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ABSTRACT

Visualizing molecular transformations in real-time requires a structural retrieval method with Ångström spatial and femtosecond temporal atomic resolution. Imaging of hydrogen-containing molecules additionally requires an imaging method sensitive to the atomic positions of hydrogen nuclei, with most methods possessing relatively low sensitivity to hydrogen scattering. Laser-induced electron diffraction (LIED) is a table-top technique that can image ultrafast structural changes of gas-phase polyatomic molecules with sub-Ångström and femtosecond spatiotemporal resolution together with relatively high sensitivity to hydrogen scattering. Here, we image the umbrella motion of an isolated ammonia molecule (NH₃) following its strong-field ionization. Upon ionization of a neutral ammonia molecule, the ammonia cation (NH₃⁺) undergoes an ultrafast geometrical transformation from a pyramidal ($\Phi_{\text{HNH}} = 107^\circ$) to planar ($\Phi_{\text{HNH}} = 120^\circ$) structure in approximately 8 femtoseconds. Using LIED, we retrieve a near-planar ($\Phi_{\text{HNH}} = 117 \pm 5^\circ$) field-dressed NH₃⁺ molecular structure 7.8–9.8 femtoseconds after ionization. Our measured field-dressed NH₃⁺ structure is in excellent agreement with our calculated equilibrium field-dressed structure using quantum chemical *ab initio* calculations.

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I. INTRODUCTION

Many important processes in nature rely on the motion of hydrogen atoms, such as the influence of proton dynamics on the biological function of proteins.^{1,2} The motion of the hydrogen atom, which is the lightest element in the periodic table, occurs on the few-femtosecond (few-fs; 1 fs = 10⁻¹⁵ s) timescale and represents the fastest possible nuclear motion in molecules. Consequently, a method is required that is both sensitive and fast enough to probe the motion of hydrogen atoms with sub-Ångström (sub-Å; 1 Å = 10⁻¹⁰ m) spatial and femtosecond temporal atomic resolutions.^{3,4} The static geometric structure of molecules can be successfully determined through a variety of

imaging and spectroscopic techniques,⁵ such as conventional electron diffraction (CED),⁶ x-ray diffraction and crystallography,⁷ optical and nuclear magnetic resonance (NMR) spectroscopies,⁸ scanning tunneling microscopy (STM),⁸ and atomic force microscopy (AFM).⁸ In particular, the time-resolved analogues of x-ray and electron diffraction, such as ultrafast x-ray diffraction (UXD)^{9,10} and ultrafast electron diffraction (UED),^{11–18} have provided a wealth of dynamical information in molecules that contain atoms much heavier than hydrogen. As a result, their scattering signal in such molecules is very large, and their respective dynamics occur on the hundreds-of-femtosecond timescale.

Laser-induced electron diffraction (LIED)^{5,19–30} is a strong-field variant of UED that can directly retrieve the geometric structure of gas-phase molecules containing hydrogen atoms with sub-Å and few-to-sub-fs spatiotemporal resolution. The LIED technique is based on probing the molecular geometric structure using the molecule's own emitted electron to elastically scatter against the atomic cores in the molecule during strong-field-induced recollisions. The intra-optical-cycle nature of the LIED process enables structural retrieval with sub-femtosecond time resolution. Moreover, because of the small de Broglie wavelength of the electrons, the technique provides picometer (pm; $1 \text{ pm} = 10^{-12} \text{ m}$) spatial resolution. Importantly, LIED is sensitive to hydrogen atom scattering as the kinetic energy of scattering electrons in LIED (i.e., 50–500 eV) is significantly lower than the tens or hundreds of keV used in UED. At these low impact energies, hydrogen exhibits significant scattering cross section values compared to those at the high energies and forward-only scattering employed in UED. Presently, improving sensitivity to hydrogen scattering with other methods is challenging. Moreover, the low-energy nature of LIED electrons also provides a probe of the angular dependence of elastic electron scattering, and thus the extraction of doubly differential scattering cross sections.

In this work, we demonstrate LIED's capability to image the motion of hydrogen atoms on the few-fs timescale by studying the umbrella (inversion) motion of the ammonia molecule (NH_3) following its strong-field ionization. Photoelectron spectra and photoionization-induced dynamics of individual ammonia molecules and clusters have been a topic of interest in the past decades, both experimentally^{31–35} and theoretically.^{34–40} Neutral ammonia at its equilibrium configuration has a pyramidal shape, described by the C_{3v} symmetry point group, with an equilibrium H–N–H bond angle,⁴¹ Φ_{HNH} , of 107° , as shown in Fig. 1. When ionized, the ammonia molecule undergoes a significant geometrical transformation as the ammonia cation in its ground electronic state has a planar equilibrium geometry of D_{3h} symmetry with an equilibrium Φ_{HNH} of 120° . Förster and Saenz (2013) developed a theoretical model to describe the inversion motion of the ammonia cation (NH_3^+) for high-harmonic spectroscopy (HHS), where they predict that the NH_3^+ nuclear wave packet reaches the potential minimum on a 5-fs timescale.³⁶ Kraus and Wörner³⁴ theoretically investigated the pyramidal-to-planar transition in NH_3^+ , which they calculated to occur on a 7.9-fs timescale. The authors also experimentally studied the same dynamics but could only indirectly provide partial evidence of the umbrella motion through high-harmonic spectroscopy (HHS). These HHS measurements were, in fact, performed at different wavelengths in the near-infrared (NIR) up to $1.8 \mu\text{m}$, reaching a temporal range of up to 3.8 fs after ionization to be investigated. In the aforementioned HHS studies, structural information could only be indirectly obtained, with no direct imaging studies previously reported. Here, we use mid-infrared (MIR)-LIED to directly retrieve structural information of the NH_3^+ cation 7.8–9.8 fs after ionization, which is on a similar (7.9-fs) timescale as that predicted for the pyramidal-to-planar transition to occur in the NH_3^+ cation.³⁴

This paper is organized as follows: First, a brief overview of the experimental setup and the theoretical methods employed in this work is given in Sec. II, followed by a discussion of the experimental and theoretical results in Sec. III, and finally, a summary and conclusion of our results are presented in Sec. IV.

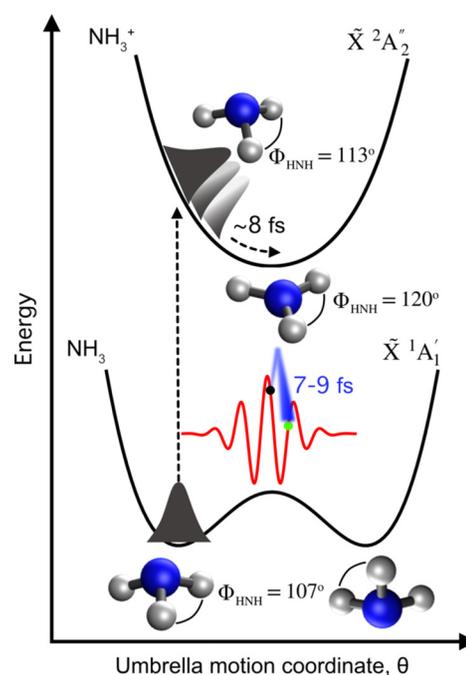


FIG. 1. Scheme of the ultrafast umbrella motion of ammonia. The potential energy curves for the neutral (cation) NH_3 (NH_3^+) in the ground electronic state \tilde{X}^1A_1' (\tilde{X}^2A_2'') are shown. Upon strong-field ionization, a nuclear wave packet is launched into the electronic ground state of the cation, \tilde{X}^2A_2'' , reaching the minimum of the cation's potential energy curve on a predicted ~ 8 -fs timescale. We probe the geometric structure of the NH_3^+ cation by ionizing a neutral NH_3 molecule (see black dot) and emitting an electron wave packet (blue shaded) that recollides back onto the target NH_3^+ ion 7.8–9.8 fs after ionization (see green dot) through the MIR-LIED process. The HNH bond angle, Φ_{HNH} , for the structures shown is indicated.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

A. Mid-infrared (MIR) OPCPA source

The MIR laser source is a home-built optical parametric chirped-pulse amplifier (OPCPA) that has been previously described.⁴² Briefly, the OPCPA setup generates a $3.2 \mu\text{m}$ laser pulse with a duration of 100 fs full-width at half maximum (FWHM) at a 160 kHz repetition rate. The high repetition rate compensates for the reduced rescattering cross section due to the λ^{-4} scaling factor.⁴³ The laser pulse is focused into the molecular beam using an on-axis paraboloid that is placed inside the reaction microscope. The focal spot size achieved was $6\text{--}7 \mu\text{m}$, resulting in a peak intensity, I_0 , of $1.3 \times 10^{14} \text{ W/cm}^2$. Such peak intensity translates to a ponderomotive energy (i.e., the average kinetic energy of a free electron in an oscillating electric field), U_p , of 120 eV, which corresponds to the maximum classical return energy ($E_r^{\text{max}} = 3.17U_p$) of about 380 eV, and the maximum backscattered energy ($E_{\text{resc}}^{\text{max}} = 10U_p$) of 1200 eV. The Keldysh parameter,⁴⁴ $\gamma = \sqrt{I_p/(2U_p)}$, was approximately 0.2.

B. Reaction microscope detection system

The detection system is based on a reaction microscope (ReMi),⁴⁵ which has been previously described in detail elsewhere⁴⁶

with only a brief summary presented here. A cold ($T < 100$ K) ammonia jet (5% NH_3 , 95% He) was supersonically expanded into an ultra-high vacuum (UHV) chamber. Here, the interaction with the laser focus takes place, ionizing the gas. Upon strong-field ionization, the generated ions and electrons were guided using homogeneous electric (\vec{E}) and magnetic (\vec{B}) fields of 34 V/cm and 13 G, respectively, toward two opposing time-sensitive microchannel plate (MCP) sensors. These sensors are interfaced with position-sensitive delay-line anode detectors. The three-dimensional (3D) momentum distribution (p_x , p_y , and p_z) of charged particles is extracted from the time-of-flight (ToF; parallel to the z -axis) and the (x, y) impact position on the two-dimensional (2D) detector plane. Charged particles are detected in full electron-ion coincidence, enabling the isolation of different reaction paths.

C. Theoretical framework of LIED retrieval

LIED is a strong field technique, in which a rescattering electron acquires structural information when scattered off its target in the presence of a laser field. Therefore, measured momenta contain two contributions: a momentum shift due to scattering off the target molecule and a momentum shift due to the vector potential of the laser at the time of rescattering. The value of the vector potential varies during the laser cycle, and thus imparts different momentum at the varying times of rescattering during the laser cycle. Under quasi-static (tunneling) conditions, the exact time variation can, however, be determined with very good accuracy from the classical recollision model. The vector potential can be extracted from a measurement of the laser's peak intensity directly. We employ another, more accurate way, to extract the vector potential directly from the identification of the $2 U_p$ turnover between direct electrons and the rescattering plateau, and the cut-off at $10 U_p$. The value of the electric field, and thus the vector potential, is found according to $U_p = E_0/4\omega^2$. In addition, we determine the laser peak intensity by fitting the momentum dependent ionization rate calculated after the Ammosov-Delone-Krainov⁵⁸ (ADK) theory to the longitudinal ion momentum distribution (p_{\parallel}) of Ar^+ ions. Both methods work very well and yield $I_0 = 1.3 \times 10^{14} \text{ W/cm}^2$ ($E_0 = 0.06 \text{ a.u.}$). As already mentioned, the measured electron rescatters from the parent ion in the laser field where it receives an additional momentum kick from the laser related to its vector potential, $A_r(t_r)$, at the time of rescattering, t_r , in polarization direction. Therefore, the final detected momentum, k_{\parallel} (k_{\perp}), parallel (perpendicular) to the laser polarization direction is related to the return momentum, k_r , and scattering angle, θ_r , as $k_{\parallel} = -A_r(t_r) \pm k_r \cos(\theta_r)$ and $k_{\perp} = k_r \sin(\theta_r)$. Fourier transform (FT)-LIED is based on the measurement of backscattered electrons (i.e., for $\theta_r = 180^\circ$), thus yields $k_r = k_{\text{resc}} - A_r(t_r)$, where $A_r(t_r)$ is calculated for a detected momentum, k_{resc} , employing the classical recollision model which is valid under our quasi-static field conditions. The position $x(t, t_b)$ of the electron in a linearly polarized electric field can be obtained from the classical equation of motion according to $x(t, t_b) = \frac{E_0}{\omega^2} [\sin(\omega t_b)(\omega \Delta t) + \cos(\omega t) - \cos(\omega t_b)] + v_0 \Delta t + x_0$, where t_b and t are the time of birth and time in the laser field, respectively, and Δt is the difference between t_b and t . For quasi-static conditions, the initial velocity, v_0 , of the electron at the tunnel exit, x_0 , is assumed zero. An electron will return to the parent ion when $x(t_r, t_b) = 0$ at the time of rescattering, t_r . The equation of motion can be solved numerically by Newton's method, and general solutions

are found for electrons tunneling between $0 \leq t_b \leq 0.25$ of an optical cycle and returning between $0.25 \leq t_r \leq 1$ of the optical cycle. For a given t_b , its corresponding t_r is calculated. In general, there exist two trajectories, called long and short, which lead to the same final momenta. However, the long trajectory is born much closer to the maximum of the laser field. The exponentially dependent ionization yield, thus, favors the early ionizing long trajectory, which is the reason why the short trajectory contribution is neglected. With one trajectory present, the vector potential at t_r is obtained as $A_r = -\frac{E_0}{\omega} \sin(\omega t_r)$, making straightforward the reconstruction of k_r and allowing to unambiguously map momentum to time of rescattering.

D. Quantum chemistry calculations

The adiabatic ground state potential energy surfaces (PESs) along the inversion coordinate of both neutral NH_3 ($\tilde{X}^1 A_1'$) and cation NH_3^+ ($\tilde{X}^2 A_2''$) were calculated at the coupled cluster singles doubles (CCSD)⁴⁷ level of theory as implemented in the Q-Chem 5.1 quantum chemistry package.⁴⁸ The augmented correlation-consistent, polarized valence, double-zeta Dunning basis set (aug-cc-pVDZ)⁴⁹ was applied. Permanent dipole moments (μ_x , μ_y , and μ_z) and static dipole polarizabilities (α_{xx} , α_{yy} , and α_{zz}) were calculated at all points of the potential energy surface (PES). The field-dressed energies were calculated as follows:

$$E(F) = E_0 - \mu \cdot F - \frac{1}{2} \alpha \cdot F^2, \quad (1)$$

where F is the electric field strength, E_0 is the field-free Born-Oppenheimer energy, μ is the permanent dipole moment, and α is the main diagonal of the polarizability tensor. The field strength was set to 0.06 a.u. (3.1 V/Å), corresponding to a laser peak intensity of $1.3 \times 10^{14} \text{ W/cm}^2$.

All geometries were previously optimized at the second-order Møller-Plesset (MP2) level of theory using the atomic natural orbital-relativistic core-correlated basis set with polarized double-zeta contraction (ANO-RCC-PVDZ)⁵⁰ in OpenMolcas 8.0.⁵¹ A dummy atom (X) was placed along the z -axis, which is parallel to the C_3 principal axis of NH_3 , at a distance of 1.0 Å above the nitrogen atom (N). The H1-N-X, H2-N-X, and H3-N-X angles (β) were constrained to vary from 130° to 90° in steps of 1° (i.e., total of 41 geometries). Planarity is therefore defined by $\beta = 90^\circ$. Here, the inversion coordinate, Q , is defined as displacement with respect to the reference geometry in degrees, where a value of 0° corresponds to planarity (i.e., $\Phi_{\text{HNH}} = 120^\circ$). For a negative (positive) value of Q , the nitrogen atom is located above (below) the plane spanned by the three hydrogen atoms. A sketch of the described coordinate is shown in Fig. 5.

III. RESULTS AND DISCUSSION

A. FT-LIED analysis

The procedure for retrieving structural information is based on the Fourier transform (FT) variant of LIED, called FT-LIED,^{20,23} which is also known as the fixed-angle broadband laser-driven electron scattering (FABLES)²⁵ method. In the FT-LIED method, Fourier transforming the coherent molecular interference signal, ρ_M , embedded within the momentum distribution of the backscattered highly energetic electrons (i.e., $\theta_r = 180^\circ$) directly provides an image of the molecular structure in the far-field. The key benefit of the FT-LIED scheme is its ability to empirically retrieve the background incoherent

sum of atomic scatterings, ρ_A , that contributes to the total detected interference signal, ρ_E . Thus, the ρ_M can be obtained from ρ_E by subtracting the empirically retrieved ρ_A to directly retrieve the molecular structure without the use of theoretical fitting, retrieval, or modeling algorithms.

Figure 2 shows the logarithmically scaled momentum distribution of longitudinal (P_{\parallel} ; parallel to the laser polarization) and transverse (P_{\perp} ; perpendicular to the laser polarization) momenta for electrons detected in coincidence with the NH_3^+ molecular ion. *Direct* electrons oscillate away from the parent ion without rescattering, with a momentum obtained initially by the vector potential of the laser field, $A(t_r)$, at the instance of rescattering, t_r . Hence, the maximum kinetic energy that the electron can gain is $2U_p$ (i.e., momentum $P_{\parallel} \leq 4.2$ a.u.). *Rescattered* electrons, however, propagate further in the field, acquiring significantly higher kinetic energy after recolliding against the parent ion at t_r with an appreciably large return momentum, k_r . Additionally, the rescattered electron is also “kicked” by the laser field at t_r , receiving an additional momentum in the polarization direction. Therefore, the total detected momentum, k_{resc} , is related to the return momentum at the instance of rescattering, k_r , and the momentum “kick” obtained by the vector potential, $A(t_r)$, of the laser field through $k_{\text{resc}} = k_r + A(t_r)$ (see the sketch in Fig. 2). The overall maximum kinetic energy obtained by the *rescattered* electrons is ten times the ponderomotive potential ($10U_p$) (i.e., $P_{\parallel} = 9.4$ a.u.) for *back-scattered* electrons. In this sense, the elastically rescattered electrons, which contain structural information, can be distinguished from the direct electrons in the kinetic energy spectrum (momentum distribution) for energies of $2U_p \leq E_{\text{resc}} \leq 10U_p$ ($4.2 \leq P_{\parallel} \leq 9.4$ a.u.).

Since the FT-LIED method is applied, only coincidence electrons with a returning momentum of $k_r > 2.1$ a.u. (i.e., $P_{\parallel} > 4.2$ a.u.) and increasing rescattering angles, $\Delta\theta_r$, from 2 to 10° around the backscattering angle of $\theta_r = 180^\circ$ are analyzed. At low k_r , a small $\Delta\theta_r$ is taken to avoid appreciable contributions from direct electrons, which do not contain structural information. While at appreciably large enough P_{\parallel} , larger values of $\Delta\theta$ can be taken for higher k_r , since direct electrons do not contribute in this momentum region as they are significantly less energetic than the rescattered electrons. The interference signal is extracted by integrating an area indicated by a block arc in momentum space, as shown schematically in Fig. 2(b), at various vector potential kicks, A_r .

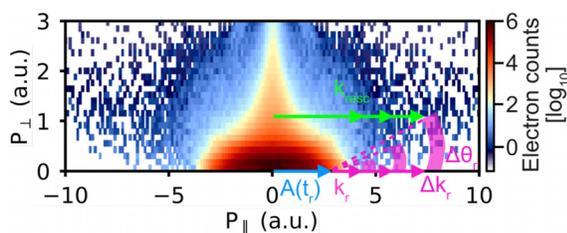


FIG. 2. FT-LIED extraction. Logarithmically scaled momentum distribution of electrons detected in coincidence with NH_3^+ fragments only, given in atomic units (a.u.). The return momentum, k_r , at the time of rescattering, t_r , is obtained by subtracting the vector potential, $A(t_r)$, from the detected rescattering momentum, k_{resc} , given by $k_r = k_{\text{resc}} - A(t_r)$. The energy-dependent interference signal is extracted by integrating the area indicated by a block arc at different vector potential kicks along $P_{\perp} = 0$. The block arc is given by a small range of rescattering angles and momenta, $\Delta\theta_r$ and Δk_r , respectively. We used $\Delta k_r = 0.2$ a.u. together with progressively increasing the $\Delta\theta_r$ values from 2° to 10° with increasing k_{resc} .

B. Electron-ion 3D coincidence detection

In strong-field LIED studies, other events aside from elastic scattering of the tunnel-ionized electrons will occur. For example, more than one electron can be removed from the molecule, leading to the Coulomb explosion of multiply charged NH_3^{n+} and the subsequent production of NH_2^+ and H^+ ions and corresponding electrons. Moreover, there may also be contributions to the overall signal from background molecules existing in the main chamber, generating ion species that are not of interest in this study (e.g., H_2O^+ , N_2^+ , or O_2^+). All of these background ions and their corresponding electrons are detected in our spectrometer along with our molecular ion of interest, NH_3^+ , which is the main peak at approximately 4.1 μs in the ion time-of-flight (ToF) spectrum shown in Fig. 3(a). Electrons corresponding to background ions contribute to an unwanted background signal in the FT-LIED analysis process, impeding structure retrieval when averaging over all molecular ionization channels. Electron-ion coincidence detection is implemented to ensure that the LIED interference signal originates only from our ion of interest (i.e., NH_3^+). To highlight the importance of coincidence detection, the total electron signal for all ions (petrol blue) and those electrons detected in coincidence with NH_3^+ (orange) are shown in Fig. 3(b). In both distributions, the $2U_p$ and $10U_p$ classical cutoffs are clearly visible (vertical dashed lines). An order-of-magnitude difference in the number of electron counts is observed in the rescattering frame. Furthermore, the inset panel in Fig. 3(b) emphasizes the more pronounced oscillations, arising from the molecular interference signal observed in the NH_3^+

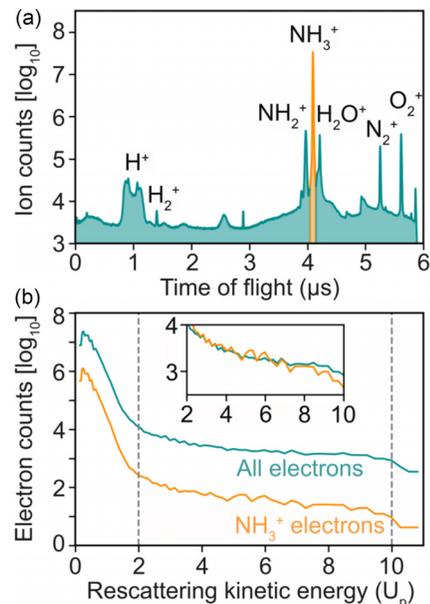


FIG. 3. Electron-ion coincidence detection. (a) Ion time-of-flight (ToF) spectrum, with the main ToF peak near 4.1 μs corresponding to the molecular ion of interest, NH_3^+ (orange). (b) The signal as a function of rescattered kinetic energy given in ponderomotive energy, U_p , for all electrons (petrol blue) and those electrons detected in coincidence with NH_3^+ (orange). The inset shows a detailed view of the electron signal in the rescattering regime (i.e., 2–10 U_p) with both distributions overlaid on top of each other, highlighting the importance of coincidence detection; the NH_3^+ electron distribution was scaled by a factor of 50.

coincidence distribution (orange) as compared to the “all electrons” distribution (petrol blue).

C. Molecular structure retrieval

Electrons detected in coincidence with NH_3^+ ions are plotted in Fig. 4(a) as a function of return kinetic energy in the range of 40–350 eV corresponding to the rescattering plateau of $2U_p$ – $10U_p$ range. The experimentally measured molecular backscattered electron distributions (ρ_E) (orange solid trace) contain contributions from both the incoherent sum of atomic scatterings—which is independent of molecular structure, and thus serves as a background (ρ_B) signal—and the coherent molecular interference signal (ρ_M). We calculate the LIED interference signal by subtracting an empirically determined background (by fitting a third-order polynomial function) from the logarithm of ρ_E ,²⁰ given by

$$\rho_M = \log_{10}(\rho_E) - \log_{10}(\rho_B) = \log_{10}(\rho_E/\rho_B), \quad (2)$$

and is plotted in Fig. 4(b) as a function of momentum transfer, $q = 2k_r$, in the back-rescattered frame. Observed oscillations in the interference signal (orange solid trace) provide a unique, sensitive signature of the molecular structure, with the orange (gray) shaded regions.

The fast Fourier transform (FFT) spectrum generated from the molecular interference signal, embedded within the interference signal [Fig. 4(b)], is shown in Fig. 4(c). Before transforming, a Kaiser window⁵² ($\beta = 0$) and zero padding⁵³ are applied. The FFT spectrum (orange solid trace), individual Gaussian fits (gray dotted traces), and the sum of the two Gaussian fits (blue solid trace) are presented. The center position of the individual Gaussian fits of the two FFT peaks appears at $1.31 \pm 0.03 \text{ \AA}$ and $2.24 \pm 0.03 \text{ \AA}$, respectively, as shown in the sketch of Fig. 4(d). Table I shows the N–H internuclear distance reported for neutral NH_3 in the ground electronic state and NH_3^+

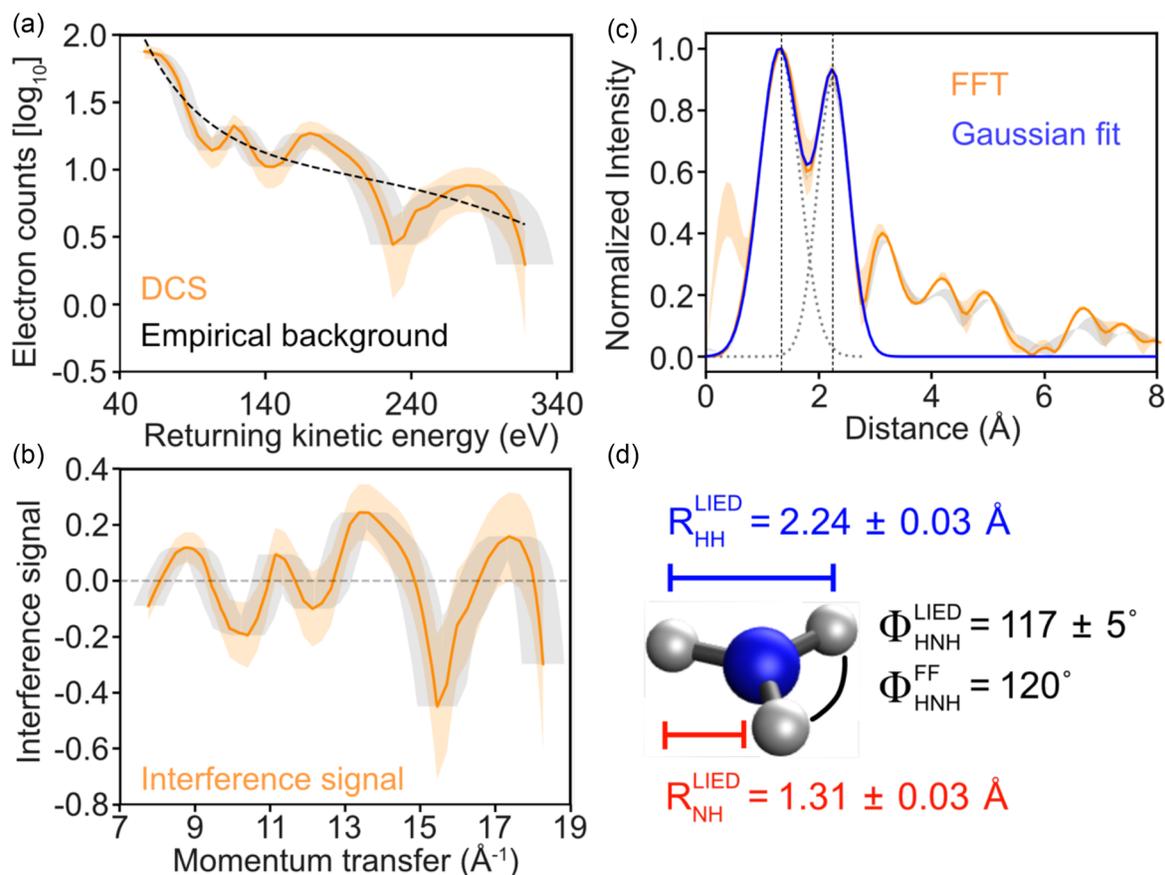


FIG. 4. Molecular structure retrieval. (a) Modulated total interference signal (orange solid trace) and its estimated Poissonian statistical error (orange shaded region) together with the measured longitudinal momentum error (gray shaded region) are shown with the background atomic signal empirically extracted using a third-order polynomial fit (black-dotted trace). (b) LIED interference signal plotted as a function of momentum transfer, $q = 2k_r$, in the back-rescattered frame. The orange shaded region corresponds to the Poissonian statistical error, and the gray shaded region corresponds to the detected longitudinal momentum error. (c) Fast Fourier spectrum (blue solid trace) along with the individual (gray dashed traces) and sum (blue solid trace) of Gaussian fits. Orange (gray) shaded region represents the FFT spectra for the two extrema of the Poissonian (momentum) error. The black vertical dotted lines indicate the mean center positions of the two Fourier peaks corresponding to the N–H and H–H internuclear distances, R_{NH} and R_{HH} , respectively. We note that the peaks above 3 \AA could arise from the formation of clusters and are in accordance with Refs. [54] and [55]. (d) Sketch of the measured NH_3^+ LIED structure together with field-free equilibrium NH_3^+ ground state structure is shown. The following geometrical parameters were extracted: $R_{\text{NH}} = 1.31 \pm 0.03 \text{ \AA}$; $R_{\text{HH}} = 2.24 \pm 0.03 \text{ \AA}$; and H–N–H bond angle, $\Phi_{\text{HNH}} = 117 \pm 5^\circ$.

TABLE I. Field-free equilibrium geometrical parameters of NH_3 and NH_3^+ . The N–H and H–H internuclear distances, R_{NH} and R_{HH} , respectively, and the H–N–H angle, Φ_{HNH} , for neutral NH_3 in the ground electronic state.⁵⁶ The same geometric parameters for NH_3^+ in the ground⁵⁷ electronic state are also presented.

| | R_{NH} (Å) | R_{HH} (Å) | Φ_{HNH} (deg) |
|--|---------------------|---------------------|---------------------------|
| NH_3 (\tilde{X}^1A_1') | 1.030 | 1.662 | 107 |
| NH_3^+ (\tilde{X}^2A_2'') | 1.023 | ... | 120 |

cation in the ground and first excited electronic state. Comparing our FFT spectrum shown in Fig. 4(c) to the data in Table I, it is clear that the first FFT peak at 1.31 ± 0.03 Å corresponds to the N–H internuclear distance, R_{NH} , while the second FFT peak at 2.24 ± 0.03 Å corresponds to the H–H internuclear distance, R_{HH} . The FT-LIED-measured internuclear distances correspond to an H–N–H bond angle, Φ_{HNH} , of $117 \pm 5^\circ$ (see the supplementary material for further details). We note that the peaks above 3 Å could arise from clusters of ammonia, which have been reported to have a center-of-mass (i.e., N–N) distance of between 3.2 and 5.2 Å and full H–H distances within a cluster of up to 8 Å.^{54,55}

D. Quantum chemistry calculations

To aid in our interpretation and understanding of the FT-LIED-measured NH_3^+ structure, we investigate the pyramidal-to-planar geometrical transition that ammonia undergoes following strong-field ionization. We perform quantum chemical *ab initio* calculations of field-free (black solid curves) and field-dressed (colored dashed curves) ground state potential energy curves (PECs) of neutral NH_3 (bottom panel) and NH_3^+ cation (top panel), as shown in Fig. 5. The inversion coordinate (Q) employed is also shown at the bottom left side of Fig. 5.

A value of 0° corresponds to planarity. For $Q < 0$ ($Q > 0$), the nitrogen atom is located above (below) the plane spanned by the three hydrogen atoms. The pyramidal-to-planar transition is initiated at the time of ionization ($t = 0$ fs), where a nuclear wave packet (NWP) in the neutral ammonia is transferred to the PES of the NH_3^+ cation. Kraus and Wörner³⁴ calculated that the NWP in field-free NH_3^+ reaches the equilibrium planar structure (i.e., $Q = 0^\circ$; $\Phi_{\text{HNH}} = 120^\circ$) at 7.9 fs.³⁴ Thus, the equilibrium planar structure could be directly retrieved with MIR-LIED since the emitted LIED electron takes 7.8–9.8 fs to be accelerated and driven back to the NH_3^+ parent ion by the laser field. In fact, we resolve an H–N–H bond angle of $\Phi_{\text{HNH}} = 117 \pm 5^\circ$ for the FT-LIED field-dressed NH_3^+ structure. Our measured near-planar structure may be due to one or a combination of the following reasons: (i) the field strength, F , used in the calculations of Ref. [34] corresponded to a significantly different peak pulse intensity (5.0×10^{13} W/cm²), compared to the one used in our experimental conditions (1.3×10^{14} W/cm²); (ii) the NWP was propagated on field-free potentials,⁵⁷ neglecting the important effects of the strong laser field; (iii) the model of Ref. 34 also neglects dynamics induced by the strong laser field that may occur in the neutral molecule prior to ionization. To account for the non-negligible contribution of the MIR laser field, we calculated field-dressed Born–Oppenheimer curves with the field strength set to the corresponding peak intensity 1.3×10^{14} W/cm² (i.e., 3.1 V/Å), as shown in Fig. 5. Orange (blue) dashed curves show the field-dressing when the polarization vector is parallel, $F > 0$

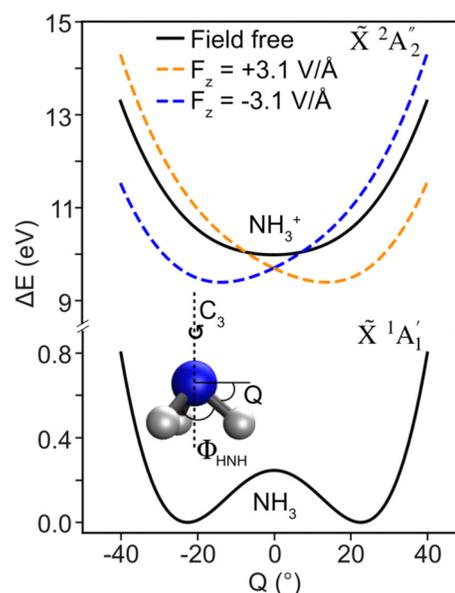


FIG. 5. Quantum chemistry calculations. Ground state field-free PECs along the inversion coordinate for neutral NH_3 (\tilde{X}^1A_1') (bottom, solid black curve) and cation NH_3^+ (\tilde{X}^2A_2'') (top, solid black curve), and the corresponding field-dressed curves (dashed colored traces) with a field strength of 3.1 V/Å (i.e., $I_0 = 1.3 \times 10^{14}$ W/cm²). The polarization vector points along the static dipole moment of the molecule. Field-dressed PECs for the field pointing parallel to the dipole moment vector of the molecule (orange dashed curve; $F > 0$) and antiparallel (blue dashed curve; $F < 0$) are shown. On the bottom left, a sketch of the geometry of the ammonia molecule is shown, showing the H–N–H bond angle, Φ_{HNH} , the inversion coordinate employed, Q , and the C_3 rotation axis.

(antiparallel, $F < 0$) to the static dipole moment of the ammonia molecule. Importantly, the field-free planar equilibrium cationic structure has now been shifted toward a bent field-dressed structure (i.e., $Q = -14^\circ$; $\Phi_{\text{HNH}} = 114^\circ$) caused by the strong laser field, dressing the molecule. There is an excellent agreement between our measured FT-LIED field-dressed NH_3^+ structure ($\Phi_{\text{HNH}} = 117 \pm 5^\circ$) and the calculated equilibrium geometry of the field-dressed ground cationic state ($\Phi_{\text{HNH}}^{\tilde{X}^2A_2''} = 114^\circ$). It should be noted that the calculations presented in this work are static in nature, and that quantum dynamical calculations will be required to further investigate the time-resolved nature of this field-dressed system, which are planned in future investigations.

IV. CONCLUSIONS

In summary, we directly retrieve the geometric structure of NH_3^+ with picometer spatial and femtosecond temporal resolution using MIR FT-LIED. We use strong external fields (i.e., 3.1 V/Å) to investigate the response of an isolated ammonia molecule to strong-field ionization and the subsequently induced pyramidal-to-planar transition dynamics. We identified a near-planar ammonia cation with a H–N–H bond angle of $\Phi_{\text{HNH}} = 117 \pm 5^\circ$. We calculate the field-dressed PECs of NH_3^+ and show that the equilibrium field-dressed structure is distorted by the intense laser field, compared to the corresponding field-free case ($\Phi_{\text{HNH}}^{\text{FF}} = 120^\circ$). The minimum of the field-dressed PEC displaced toward a more bent, near-planar

structure ($\Phi_{\text{HNH}}^{\text{FD}} = 114^\circ$), which has an excellent agreement with our FT-LIED-measured NH_3^+ structure. Additionally, it would be beneficial to study the dynamics of the ammonia system through quantum-dynamical wave-packet calculations that also include the interaction of the molecule with the intense laser field to further confirm the experimental results.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for the description of the structural retrieval process and the determination of the uncertainty in the extracted structural parameters.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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