectron energy distribution measured along the laser polarization with our apparatus. In the tunneling theory, electrons are created at \( t_b \) (initial phase in Fig. 1a) with zero velocity. The electron can then gain energy from the laser field. In the case of direct electrons, the maximum detected kinetic energy is \( 2U_P \). For an electron that returns to collide with the parent ion, the maximum detected energy is \( 10U_P \)\(^3\). Both these cutoff energies are evident in the detected energy distribution shown in Fig. S2a. In addition, the maximum kinetic energy at the return time, \( t_r \), is \( 3.2U_P \). Note that since rescattering occurs in the laser field, backscattered electrons gain an additional field momentum, \( A_r \), as can be seen from Fig. 1a if \( p_r \) is parallel to \( A_r \).

Fig. S2a also shows that low-energy electrons are more abundant (< \( 2U_P \)). The low-energy distribution is composed of direct electrons and electrons that rescatter in the forward direction. The interference between these two groups of electrons makes the analysis of this portion of the momentum distribution (inside the black dashed circle of Fig. 1a) nearly intractable. In the LIED method, analysis is restricted to high-energy electrons (> \( 2U_P \)) which result from elastic backscattering. For large scattering angles, the electron undergoes a large momentum transfer \( q \) which occurs only when the electron is deflected near the atomic centers of the molecule. Since \( |q| = 2p\sin(\theta/2) \) (see vector inset of Fig. 1a), a 100 eV electron scattered at \( \theta = 180^\circ \) would produce similar \( q \)-values as in a standard CED experiment where a multi-kilovolt electron is forward scattered (\( \theta \leq 5^\circ \)). Since CED is a well established method for precisely determining bond length distances, if the field-free DCS can be extracted from the LIED experiment, as described herein, than the bond retrieval method used in CED is directly applicable.\(^1\)
The principle of utilizing rescattering for extracting molecular structure has been discussed in several theoretical papers. These investigations use a space-fixed, one-electron molecular model exposed to a well-defined laser pulse. However, these approximations do not translate well to real experiments where the molecules are only partially aligned and ionization occurs from a
distribution of intensities. Experimentally, bond length relaxations extracted from fragment kinetic energy release7,39,40 following dissociation or Coulomb explosion of H$_2^+$ or D$_2^+$ have been studied at different laser wavelengths. Investigations using high harmonic generation by the so-called PACER method$^{41,42}$ probes the bond length relaxation by comparing spectra from different isotopes and at different wavelengths. Earlier LIED experiments using 0.8 µm lasers have been reported$^{24-27}$. While the DCS can be extracted, the return energy (momentum exchange) from these experiments is too low to extract the bond length directly. The current LIED investigation bridges all the critical elements for a direct and precise general method of determining atomic position using the attributes of long wavelength lasers: high-energy electron production, core penetrating collisions and tunnel ionization.

**S.1.C. Quantitative Rescattering Theory**

According to the quantitative rescattering (QRS) theory$^{11,22,23}$, the experimental photoelectron momentum distribution $I(p)$ is related to elastic electron-ion differential scattering cross section $\hat{\sigma}(p_r, \theta)$ via,

$$I(p) = W(p_r)\hat{\sigma}(p_r, \theta).$$  \hspace{1cm} (S1)

This equation interprets that $I(p)$ is the result of a beam of field-driven electrons elastically scattered by the ion into a range of angles $\theta$. The proportional constant $W(p_r)$ is the electron wave packet flux integrated over the laser pulse duration and the laser focus volume. The detected momentum of the photoelectron $p$ displayed in Fig. 1a is related to the momentum of the electron $p_r$ at rescattering by $p = p_r - A_r$. The additional momentum $A_r = A(t_r)$ is the vector potential of the laser field at time of rescattering, $t_r$. Since the return time varies only slightly with the electron momentum and intensity, a single return time (and $A_r$) is used to extract the DCS from Eqn. (S1).

Following Eqn. (S1), the unnormalized DCS, $\hat{\sigma}(p_r, \theta)$, (the experiment is not an absolute measurement) can be extracted from $I(p)$ by tracing an elastic scattering circle (or more generally, a sphere), e.g. the magenta dashed circle in Fig. 1a. The central point is that the resulting DCS is independent of laser parameters, e.g. intensity, wavelength and pulse duration. In the LIED approach the laser’s only role is to act as a source of returning electrons for scattering measurements with momentum $p_r$. The validity of Eqn. (S1) has been confirmed by several experiments using atomic and molecular targets, although limited to studies at a 0.8 µm wavelength$^{24-27}$. It has also been verified for different atoms and molecules using our unique mid-infrared lasers, Fig. 1b being a typical example. For longer wavelength drivers, the scattering events are significantly more energetic$^{16}$ ($\lambda^2$-scaling of $U_P$), a prerequisite for the IAM structural analysis.

**S.1.D. Basic electron diffraction theory and independent atom model (IAM) for CED**

The goal in conventional electron diffraction (CED) experiments is to determine the positions of atoms composing a molecule. Experimentally, an external source of a monochromatic electron beam is scattered from a molecular gas target. Typically, the beam has an energy of 10-100 keV and the elastic scattered electrons are detected in the forward direction at small angles$^{12}$. The electron-molecule collision can be defined as “soft” or “hard” by the momentum transfer $q = 2p_0\sin(\theta/2)$, where $p_0$ is the momentum of the incident electron and $\theta$ is the scattering angle. For a typical CED experiment, $q$ has a range of values from 5-20 Å$^{-1}$ which implies a scattering distance of closest approach of ≤0.1 Å. For these “hard” collisions, the large momentum transfer is affected by the strong electric field near the atomic core and less by the weaker field of the outer-shell valence electrons. Consequently, the molecular image can be viewed as derived from
a collection of independent atoms fixed in space, i.e., one can employ the simplest ball-and-stick model of a molecule. The goal of electron diffraction is to identify the balls and the length of the sticks in the molecule.

Based on the above picture, the diffraction image of a CED experiment is described by the coherent scattering on all atoms in the molecule. Let atom \( j \) be located at position \( \mathbf{R}_j \); then, the scattering amplitude of the incident electron by the entire molecule is given by:

\[
F_M(\mathbf{q}, \Omega) = \sum_j f_j(\theta) e^{-i\mathbf{q} \cdot \mathbf{R}_j}, \tag{S2}
\]

where \( \Omega \) describes the orientation angle of the molecule with respect to the incident beam and \( f_j(\theta) \) is the complex elastic differential scattering amplitude with momentum transfer \( \mathbf{q} \) for the \( j \)th atom. The diffracted image is defined by \( |F_M(\mathbf{q}, \Omega)|^2 \). To obtain the image from randomly oriented molecules, as is the case for most CED experiments, \( |F_M(\mathbf{q}, \Omega)|^2 \) is averaged over the orientation angles \( \Omega \). For homonuclear diatomic molecules, this yields the DCS as

\[
\sigma_M = 2\sigma_A + 2\sigma_A \sin(qR)/qR,
\]

where \( \sigma_A \) is the atomic DCS. For more complex molecules, the DCS will depend explicitly on the phase and magnitude of the scattering amplitudes \( f_j(\theta) \). Note that the scattering amplitudes are not calculated using the Born approximation, even at the 10-100 keV energies used in CED. Instead they are derived using a partial wave expansion method as described in elementary quantum mechanics. For atoms, such calculations for elastic collisions at energies above 100 eV are quite simple and accurate.

As discussed above, for a CED experiment a momentum transfer in the range of 5-20 Å\(^{-1}\) for electrons scattered in the forward direction is satisfied by 10-100 keV beam energies. However, field-driven electrons produced by an intense mid-infrared laser in a LIED experiment yields rescattering energies of ~100-250 eV. Nonetheless, a similar range of q-values can be realized at lower energies by backscattered electrons. For instance, a 100 eV incident energy scattered into angles from 60° to 180° would yield q-values from 5.1-10.3 Å\(^{-1}\). Likewise, 200 eV electrons produce q’s of 7.2-14.5 Å\(^{-1}\). Assuming the validity of the IAM model, then we can procedurally retrieve the molecular bond length from the measured LIED images. This conjecture was theoretically investigated previously using the DCS obtained for large-angle CED measurements for CO\(_2\) and C\(_2\)H\(_4\) at incident energies ≥100 eV. The following discussion summarizes these principles for \( e^-\)N\(_2\) collisions.

Figs. S3a and b show CED measured DCS for 100 eV (solid red squares) and 200 eV (solid orange circles) electrons colliding with N\(_2\) at large scattering angles. The \( e^-\)N interaction is modeled via a Yukawa potential \( V(r) = Ze^{-\alpha r}/r \) with \( Z = 7 \) and \( \alpha = 1.695 \). For oxygen (not shown), the Yukawa potential has \( Z = 8 \) and \( \alpha = 1.720 \). Using standard quantum mechanical scattering theory, the complex scattering amplitudes \( f(\theta) \) in Eqn. (S2) can be calculated. Fig. S3a shows the calculated DCS curve (dotted green line) with the known N-N equilibrium bond length, \( R_{eq} \), of 1.10 Å. The atomic term is also shown (blue dashed line). Note that the experimental data and the IAM predictions oscillate about the atomic term. The phase of the oscillation from the IAM model agrees well with the experiment, even though the amplitude shows deviations. A consistency check of our bond length retrieval method is performed by using the same scattering amplitudes and taking the N-N distance as a free parameter to fit the experimental data. This procedure yields a N-N bond length \( R_{fit} = 1.13 \) Å for 100 eV and 1.09 Å for 200 eV, in very good agreement with the accepted value of 1.10 Å. The resulting DCS curves are also plotted in Figs. S3a and b. This, along with other examples, establishes that CED data at 100 eV can achieve an accuracy of ~0.05 Å or smaller. Of course, higher collision energies will improve the accuracy for comparable counting statistics. However, scattering cross sections typically decrease with increasing electron energies, leading to lower counting rates and longer acquisition times.
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Figure S3: Validity of IAM: retrieval of \( \text{N}_2 \) bond lengths using DCSs from CED data. Full solid squares and circles are experimental DCSs from electron-molecule collisions at large angle for incident energy of (a) 100 eV and (b) 200 eV, respectively. In both (a) and (b), the DCSs (green dotted lines) with the known equilibrium bond length, \( R_{eq} = 1.10 \, \text{Å} \) are calculated using IAM, and the atomic terms (blue dashed lines) give the DCS for electron-nitrogen-atom collisions. Fitting the experimental data to IAM with the bond length as a parameter, we retrieved the N-N bond lengths \( R_{fit} \) of 1.13 Å at 100 eV and 1.09 Å at 200 eV, in very good agreement with the accepted length \( R_{eq} = 1.10 \, \text{Å} \). The DCSs from IAM with fitted bond lengths \( R_{fit} \) are also shown by the red curve in (a) and the orange curve in (b). In (c), MCF from experimental DCSs in (a) and (b) and their corresponding best fits are plotted against the momentum transfer \( q \). For 100 eV, the experimental MCF curve has been multiplied by 0.3 from the actually calculated ones. Note that scaling does not change the position of the peak of the curve or the values of \( q \) where it changes sign. The IAM approximation may not lose accuracy at 100 eV but the global oscillation in the MCF still provides an accurate method for retrieval of the bond distance.
Figure S3c shows the molecular contrast factor (MCF) calculated via IAM using the two fitted R’s from Figs. S3a and b (maintaining the same label convention used above). The two curves should be continuous if the derived R’s are identical. The 200 eV CED data does agree well with the IAM curve except the deviations of the last three points, possibly due to the small cross section at large angles. The 100 eV experimental data points have been scaled by 0.3 but this does not affect the peak (fringe) position or the q-value where the MCF changes sign. Note that the R was fitted from the DCS directly, i.e. without scaling. The MCF shows that the experiment still follows the oscillation in q as predicted by the IAM, even though the magnitude does not. Despite this limitation, the retrieved R is accurate (1.13 Å versus 1.10 Å) and clearly demonstrates that the retrieval method of R is sensitive to the oscillatory behavior (fringe pattern) of the molecular term and not the magnitude of MCF. This same conclusion can be drawn with respect to Young’s double slit experiment where the information on the slit separation is contained in the global oscillation of the fringe pattern and not the fringe luminosity.

We comment that the method used above follows the standard gas-phase CED method. In CED, corrections due to vibrational motion of the molecules can also be included. In addition for multi-keV collision energies the electron’s deBroglie wavelength is much smaller than our LIED study, thus bond length accuracy can approach 0.01 Å. In dynamic systems we are looking for large bond length change of a fraction to a few Angstroms, thus such high spatial resolution is not necessary. Based on the analysis discussed above, we conservatively estimate that the accuracy of our LIED method is ∼0.05 Å for rescattering electron energies of ∼100 eV.

S.1.E. Using IAM to retrieve N-N and O-O bond lengths from LIED

In a LIED experiment, the returning electron scatters from its parent ion, not the neutral. In the IAM approximation, this implies that one needs to consider N$_2^+$ as composed of N$^+$+N or N+N$^+$. For application to large polyatomic molecules this procedure would make the IAM model extremely complicated. However, the LIED diffraction images at long wavelength result from core penetrating (hard) collisions with N or N$^+$. At short ranges the potentials between e--N and e--N$^+$ are essentially identical, thus the DCS for both should be the same for large q. In other word at the energies considered, the e--N$_2^+$ collision will be treated as an e--N$_2$ collision for large scattering angles.

The validity of this approximation has been investigated by various methods. Experimentally, the measured DCS at large angles (> 60°) in rescattering collisions extracted from the laser experiment agree well with those from e--Ar CED collision experiment for energies at ≥100 eV. This is further illustrated in Fig. 1b for N$_2$ LIED and CED measurements. Furthermore, theoretical calculations based on the model potential for e--O$^+$ and e--N$^+$ collisions agree with the corresponding neutral targets at 100 eV and higher for scattering angles greater than 70 degree.

In the present experiment, the molecules are unaligned. Thus the DCS is obtained by averaging over the randomly distributed molecules. In a CED experiment the electron beam flux is constant for all orientations of the molecule but in LIED the electron wave packet is generated from the molecule itself. Thus, the flux of the returning electron wave packet which is proportional to the tunneling ionization rates depends on the orientation of the molecules. Let $\Omega$ be the orientation angle between the molecular axis and the polarization axis for a linearly polarized laser. The $\Omega$-dependence of the ionization rate $N(\Omega)$ can be calculated using the molecular tunneling ionization theory. For O$_2$ and N$_2$ molecules, the MCF has the simple form

$$MCF = \int \cos(\mathbf{q} \cdot \mathbf{R}) N(\Omega)d\Omega/\int N(\Omega)d\Omega$$  

(S3).
Unlike CED, in LIED the $N(\Omega)$ makes the MCF to depend not only on $q$, but also weakly on the electron’s return energy. Furthermore, the ionization rate $N(\Omega)$ might also have a weak dependence on the laser intensity$^{17}$. These effects have all been included in the theory.

**S.1.F. Role of excitations in CED and LIED**

Both CED and LIED experiments measure the differential cross sections (DCS) of molecular targets produced by energetic electrons. Typical neutral molecules have excited electronic (in addition to rotational and vibrational) states that are only a few eV’s above the ground state, thus the measured DCS would inevitably include contributions from both the elastic and inelastic scattering. However, theoretical DCS calculated within IAM does not explicitly include the DCS from inelastic collisions. How much error does this approximation introduce? This issue could potentially compound the interpretation of an LIED experiment. Below we show through a combination of theoretical analysis and experimental evidence that the contribution of inelastic collisions to the DCS is small.

In the IAM model, a molecule is approximated as a collection of non-interacting atoms. If the interactions among the atoms are included, then molecular orbitals are formed by a combination of atomic orbitals. Thus for $N_2$, the set of molecular orbitals that are constructed from the 2p orbitals of the two nitrogen atoms should be degenerate, and included as elastic channels within the IAM model. [Analogously: if spin-orbit interaction is not included, then the fine structure levels are treated as degenerate.] Clearly this is a good approximation only when the collision energy is large compared to the excitation energies. For excitation energies of 10 eV and collision energies of 100 eV, at each scattering angle, the difference of momentum transfer for the elastic and inelastic processes will differ by $\sim 2.5\%$. Assuming that the inelastic collision is as important as elastic scattering then a 2.6\% error is introduced into the bond length determination. However, typical experimental data for neutral targets shows that for incident energies of 100 eV or higher the inelastic cross sections are only a few percent of the elastic channel$^{49,50}$. Differential measurements for $e^+ + ion$ collisions, such as $N_2^+$ and $O_2^+$, are rarer and unfortunately, to the best of our knowledge, nonexistent, including the energies covered in our experiment. Therefore, we take the ratio of a few percent or less for the inelastic collision as compared to the elastic one around 100 eV to be true for molecular ion targets just as it was found for neutrals. In addition, the elastic and inelastic DCS recorded at the same collision energy for an $N_2O$ experiment$^{51}$ display a very similar angular dependence for both channels at large scattering angles. This is easily understood since large-angle scattering occurs only when the electron is scattered close to the atomic core, thus a loss of a few eV’s in the incident energy due to excitation will not significantly alter the scattering angle or shift the interference fringe pattern. Thus we conclude, as has been done for decades in CED experiments, that IAM is a valid model for DCS analysis in our LIED measurement.

**S.1.G. Data analysis**

**1) Extracting DCS from measured photoelectron momentum distributions**

For each momentum distribution measurement at a given laser peak intensity, select an electron return energy, e.g. 100 eV ($p_r=2.71$ a.u.). Using the classical dynamics for long trajectories, calculate the birth ($t_b$) and return ($t_r$) times for the prescribed experimental wavelength $\lambda$. Note that $p_r=A(t_r)-A(t_b)$ since the electron is assumed to have zero initial velocity (additional details can be found elsewhere$^{23}$). Using the return time the laser’s vector potential, $A(t_r)$, is determined and finally, using the values of $p_r$ and $A(t_r)$, a scattering circle at constant scattering energy is constructed (see magenta circle in Fig.1a).
To improve the statistics, a desired uncertainty, \( \Delta p_r \), is selected, typically a few percent. From \( p_r^{\text{min}} = p_r - \Delta p_r \) and \( p_r^{\text{max}} = p_r + \Delta p_r \), the corresponding values for the vector potential, \( A_r^{\text{min}} \) and \( A_r^{\text{max}} \) are estimated, respectively. Next, for a given detected angle, \( \alpha \), we determine the detected momenta \( p_{\text{min}} \) and \( p_{\text{max}} \) and scattering angles \( \theta_{\text{min}} \) and \( \theta_{\text{max}} \) using the sine law for the triangles formed by \((p_r^{\text{min}}, A_r^{\text{min}}, \alpha)\) and \((p_r^{\text{max}}, A_r^{\text{max}}, \alpha)\), respectively. Then, using the raw electron time-of-flight data recorded at an angle \( \alpha \), we integrate the counts in the time interval, \( \tau \), corresponding to the momentum interval \( \Delta p = p_{\text{max}} - p_{\text{min}} \). Each time bin \( t \) is weighted by the Jacobian, \( J = p^3 \), and the yield of electrons scattered at the angle \( \theta(\alpha) = (\theta_{\text{max}} + \theta_{\text{min}})/2 \) is obtained. Finally, repeating the above procedure for every detected angle \( \alpha \), we obtain the yields for electrons scattered with momentum \( p_r \). The statistical error bars plotted in the figures are obtained from the total number of counts \( N \) contained in the interval \( \tau \), assuming Poisson statistics, \( i.e. \Delta N = N^{1/2} \). Obviously, the uncertainty \( \Delta N \) is directly related to the chosen uncertainty \( \Delta p_r \) and in practice the value is selected to obtain a relative uncertainty \( \Delta N/N \) better than 10%.

(2) The Genetic Algorithm fitting procedure

Using the experimental DCS, we fit the interatomic distance \( R \) using a genetic algorithm\(^\text{17}\). The fitness function is defined as,

\[
\chi^2(R, \beta) = \sum_i \left[ \frac{\sigma_i^{\text{exp}}}{\sigma_i^{\text{atom}}} - \beta \frac{\sigma_i^{\text{theory}}(R)}{\sigma_i^{\text{atom}}} \right]^2 \tag{S4}
\]

where \( i \) refers to discretized values of \( q \) and \( \beta \) is a normalization constant since the experimental DCS is not absolute. At each angle, the experimental and theoretical cross sections are normalized by the atomic cross sections in order to have equal weighting at all angles. Recall from Section S.1.D that the molecular DCS oscillates around the smooth atomic DCS. At the energies treated here, the atomic DCS has a minimum at some angle. The smallest value of \( q \) is selected close to where the atomic DCS and the extracted DCS begin to deviate. For computational efficiency, we limit the search to a range of \( R \) [0.95 Å, 1.60 Å].

S.1.H. Error estimate of the recollision time

In our experiment, pulses of 50 fs duration are used (7-8 cycles at 2 µm). The time propagation of the electron between birth and recollision \( \Delta t = t_r - t_b \) is calculated from 1D classical mechanics, ignoring the ionic potential. For the long trajectories, \( \Delta t \) is 4.3, 5.4 and 6.3 fs for the wavelengths of 1.7, 2.0 and 2.3 µm, respectively. These estimated times can be modified by several factors and are discussed below.

First, as discussed earlier, \( \Delta t \) depends on the value of the vector potential at the atom position and therefore must be averaged over the focal volume intensity distribution. It is reasonable to limit the range of intensities to ±15% because of the exponential dependence of the tunneling rate. The resulting uncertainty on the propagation time is approximately 0.2-0.3 fs.

Second, the classical model predicts two classes of rescattering trajectories, dubbed short and long. Our analysis of the high-energy rescattering events is based on long trajectories but the short trajectories will affect the propagation time for all detected energies except at the 10U\( p \) cutoff where the two trajectories merge. The corresponding times are approximately a quarter-cycle shorter (2 fs at 2µm) than the long but this difference decreases rapidly with increasing return energy and vanishes at the cutoff. The exact contribution of the short and long trajectories
to the LIED image is difficult to evaluate but some general statements can be inferred. For one, the short trajectories have an initial phase that is later in the field-cycle (low field amplitude) than the long trajectories. Consequently, the exponential dependence of the tunnel rate on the electric field strength favors long trajectory production. For the return energies of 1.5-2U_p typically used in our LIED analysis and a peak intensity at 1.3×10^{14} W/cm^2, the short trajectory contribution is 6-14% of the long one. For a 2.3 µm LIED experiment this would give return times of 3.3±0.2 fs and 6.3±0.2 fs for the short and long trajectories, respectively. For our current LIED investigation, a conservative estimate of the temporal resolution is 2-3 fs. However, improvement in future experiments can increase the temporal resolution by analyzing the electron momentum near the classical cutoff or using bichromatic fields for differential control over the short and long trajectories. Resolution of this issue needs further experimental and theoretical investigations.

Third, the electron wave packet continues to oscillate in the field after the first rescattering and may re-encounter the ion several more times, resulting in a large uncertainty in the recollision time. These multiple returns are all children of the long trajectory discussed above and as it continues to propagate the wave packet spreads (∝ λ^2) in the transverse dimension, thus diminishing the electron flux with each subsequent return. In addition, the rescattering energy is reduced below 2.4U_p for these multiple returns, as compared to 3.2U_p for the first returns. Thus the high energy portion of the momentum distribution is produced mostly by single return events. Furthermore, if the multiple returns were significant, then the recollision events in LIED would temporally sample the molecular core at very different internuclear distances. Consequently, the MCF fringe visibility would be strongly reduced due to the sum of shifted patterns and it would be impossible to fit the data with a single R value, let alone derive physically significant bond lengths. In fact, the importance of multiple returns has been previously analyzed for 0.8 µm ionization^52. Using the second-order strong-field approximation^52, we calculate the wave packets for the first and third returns for 2 µm pulses.
The result is plotted in Fig. S4 and includes the average over the focal volume intensity distribution. The figure shows that at a 2Up return energy, the 3rd-return is only 12% of the 1st-return and its contribution diminishes at higher energies. Up is defined by the peak intensity at the focus. The 2nd-return (not shown) is not a relevant trajectory since the field drives the recollision with the ion from the opposite direction relative to the 1st and 3rd returns. We comment that the above conclusion was obtained for different atomic targets and laser intensities. In the calculation, each multielectron atom is approximated by a model potential, and the effect of core potential on the electron motion is found to be very weak. This is consistent with the QRS model where the wave packet is determined mostly by the laser field. In conclusion, the effect of multiple returns in our LIED measurements is considered negligible. In the future, experiments using few-cycle (2-3) long wavelength pulses can further reduce this effect.

Supplement references: