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Christopher J. Hensley
University of Nebraska—Lincoln,, chensley22@unl.edu

Jie Yang
University of Nebraska—Lincoln, wyyajy@gmail.com

Martin Centurion
University of Nebraska - Lincoln, martin.centurion@unl.edu

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Imaging of Isolated Molecules with Ultrafast Electron Pulses

Christopher J. Hensley, Jie Yang, and Martin Centurion
University of Nebraska—Lincoln, Lincoln, Nebraska 68588, USA
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Imaging isolated molecules in three dimensions with atomic resolution is important for elucidating complex molecular structures and intermediate states in molecular dynamics. This goal has so far remained elusive due to the random orientation of molecules in the gas phase. We show that three-dimensional structural information can be retrieved from multiple electron diffraction patterns of aligned molecules. The molecules are aligned impulsively with a femtosecond laser pulse and probed with a femtosecond electron pulse two picoseconds later, when the degree of alignment reaches a maximum.

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The majority of known molecular structures have been determined using either x-ray diffraction for crystallized molecules or NMR spectroscopy for molecules in solution. However, for isolated molecules there has been no method demonstrated to measure the three-dimensional structure. Intense x-ray pulses from a free electron laser could potentially be used to image single molecules with atomic resolution, if the pulses were intense and short enough to diffract from the molecule before destroying it [1,2]. Electron diffraction has been the main tool to determine the structure of molecules in the gas phase [3] and also to investigate ultrafast changes in structure [4–6]. In this method, the diffraction pattern is compared with a calculated structure iteratively until an appropriate match between experiment and theory is found [7]. Diffraction patterns from randomly oriented molecules in the gas phase contain only one-dimensional information, and thus input from theoretical models is needed to recover the structure. Here, we show that a three-dimensional image of a molecule can be reconstructed from electron diffraction patterns of laser-aligned molecules without any prior knowledge of the structure. For this Letter, we assume that the constituent atoms are known, but their spatial distribution is unknown.

The molecules are impulsively aligned with a femtosecond laser pulse and probed with femtosecond electron pulses in a field-free environment at the peak alignment. This method opens the door to image molecules that cannot be crystallized and to investigate dynamics on ultrafast time scales with newly available femtosecond electron sources [8,9]. It has been shown recently that laser-induced electron diffraction (LIED) can be used to measure changes in the interatomic distance of diatomic molecules with sub-Angstrom resolution [5]. In LIED, a strong laser field was used to remove an electron from the molecule and then rescatter it from the same molecule a few femtoseconds later, at which point the interatomic distance was significantly different from the known equilibrium value. The method presented in this Letter is fundamentally different in that we image a neutral molecule in a field-free environment to avoid structural distortions induced by the laser field. We believe that LIED is ideally suited to study the recollision process and the effect of strong laser fields on molecules, while the method presented here is better suited to image the structure and dynamics of free molecules.

In gas-electron diffraction, a continuous electron beam scatters from a molecular target. The transverse coherence of the electron beam is typically larger than the molecules but smaller than the distance between the molecules. The diffraction pattern is formed by the incoherent sum of the diffraction pattern of individual molecules, averaged over all possible orientations. The resulting diffraction pattern is circularly symmetric, and the intensity depends only on the scattering angle θ. The intensity of the diffraction pattern can be written as a sum of the atomic and molecular scattering:

$$I(s) = I_{\mathrm{AT}}(s) + I_{\mathrm{MOL}}(s),$$

where $s = \frac{4\pi}{\lambda}\sin(\frac{\theta}{2})$ is the magnitude of the momentum change of a scattered electron, I_{AT} is the intensity due to scattering from individual atoms, and I_{MOL} contains the interference terms between different atoms:

$$I_{\mathrm{AT}} = \sum_i |f_i|^2,$$

$$I_{\mathrm{MOL}} = \sum_{i,j} f_i f_j \cos(\eta_i - \eta_j)\frac{\sin(r_{ij}s)}{r_{ij}s},$$

where f_i and η_i are the elastic scattering cross section and phase factor of the ith atom, respectively, and r_{ij} is the distance between the ith and jth atoms. Structural information is contained in I_{MOL} through this interference between different atoms.

A Fourier analysis of I_{MOL} yields the interatomic distances. Because of the limited resolution and the one-dimensional nature of the data, distances that are similar cannot be distinguished. For larger molecules, this problem becomes more severe, as there are more overlapping distances. In the ideal case, imaging could be accomplished

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by scattering from a single molecule, but currently it is not possible to deliver sufficient radiation to do this without damaging the molecule. Here, we pursue a different solution, which is to scatter from a sample of isolated molecules that are aligned. In previous experiments, electron diffraction patterns of aligned molecules have been recorded using adiabatic alignment with long laser pulses (in this case, the laser is longer than the rotational period and is present during the alignment) [10] and by selective alignment in a photodissociation reaction [11]. However, in both cases, the degree of alignment was found to be too weak to extract structural information. Additionally, in adiabatic alignment, the presence of a strong laser field can distort the molecular structure, while selective alignment relies on a change in the structure. We have used nonadiabatic alignment, in which the molecules reach their maximum alignment a short time after interacting with the laser, so that they can be probed in a field-free environment. Furthermore, we show that the three-dimensional structure of the molecule can be retrieved using multiple diffraction patterns, even if the degree of alignment is not very high, making our method very promising for imaging complex molecules.

Impulsive, or nonadiabatic, alignment with short laser pulses creates a rotational wave packet that evolves to produce a distribution of aligned molecules after interaction with the laser [12]. Nonadiabatic laser alignment has been demonstrated both for one-dimensional and three-dimensional alignment [13–15]. Here, we use a linearly polarized laser pulse to align the molecule along the direction of the laser polarization. For a first demonstration, we chose trifluoroiodomethane (CF_3I), a symmetric top molecule along the *C-I* axis (Fig. 1). This molecule has four distinct interatomic distances: $r_{CF} = 1.33$ Å, $r_{CI} = 2.14$ Å, $r_{FF} = 2.15$ Å, and $r_{FI} = 2.89$ Å [16]. The molecule remains free to spin about this axis, which, when averaged over many molecules, results in a cylindrically symmetric structure. Figure 1 shows the 3D experimental molecular structure reconstructed from several diffraction patterns of aligned molecules. This image of the molecule was recovered without any prior knowledge of the structure. Because of the rotational symmetry, the reconstructed image alone does not determine the number of fluorine atoms. Additional information, such as the constituent atoms, would be sufficient to determine the position of each fluorine atom.

The experimental setup is shown schematically in Fig. 2. The directions of the alignment laser, electron pulse, and gas jet are all mutually orthogonal. The width of the three beams is approximately 100 μm at the intersection point. A supersonic gas jet is produced by flowing a mixture of CF_3I and helium through a convergent-divergent nozzle. The supersonic beam is advantageous for alignment because it results in a lower rotational temperature of the molecules, which we estimate to be about 30 K [17]. Pulses

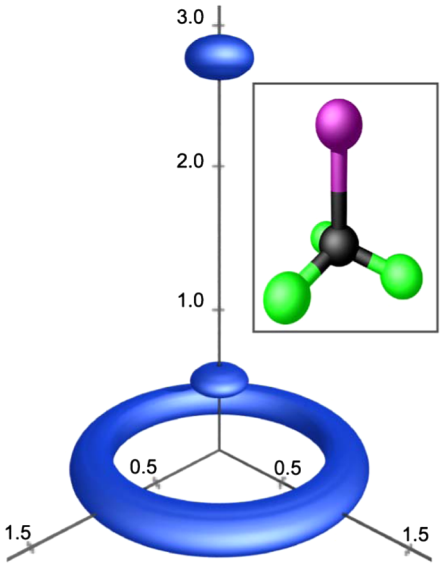


FIG. 1 (color online). Experimental reconstruction of the CF_3I molecule. The CF_3I molecules rotate freely about the *C-I* axis, which results in a cylindrically symmetric structure. The units are in angstroms. See the Supplemental Material [24] for details on the reconstruction. The inset shows a theoretical model of the CF_3I molecule for comparison. The fluorine atoms are colored light gray (green online), carbon is black, and the iodine atom is dark gray (purple online).

from our amplified Ti-sapphire laser are split in two for alignment and triggering the electron pulse. The alignment laser pulse has a duration of 300 fs and is focused to an intensity of 2.2×10^{13} W/cm^2 on the target. A small fraction of the laser pulse energy is frequency tripled and focused on a photocathode to trigger the emission of electrons. The electrons are accelerated to 25 keV using a

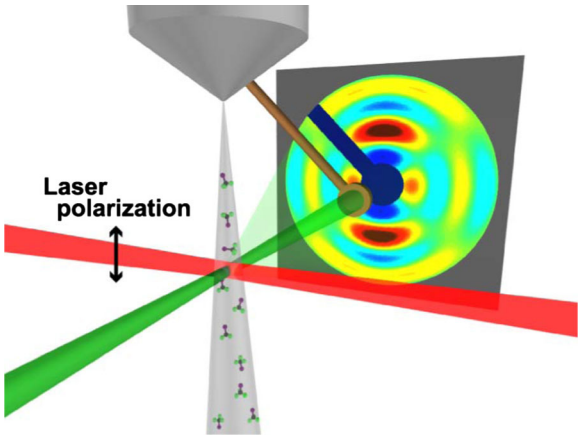


FIG. 2 (color online). Scattering region in the target chamber. The diagram shows the laser beam traveling left to right (red online), electron beam into the page (green online), and molecular beam entering the chamber from the top (gray online). The directly transmitted electron beam is blocked, and the diffraction pattern is recorded on an imaging detector.

static electric field and collimated by a magnetic lens. Each electron pulse contains approximately two thousand electrons and has a duration of 500 fs at the target. The overall resolution of the experiment is 850 fs, considering velocity mismatch in the finite size interaction volume and the duration of the pulses. After traversing the sample, the unscattered electron beam is stopped by a copper beam block, and the diffraction pattern is captured using a 2D detector comprised of a phosphor screen, an image intensifier, and a CCD camera.

For this laser pump-electron probe investigation, time zero is defined as the arrival of the laser pulse at the gas jet. This was measured independently with the same plasma-induced lensing method used in previous ultrafast electron diffraction studies [18]. We tracked the temporal evolution of the alignment by measuring the anisotropy of the diffraction pattern, which increases as the degree of alignment increases. The peak alignment was found when the electron pulse arrives 2 ps after time zero [Fig. 3(a)]. The diffraction patterns used for structure reconstruction are recorded at the time of maximum alignment.

We define a difference molecular scattering $\Delta sM(t) = sM(t) - sM(t<0)$, where $sM(t) = I_{\mathrm{MOL}}(t)s/I_{\mathrm{AT}}$ is a modified molecular scattering. ΔsM represents the difference between diffraction patterns from aligned and randomly oriented molecules and can be readily obtained from the experimental data. I_{AT} is calculated using known values for atomic elastic scattering cross sections. Figure 3(b) shows the diffraction pattern of randomly oriented molecules sM_{RANDOM}. Figure 3(c) shows the ΔsM_{90} corresponding to the case of the alignment axis at a 90° angle with the propagation of the electron beam. The anisotropy in the pattern is clearly visible and is in good agreement with our theoretical calculation [Fig. 3(d)]. This theoretical pattern is constructed by calculating the diffraction pattern of a single molecule and then averaging over the angular distribution of the aligned molecules. A degree of alignment of $\langle\cos^2\alpha\rangle = 0.5$ is calculated by comparing the experimental diffraction pattern with theory, where α is the angle between the alignment axis and the long axis of the molecules. The relative angle between the alignment axis and the electron beam can be changed continuously by rotating the polarization of the laser with a half wave plate. Figure 3(e) shows ΔsM_{60} for the alignment axis at a 60° angle with the direction of the electron beam. Again, there is good agreement with the corresponding theoretical pattern in Fig. 3(f).

The final step is to retrieve the molecular structure from the diffraction patterns. Considerable theoretical work has been devoted to this problem [19–23]. For the case of molecules with cylindrical symmetry, a single diffraction pattern sM_{PERFECT} is sufficient to fully retrieve the structure using a holographic method if two conditions are met: (i) the alignment axis is perpendicular to the electron beam and (ii) the molecules are aligned perfectly (angular distribution of $\langle\cos^2\alpha\rangle = 1$) [21]. However, significant blurring occurs for experimentally achievable alignment even if the degree of alignment is very high. We have used a genetic algorithm and three experimental diffraction patterns (sM_{RANDOM}, ΔsM_{60}, and ΔsM_{90}) to construct a single pattern sM_{EXP} that approximates sM_{PERFECT}. Once this pattern is constructed, we use the holographic algorithm [21] to retrieve an image of the molecule (see the Supplemental Material [24]).

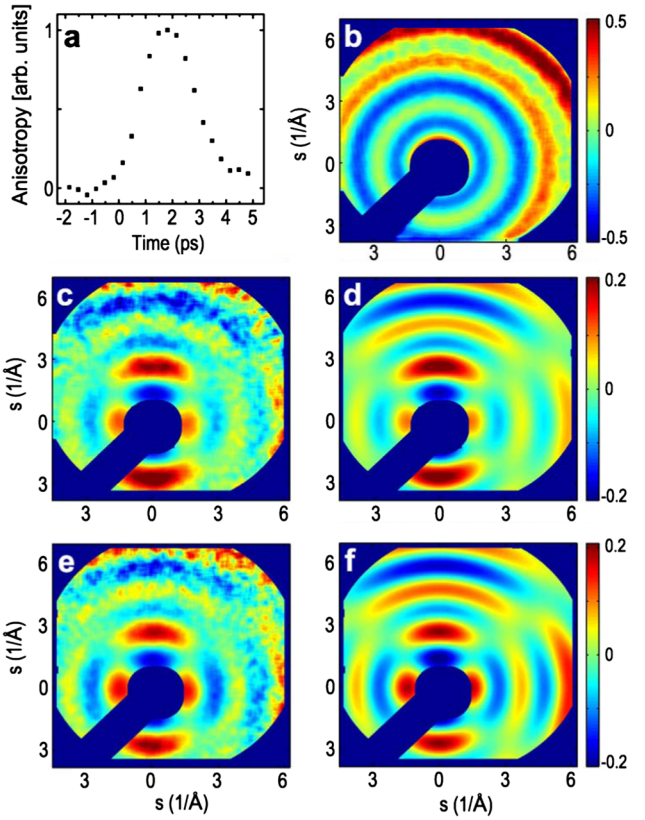


FIG. 3 (color online). (a) Temporal evolution of the anisotropy in the diffraction pattern, normalized to the peak value. (b) Rescaled molecular scattering pattern (sM) of randomly oriented molecules. (c),(d) Experimental and theoretical difference diffraction patterns (ΔsM) for an alignment axis perpendicular to the electron beam. (e),(f) Experimental and theoretical difference diffraction patterns (ΔsM) for an alignment axis at a 60° angle with respect to the electron beam. A different normalization procedure is used for the diffraction pattern of randomly oriented molecules and for the difference diffraction patterns (see the Supplemental Material [24]).

The angular distribution for a given degree of alignment can be calculated by solving the Schrödinger equation for a symmetric top rigid rotor in a laser field [25]. Once the angular distribution is known, a simple transformation can be used to convert the sM_{PERFECT} into the diffraction pattern corresponding to any angular distribution. However, there is no inverse transformation from the measured diffraction patterns to sM_{PERFECT}. Thus, we have constructed a genetic algorithm to retrieve a sM_{EXP} that

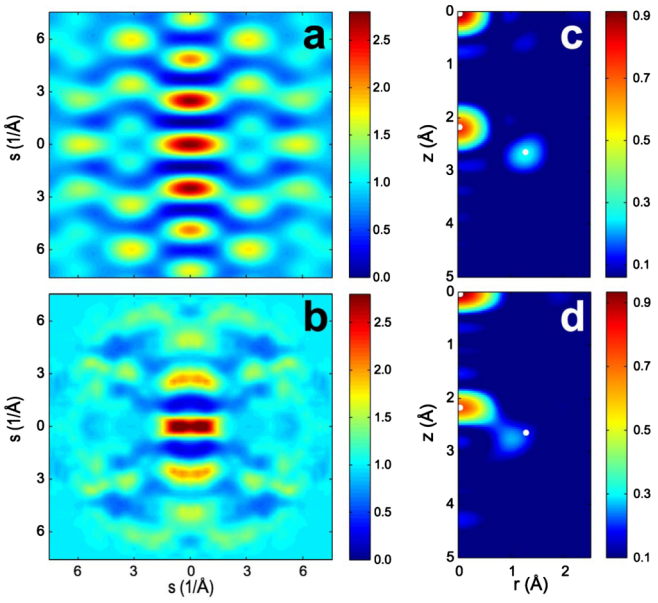


FIG. 4 (color online). (a),(c) Theoretical diffraction pattern (sM/s) for perfectly aligned molecules and the corresponding molecular image. (b),(d) Experimentally retrieved pattern for perfectly aligned molecules and the corresponding molecular image. The white dots in panels (c) and (d) indicate the expected position of each atom.

approximates the ideal pattern, starting from an initial guess of a uniform diffraction pattern. The algorithm iteratively makes a random change to the guessed pattern, then calculates the diffraction patterns corresponding to the experimental angular distributions and compares with the experimental sM_{RANDOM}, ΔsM_{60}, and ΔsM_{90} to calculate an error. Only the changes that reduce the error are kept. The degree of alignment, which determines the angular distribution, is left as a free parameter and optimized by the iterative algorithm. We have found that three diffraction patterns are sufficient to retrieve an image of the molecule.

Figures 4(a) and 4(b) show the theoretical sM_{PERFECT}/s and the experimental sM_{EXP}/s recovered using the genetic algorithm. Figures 4(c) and 4(d) show the images of the molecule in cylindrical coordinates reconstructed from the theoretical and experimental patterns, respectively, using the holographic method. The structure is best displayed in cylindrical coordinates because all three fluorine atoms overlap, even though the molecule is spinning freely about its long axis. The data in Fig. 4(d) were used to generate the 3D representation in Fig. 1. Table I compares our experimental values with previous measurements of the r_{CI} and r_{FI} distances and the angle formed by the *I-C-F* backbone, which in the case of CF_3I fully determines the structure. The experimental values were calculated from the peak values in Fig. 4(d). The previous results [16] in Table I were obtained by combining theoretical models, electron diffraction patterns, and measurements of the rotational constant of the molecule. There is very good agreement

TABLE I. CF_3I interatomic distances and angles

	Experimental results	Previous results
r_{CI}	2.19 ± 0.07 Å	2.14 Å
r_{FI}	2.92 ± 0.09 Å	2.89 Å
I-C-F angle	120 ± 9°	111°

with previously measured values, with a maximum difference of less than 10% in the angle. We believe this could be improved by increasing either the degree of alignment or the range of s values recorded. The current values, however, were sufficient to obtain a clear image of the molecule. We expect the main challenge in extending this method to larger molecules will be in achieving sufficient alignment with the laser-induced nonadiabatic method. In addition, three-dimensional alignment, along with more sophisticated phase retrieval algorithms, will need to be implemented to image more complex molecules.

In summary, we have retrieved the three-dimensional structure of isolated symmetric top molecules. The molecules are impulsively aligned using a femtosecond laser pulse and probed with a femtosecond electron pulse. The long axis of the molecule aligns parallel to the direction of laser polarization, and the molecule spins freely about this axis. The electron pulse diffracts from the molecules in a field-free environment, two picoseconds after the arrival of the laser pulse. The structure of the molecule was reconstructed using three diffraction patterns corresponding to different angular distributions. This method can be applied to image conformational changes with high temporal resolution and to determine the structure of more complex molecules.

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