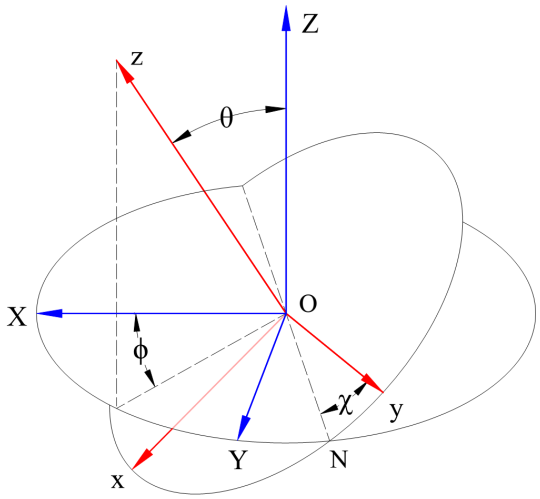
Supplementary information for
Diffractive imaging a rotational wave packet in nonlinear molecules

Yanwei Xiong, Kyle J. Wilkin, Sajib Kumar Saha, Sri Bhavya Muvva, Haoran Zhao, Martin Centurion

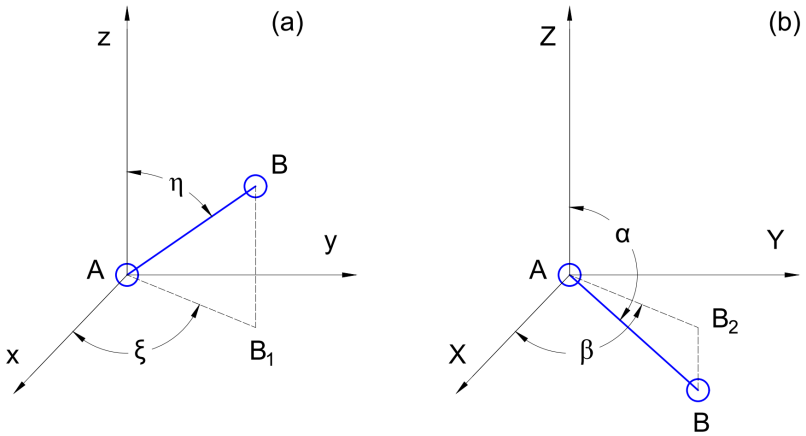
Department of Physics and Astronomy, University of Nebraska-Lincoln, Lincoln, Nebraska, 68588, USA

SUPPLEMENTARY NOTE 1

1. Probability density and atom-pair angular distribution



Supplementary Figure 1. The space-fixed (lab) frame XYZ and molecule-fixed (body) frame xyz are related by the three rotations defined by the Euler angles (ϕ, θ, χ). The details of the rotation process is shown in [1].



Supplementary Figure 2. (a) xyz is the molecule-fixed (body) frame, typically defined by the principal axes of the moment of inertia and symmetry [2]. (b) XYZ is the space-fixed (lab) frame. The orientation of the vector $\vec{r}_{AB}$ connecting the position of atoms A and B in a molecule is described by the polar and azimuthal

angles defined in the body frame and lab frame. The orientation of $\vec{r}_{AB}$ is described by (η, ξ) in the body frame, and (α, β) in the lab frame. The projection of B on the x-y plane is B_1, and the projection on the X-Y plane is B_2. The rotation from the lab frame to the body frame is shown in Supplementary Figure 1.

After the three rotations defined by (ϕ, θ, χ) are applied to the molecule, the atom pair in the molecule ends up with an orientation that is determined by both (η, ξ) and (ϕ, θ, χ). Here we show how the angular distributions of vector $\vec{r}_{AB}$ is related to the probability density distribution of the molecular ensemble. First, we will show how the angles (α, β) that describe the orientation of $\vec{r}_{AB}$ is related to the Euler angles. Second, we derive the probability distribution of $\vec{r}_{AB}$ by using the transformation technique of bivariate random variables.

Suppose $\boldsymbol{r}$ is an arbitrary vector having the Cartesian components (X,Y,Z) in the space-fixed (lab) frame and components (x,y,z) in the molecule-fixed (body) frame. The body frame vector is obtained by applying the unitary transformation expressed by the product of three Euler angle rotations $\boldsymbol{\Phi}(\phi, \theta, \chi) = \mathbf{R_Z}(\chi)\mathbf{R_N}(\theta)\mathbf{R_Z}(\phi)$ to the lab frame, as shown in Supplementary Figure 1. The two representations of the vector $\boldsymbol{r}$ in two frames are related by direction cosine matrix $\boldsymbol{\Phi}$ parametrized by the Euler angles (ϕ, θ, χ) [1].

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{bmatrix} \mathrm{c}\phi\mathrm{c}\theta\mathrm{c}\chi - \mathrm{s}\phi\mathrm{s}\chi & -\mathrm{c}\phi\mathrm{c}\theta\mathrm{s}\chi - \mathrm{s}\phi\mathrm{c}\chi & \mathrm{c}\phi\mathrm{s}\theta \\ \mathrm{s}\phi\mathrm{c}\theta\mathrm{c}\chi + \mathrm{c}\phi\mathrm{s}\chi & -\mathrm{s}\phi\mathrm{c}\theta\mathrm{s}\chi + \mathrm{c}\phi\mathrm{c}\chi & \mathrm{s}\phi\mathrm{s}\theta \\ -\mathrm{s}\theta\mathrm{c}\chi & \mathrm{s}\theta\mathrm{s}\chi & \mathrm{c}\theta \end{bmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{S1}$$

where cosine and sine are denoted by c and s for simplification when the expression is long. The orientation of an atom pair AB in a molecule is described by the polar and azimuthal angles defined in the body frame (η, ξ), shown in Supplementary Figure 2 (a), and the unit vector of the atom pair is $\boldsymbol{b} = (\sin\eta\cos\xi, \sin\eta\sin\xi, \cos\eta)$. Note that we do not distinguish the row and column vectors here. The orientation of the atom pair vector in the lab frame after the rotations can be obtained using equation (S1).

$$\boldsymbol{B} = \boldsymbol{\Phi b} = \begin{pmatrix} \mathrm{c}\phi\mathrm{c}\theta s\eta\mathrm{c}(\chi+\xi) - \mathrm{s}\phi s\eta\mathrm{s}(\chi+\xi) + \mathrm{c}\phi\mathrm{s}\theta\mathrm{c}\eta \\ \mathrm{s}\phi\mathrm{c}\theta s\eta\mathrm{c}(\chi+\xi) + \mathrm{c}\phi s\eta\mathrm{s}(\chi+\xi) + \mathrm{s}\phi\mathrm{s}\theta\mathrm{c}\eta \\ -\mathrm{s}\theta s\eta\mathrm{c}(\chi+\xi) + \mathrm{c}\theta\mathrm{c}\eta \end{pmatrix} \tag{S2}$$

The atom pair in the lab frame is described by the polar and azimuthal angles (α, β), shown in Supplementary Figure 2 (b), and $\boldsymbol{B} = (\sin\alpha\cos\beta, \sin\alpha\sin\beta, \cos\alpha)$. Thus, we have

$$\mathrm{c}\alpha = -\mathrm{s}\theta s\eta\mathrm{c}(\chi+\xi) + \mathrm{c}\theta\mathrm{c}\eta \tag{S3-1}$$

$$\mathrm{s}\alpha\mathrm{s}\beta = \mathrm{s}\phi\mathrm{c}\theta s\eta\mathrm{c}(\chi+\xi) + \mathrm{c}\phi s\eta\mathrm{s}(\chi+\xi) + \mathrm{s}\phi\mathrm{s}\theta\mathrm{c}\eta \tag{S3-2}$$

By organizing the right side of (S3-2), we have

$$\sqrt{[\mathrm{c}\theta s\eta\mathrm{c}(\chi+\xi) + \mathrm{s}\theta\mathrm{c}\eta]^2 + [s\eta\mathrm{s}(\chi+\xi)]^2}\left[\mathrm{s}\phi\frac{\mathrm{c}\theta s\eta\mathrm{c}(\chi+\xi)+\mathrm{s}\theta\mathrm{c}\eta}{\sqrt{[\mathrm{c}\theta s\eta\mathrm{c}(\chi+\xi)+\mathrm{s}\theta\mathrm{c}\eta]^2+[s\eta\mathrm{s}(\chi+\xi)]^2}} + \mathrm{c}\phi\frac{s\eta\mathrm{s}(\chi+\xi)}{\sqrt{[\mathrm{c}\theta s\eta\mathrm{c}(\chi+\xi)+\mathrm{s}\theta\mathrm{c}\eta]^2+[s\eta\mathrm{s}(\chi+\xi)]^2}}\right]$$

The term $[\mathrm{c}\theta s\eta\mathrm{c}(\chi+\xi) + \mathrm{s}\theta\mathrm{c}\eta]^2 + [s\eta\mathrm{s}(\chi+\xi)]^2 + [-\mathrm{s}\theta s\eta\mathrm{c}(\chi+\xi) + \mathrm{c}\theta\mathrm{c}\eta]^2 = 1$; Thus $\mathrm{s}\alpha = \sqrt{[\mathrm{c}\theta s\eta\mathrm{c}(\chi+\xi) + \mathrm{s}\theta\mathrm{c}\eta]^2 + [s\eta\mathrm{s}(\chi+\xi)]^2}$. (S3-2) becomes

$$\mathrm{s}\beta = \mathrm{s}\phi\mathrm{c}\delta + \mathrm{c}\phi\mathrm{s}\delta = \mathrm{s}(\phi + \delta) \tag{S3-3}$$

$$\text{or} \quad \beta = \phi + \delta \tag{S3-4}$$

where $\mathrm{s}\delta = \frac{\mathrm{s}\eta\mathrm{s}(\chi+\xi)}{\sqrt{[\mathrm{c}\theta\mathrm{s}\eta\mathrm{c}(\chi+\xi)+\mathrm{s}\theta\mathrm{c}\eta]^2+[\mathrm{s}\eta\mathrm{s}(\chi+\xi)]^2}}$ and $\mathrm{c}\delta = \frac{\mathrm{c}\theta\mathrm{s}\eta\mathrm{c}(\chi+\xi)+\mathrm{s}\theta\mathrm{c}\eta}{\sqrt{[\mathrm{c}\theta\mathrm{s}\eta\mathrm{c}(\chi+\xi)+\mathrm{s}\theta\mathrm{c}\eta]^2+[\mathrm{s}\eta\mathrm{s}(\chi+\xi)]^2}}$. The relation between (α, β) and (ϕ, θ, χ) is given by (S3-1) and (S3-4). Using $\mathrm{c}(\chi + \xi) = \frac{\mathrm{c}\theta\mathrm{s}\eta - \mathrm{c}\alpha}{\mathrm{s}\theta\mathrm{s}\eta}$ from (S3-1), we have

$$\mathrm{c}\delta = \frac{\mathrm{c}\theta\mathrm{s}\eta\mathrm{c}(\chi+\xi)+\mathrm{s}\theta\mathrm{c}\eta}{\sqrt{[\mathrm{c}\theta\mathrm{s}\eta\mathrm{c}(\chi+\xi)+\mathrm{s}\theta\mathrm{c}\eta]^2+[\mathrm{s}\eta\mathrm{s}(\chi+\xi)]^2}} = \frac{\mathrm{c}\eta - \mathrm{c}\theta\mathrm{c}\alpha}{\mathrm{s}\theta\mathrm{s}\alpha} \tag{S4}$$

According to (S3-1), (S3-4) and (S4), (ϕ, χ) can be expressed in terms of (α, β) as follows. For $\chi + \xi \leq \pi$

$$\begin{cases} \phi_1 = \beta - \cos^{-1}\left(\frac{\cos\eta - \cos\theta\cos\alpha}{\sin\theta\sin\alpha}\right) \\ \chi_1 = \cos^{-1}\left(\frac{\cos\eta\cos\theta - \cos\alpha}{\sin\theta\sin\eta}\right) - \xi \end{cases} \tag{S5-1}$$

For $\chi + \xi > \pi$

$$\begin{cases} \phi_2 = \beta - 2\pi + \cos^{-1}\left(\frac{\cos\eta - \cos\theta\cos\alpha}{\sin\theta\sin\alpha}\right) \\ \chi_2 = 2\pi - \cos^{-1}\left(\frac{\cos\eta\cos\theta - \cos\alpha}{\sin\theta\sin\eta}\right) - \xi \end{cases} \tag{S5-2}$$

Now we calculate the probability density function of (α, β) for a certain θ, denoted as $w(\alpha, \beta, \theta)$, according to the theory of bivariate transformation in [3]. The Jacobians are given by

$$J_1 = \begin{vmatrix} \frac{\partial\phi_1}{\partial\alpha} & \frac{\partial\phi_1}{\partial\beta} \\ \frac{\partial\chi_1}{\partial\alpha} & \frac{\partial\chi_1}{\partial\beta} \end{vmatrix} = -\frac{\partial\chi_1}{\partial\alpha} = \frac{\sin\alpha}{\sqrt{(\sin\theta\sin\eta)^2 - (\cos\theta\cos\eta - \cos\alpha)^2}} \tag{S6-1}$$

$$J_2 = \begin{vmatrix} \frac{\partial\phi_2}{\partial\alpha} & \frac{\partial\phi_2}{\partial\beta} \\ \frac{\partial\chi_2}{\partial\alpha} & \frac{\partial\chi_2}{\partial\beta} \end{vmatrix} = -\frac{\partial\chi_2}{\partial\alpha} = \frac{-\sin\alpha}{\sqrt{(\sin\theta\sin\eta)^2 - (\cos\theta\cos\eta - \cos\alpha)^2}} \tag{S6-2}$$

The joint probability density function of (ϕ, θ, χ) is $\rho(\phi, \theta, \chi)$, which is in our case the probability density of the molecule ensemble. Then $w(\alpha, \beta, \theta)$ is given by

$$w(\alpha, \beta, \theta) = |J_1|\rho(\phi_1, \theta, \chi_1) + |J_2|\rho(\phi_2, \theta, \chi_2) = \frac{\sin\alpha}{\sqrt{(\sin\theta\sin\eta)^2 - (\cos\theta\cos\eta - \cos\alpha)^2}}[\rho(\phi_1, \theta, \chi_1) + \rho(\phi_2, \theta, \chi_2)] \tag{S7}$$

where $\phi_1, \chi_1, \phi_2, \chi_2$ are given by (S5-1) and (S5-2). The atom-pair angular distribution, denoted as $g(\alpha, \beta)$, is given by $g(\alpha, \beta)\sin\alpha = \int_0^\pi w(\alpha, \beta, \theta)\ \sin\theta\, d\theta$. Therefore, we have

$$g(\alpha, \beta)\sin\alpha = \int_0^\pi \frac{\sin\alpha}{\sqrt{(\sin\theta\sin\eta)^2 - (\cos\theta\cos\eta - \cos\alpha)^2}}\left[\rho\left(\phi_1, \theta, \chi_1\right) + \rho\left(\phi_2, \theta, \chi_2\right)\right]\sin\theta\, d\theta \tag{S8}$$

Generally, we can write equation (S8) for an atom pair in a molecule marked with jk as

$$g_{jk}(\alpha,\beta)\sin\alpha = \int_0^{\pi} \frac{\sin\alpha}{\sqrt{\left(\sin\theta\sin\eta_{jk}\right)^2-\left(\cos\theta\cos\eta_{jk}-\cos\alpha\right)^2}}\left[\rho\left(\phi_1,\theta,\chi_1\right)+\rho\left(\phi_2,\theta,\chi_2\right)\right]\sin\theta\, d\theta \qquad \text{(S9)}$$

where $g_{jk}(\alpha,\beta)$ is the angular distribution of the atom pair labeled by jk, and the orientation of vector $\vec{r}_{jk}$ pointing from atom j to atom k in the body frame is indicated by $(\eta_{jk},\ \xi_{jk})$. The $\phi_1,\chi_1,\phi_2,\chi_2$ are calculated using (S5-1), (S5-2) by replacing (η,ξ) with $(\eta_{jk},\ \xi_{jk})$. The inequality $\left(\sin\theta\sin\eta_{jk}\right)^2-\left(\cos\theta\cos\eta_{jk}-\cos\alpha\right)^2>0$ requires that $\left|\eta_{jk}-\theta\right|<\alpha<\eta_{jk}+\theta$ for $\eta_{jk}+\theta\le\pi$, and $\left|\eta_{jk}-\theta\right|<\alpha<2\pi-\left(\eta_{jk}+\theta\right)$ for $\eta_{jk}+\theta>\pi$.

2. Retrieval of probability density

Since $\rho(\phi,\theta,\chi)$ cannot be measured directly, equation (S9) could be used to retrieve the probability density of the molecules from the experimentally measured atom-pair angular distributions through UED, X-ray diffraction or ion imaging. In principle, $\rho(\phi,\theta,\chi)$ can be simulated by the use of the experimental conditions; then the corresponding $g_{jk}(\alpha,\beta)$ can be theoretically calculated using equation (S9). $g_{jk}(\alpha,\beta)$ can be measured experimentally and compared with its theoretical counterpart to determine $\rho(\phi,\theta,\chi)$. However, (S9) in some cases can be simplified to retrieve $\rho(\phi,\theta,\chi)$ from $g_{jk}(\alpha,\beta)$ directly. We show the method of retrieving $\rho(\phi,\theta,\chi)$ for symmetric top molecules aligned by a linearly polarized laser field (1D alignment), and then discuss the possible methods without simulations to determine $\rho(\phi,\theta,\chi)$, for 2D and 3D alignments, detailed below.

1D alignment. Now we apply equation (S9) to the case of symmetric top molecules aligned by a linearly polarized laser field. The polarization of the laser field is parallel to the Z axis of the lab frame, shown Figure 1 of main text. The symmetry axis of the molecule is defined as the z axis of the body frame, and the two other principal axes of inertia are defined as the x and y axes. According to [4], both quantum numbers *K* and *M* are conserved during the interaction of the symmetric top molecule and the linearly polarized laser field. Therefore, the molecules can be rotated freely about Z axis of the lab frame and the z axis in the body frame, which are depicted by the angles ϕ and χ respectively. The probability density distribution $\rho(\phi,\theta,\chi)$ is isotropic on ϕ and χ, which can be written as

$$\rho(\phi,\theta,\chi) = (\frac{1}{2\pi})^2\rho_1(\theta) \qquad \text{(S10)}$$

$$g_{jk}(\alpha,\beta)\sin\alpha = \int_0^{\pi}\frac{1}{2\pi^2}\frac{\sin\alpha}{\sqrt{\left(\sin\theta\sin\eta_{jk}\right)^2-\left(\cos\theta\cos\eta_{jk}-\cos\alpha\right)^2}}\rho_1(\theta)\sin\theta\, d\theta \qquad \text{(S11)}$$

$g_{jk}(\alpha,\beta)$ is independent of β; thus, we define $g_{jk}(\alpha)\sin\alpha = \int_0^{2\pi} g_{jk}(\alpha,\beta)\sin\alpha\, d\beta$.

$$g_{jk}(\alpha)\sin\alpha = \int_0^{\pi}\frac{1}{\pi}\frac{\sin\alpha}{\sqrt{\left(\sin\theta\sin\eta_{jk}\right)^2-\left(\cos\theta\cos\eta_{jk}-\cos\alpha\right)^2}}\rho_1(\theta)\sin\theta\, d\theta \qquad \text{(S12)}$$

The angular distribution of atom pair labeled as jk is related to the probability density of the ensemble by an integral transform given by (S12). By defining the kernel function $u(\alpha,\theta,\eta_{jk}) = \frac{1}{\pi}\frac{\sin\alpha}{\sqrt{(\sin\theta\sin\eta_{jk})^2-(\cos\theta\cos\eta_{jk}-\cos\alpha)^2}}$, (S12) can be written as

$$g_{jk}(\alpha)\sin\alpha = \int_0^\pi \rho_1(\theta)u(\alpha,\theta,\eta_{jk})\sin\theta\, d\theta \tag{S13}$$

The kernel function has the property that $u(\alpha,\theta,\eta_{jk}) = u(\alpha,\pi-\theta,\pi-\eta_{jk})$; and by using $\rho_1(\theta) = \rho_1(\pi-\theta)$ we can write

$$g_{jk}(\alpha)\sin\alpha = \int_0^\pi \rho_1(\theta)\sin\theta\, u(\alpha,\theta,\eta_{jk})d\theta = \int_0^\pi \rho_1(\theta)\sin\theta\, u(\alpha,\theta,\pi-\eta_{jk})d\theta \tag{S14}$$

We can show that the probability density of the ensemble with a constant offset is subject to the integral transform (S13) as well. We replace $\rho_1(\theta)$ by $\rho_1(\theta)+C$, where *C* is a constant.

$$\int_0^\pi [\rho_1(\theta)+C]u(\alpha,\theta,\eta_{jk})\sin\theta d\theta = [g_{jk}(\alpha)+C]\sin\alpha \tag{S15}$$

$\int_0^\pi C\, u(\alpha,\theta,\eta_{jk})\sin\theta d\theta = 2C\int_0^\pi \frac{1}{2}u(\alpha,\theta,\eta_{jk})\sin\theta d\theta = C\cdot\sin\alpha$ is used since the transformation of a uniform distribution ½ keeps the same. Equation (S13) can be written into a discrete form to retrieve the probability density of the ensemble from an atom-pair angular distribution, which can be determined experimentally.

$$g_{jk}(\alpha)\sin\alpha = \int_0^\pi \rho_1(\theta)u(\alpha,\theta,\eta_{jk})\sin\theta d\theta \cong \sum_{m=1}^N \rho_1(\theta_m)u(\alpha,\theta_m,\eta_{jk})\sin\theta_m\,\Delta\theta \tag{S16}$$

where $\Delta\theta = \pi/N$ and $\theta_m = m\Delta\theta$. By defining $y_n = g_{jk}(\alpha_n)\sin\alpha_n$, $x_m = \rho_1(\theta_m)\sin\theta_m$, and $U_{n,m} = u(\alpha_n,\theta_m,\eta_{jk})\Delta\theta$, (S16) becomes

$$y_n = \sum_{m=1}^N U_{n,m}\cdot x_m \tag{S17}$$

When the number of x_m and y_n are equal to *N*, the matrix $U_{n,m}$ is a $N\times N$ square matrix, and (S16) is a linear transformation $\boldsymbol{y} = \mathrm{U}\boldsymbol{x}$. Vector $\boldsymbol{y}$ is determined experimentally, the matrix U is calculated using the known structure of molecule. The retrieval process comes down to a problem of looking for solutions of $\boldsymbol{x}$ in a system of linear equations.

2D alignment. In this part we show the retrieval method for the case of an asymmetric top molecule ensemble aligned by a linearly polarized laser. During the interaction, the quantum number *M* is conserved according to [4]; thus the probability density of the ensemble is a function of θ and χ. We can define $\rho(\phi,\theta,\chi) = \frac{1}{2\pi}\rho_2(\theta,\chi)$, and insert it into (S9).

$$g_{jk}(\alpha,\beta)\sin\alpha = \frac{1}{2\pi}\int_0^\pi \frac{\sin\alpha}{\sqrt{(\sin\theta\sin\eta_{jk})^2-(\cos\theta\cos\eta_{jk}-\cos\alpha)^2}}[\rho_2(\theta,\chi_1)+\rho_2(\theta,\chi_2)]\sin\theta\, d\theta \tag{S18}$$

χ_1 and χ_2 are not functions of β; thus the $g_{jk}(\alpha,\beta)$ has no dependence on β. By defining $g_{jk}(\alpha)\sin\alpha = \int_0^{2\pi} g_{jk}(\alpha,\beta)\sin\alpha\, d\beta$.

$$g_{jk}(\alpha)\sin\alpha = \int_0^{\pi} \frac{\sin\alpha}{\sqrt{(\sin\theta\sin\eta_{jk})^2-(\cos\theta\cos\eta_{jk}-\cos\alpha)^2}}[\rho_2(\theta,\chi_1)+\rho_2(\theta,\chi_2)]\sin\theta\, d\theta \quad \text{(S19)}$$

ρ_2 is a real function, which can be expanded by the real spherical harmonics $S_{lm}(\theta,\chi)$ introduction in [5].

$$\rho_2(\theta,\chi) = \sum_{l,m} f_{lm}\, S_{lm}(\theta,\chi) \quad \text{(S20)}$$

where f_{lm} are the coefficient for each S_{lm}. Inserting (S20) into (S19)

$$g_{jk}(\alpha)\sin\alpha = \sum_{l,m} f_{lm} \int_0^{\pi} \frac{\sin\alpha}{\sqrt{(\sin\theta\sin\eta_{jk})^2-(\cos\theta\cos\eta_{jk}-\cos\alpha)^2}}[S_{lm}(\theta,\chi_1)+S_{lm}(\theta,\chi_2)]\sin\theta\, d\theta \quad \text{(S21)}$$

Define $V_{lm}(\alpha) = \int_0^{\pi} \frac{\sin\alpha}{\sqrt{(\sin\theta\sin\eta_{jk})^2-(\cos\theta\cos\eta_{jk}-\cos\alpha)^2}}[S_{lm}(\theta,\chi_1)+S_{lm}(\theta,\chi_2)]\sin\theta\, d\theta$, which can be calculated numerically. The equation is

$$g_{jk}(\alpha)\sin\alpha = \sum_{l,m} f_{lm}\, V_{lm}(\alpha) \quad \text{(S22)}$$

The coefficients f_{lm} can be determined by fitting experimentally measured $g_{jk}(\alpha)\sin\alpha$ to right side of (S22). The χ^2_{jk} defined as $\chi^2_{jk}(f_{lm}) = \frac{1}{N-w}\sum_{\alpha_n}\left[\frac{g_{jk}(\alpha_n)\sin\alpha_n - \sum_{l,m} f_{lm} V_{lm}(\alpha_n)}{\sigma(\alpha_n)}\right]^2$, where N is the number of data points, w is the number of f_{lm}, and $\sigma(\alpha_n)$ the standard error of the data. Then we can define $\chi^2 = \sum_{j\neq k}\chi^2_{jk}$, where the summation is over the atoms in the molecule and $j \neq k$. The minimum of χ^2 gives the coefficients f_{lm}. In practice, signals of two atom pairs that are not parallel are enough for the fitting to determine the f_{lm} since the orientations of such two atom pairs can determine the orientation of the molecule.

3D alignment. Here we consider the case of asymmetric top molecules aligned in 3D, for example using elliptically polarized laser pulses or two linearly polarized pulses with orthogonal polarization. In this case $g_{jk}(\alpha,\beta)$ is a function of both α and β, and $\rho(\phi,\theta,\chi)$ a non-negative function of ϕ,θ and χ. The eigenfunctions of symmetric top $|JKM\rangle = \left(\frac{2J+1}{8\pi^2}\right)^{\frac{1}{2}} e^{iM\phi} d^J_{MK}(\theta) e^{iK\chi}$ can be used as the basis to expand $\rho(\phi,\theta,\chi)$. However, since $|JKM\rangle$ are a complex funcitons and $\rho(\phi,\theta,\chi)$ is real, there are conditions for coefficient of each $|JKM\rangle$ to fulfill. Equation (3.70) in [1] shows that $d^J_{MK}(\theta)$ has the following properties.

$$d^J_{MK}(\theta) = (-1)^{M-K} d^J_{KM}(\theta) = (-1)^{M-K} d^J_{-M-K}(\theta) \quad \text{(S23)}$$

Therefore, for $M-K =$ even,

$$|JKM\rangle + |J-K-M\rangle = 2\left(\frac{2J+1}{8\pi^2}\right)^{\frac{1}{2}} d^J_{MK}(\theta)\cos(M\phi+K\chi) \quad \text{(S24-1)}$$

For $M-K =$ odd,

$$|JKM\rangle + |J-K-M\rangle = 2i\left(\frac{2J+1}{8\pi^2}\right)^{\frac{1}{2}} d^J_{MK}(\theta)\sin(M\phi+K\chi) \quad \text{(S24-1)}$$

The probability density can be expanded as

$$\rho(\phi,\theta,\chi) = \sum_{JKM} f_{JKM}|JKM\rangle \tag{S25}$$

The conditions for the right side of (S25) to be real are that $f_{JKM} = f_{J-K-M}$, and f_{JKM} is real for $M-K=$ even, f_{JKM} is purely imaginary for $M-K=$ odd. Equivalently, $\rho(\phi,\theta,\chi)$ can be expanded by the basis that consist of $|JKM\rangle + |J-K-M\rangle$. By defining $E_{JKM}(\phi,\theta,\chi) = 2\left(\frac{2J+1}{8\pi^2}\right)^{\frac{1}{2}} d^J_{MK}(\theta)\cos(M\phi+K\chi)$, and $O_{JKM}(\phi,\theta,\chi) = 2\left(\frac{2J+1}{8\pi^2}\right)^{\frac{1}{2}} d^J_{MK}(\theta)\sin(M\phi+K\chi)$, (S25) can be rewritten as

$$\rho(\phi,\theta,\chi) = \sum_{JKM}\left[a_{JKM}E_{JKM}(\phi,\theta,\chi) + b_{JKM}O_{JKM}(\phi,\theta,\chi)\right] \tag{S26}$$

where a_{JKM}, b_{JKM} are the real coefficients for $M-K=$ even, and $M-K=$ odd, respectively. Inserting (S26) into (S9), we have

$$g_{jk}(\alpha,\beta)\sin\alpha = \sum_{JKM}\left[a_{JKM}C_{JKM}(\alpha,\beta) + b_{JKM}S_{JKM}(\alpha,\beta)\right] \tag{S27-1}$$

$$C_{JKM}(\alpha,\beta) = \int_0^{\pi} \frac{\sin\alpha}{\sqrt{\left(\sin\theta\sin\eta_{jk}\right)^2 - \left(\cos\theta\cos\eta_{jk} - \cos\alpha\right)^2}}\left[E_{JKM}(\phi_1,\theta,\chi_1) + E_{JKM}(\phi_2,\theta,\chi_2)\right]\sin\theta\, d\theta \tag{S27-2}$$

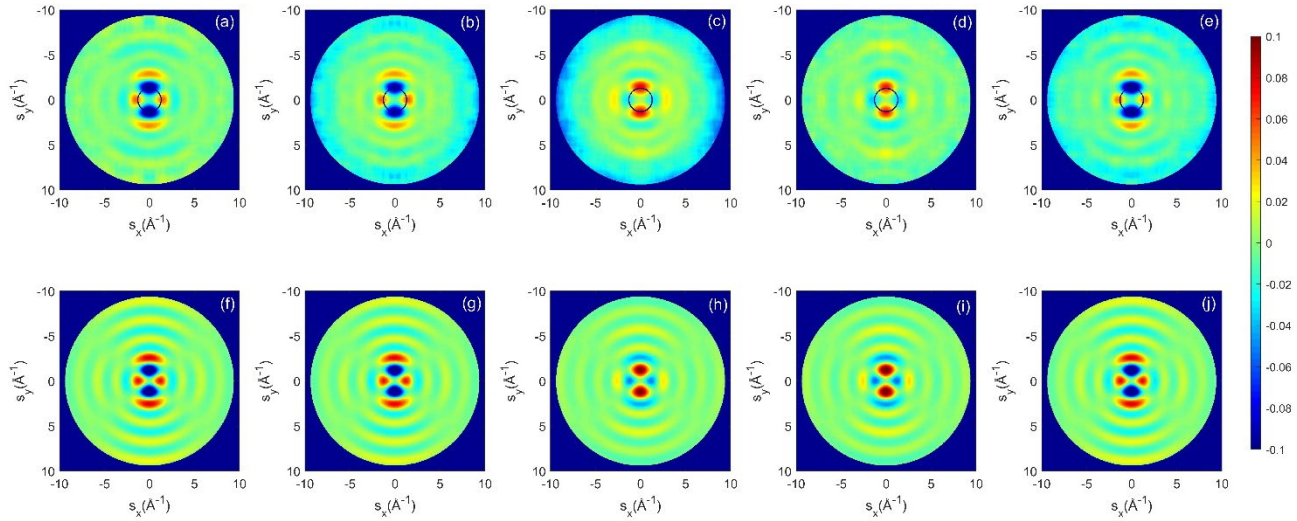
$$S_{JKM}(\alpha,\beta) = \int_0^{\pi} \frac{\sin\alpha}{\sqrt{\left(\sin\theta\sin\eta_{jk}\right)^2 - \left(\cos\theta\cos\eta_{jk} - \cos\alpha\right)^2}}\left[O_{JKM}(\phi_1,\theta,\chi_1) + O_{JKM}(\phi_2,\theta,\chi_2)\right]\sin\theta\, d\theta \tag{S27-3}$$

(S27-1),(S27-2) can be used to numerically calcualte $C_{JKM}(\alpha,\beta)$ and $S_{JKM}(\alpha,\beta)$, and the coefficients a_{JKM} and b_{JKM} can be determined by the 2-dimensional fitting of experimentally measured $g_{jk}(\alpha,\beta)\sin\alpha$ to the right side of (S27-1). The χ^2_{jk} is defined below, and $\chi^2 = \sum_{j\neq k}\chi^2_{jk}$, where the summation is over the atoms in the molecule and $j \neq k$. The coefficients a_{JKM} and b_{JKM} are determined by the minimum of χ^2.

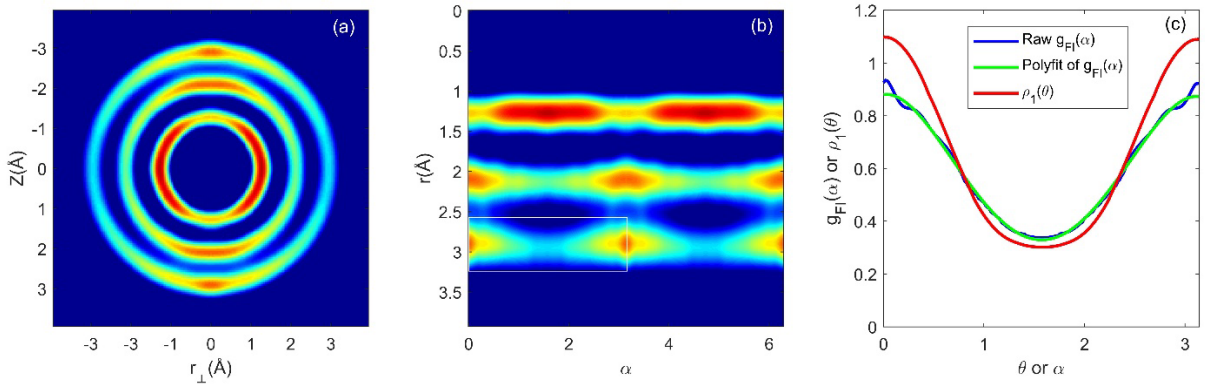
$$\chi^2_{jk}(a_{JKM}, b_{JKM}) = \frac{1}{N-w}\sum_{\alpha_m,\beta_n}\left\{\frac{g_{jk}(\alpha_m,\beta_n)\sin\alpha - \sum_{JKM}\left[a_{JKM}C_{JKM}(\alpha_m,\beta_n) + b_{JKM}S_{JKM}(\alpha_m,\beta_n)\right]}{\sigma(\alpha_m,\beta_n)}\right\}^2 \tag{S28}$$

where N is the number of data points, w is the number of fitted parameters, and $\sigma(\alpha_m,\beta_n)$ the standard error of the data.

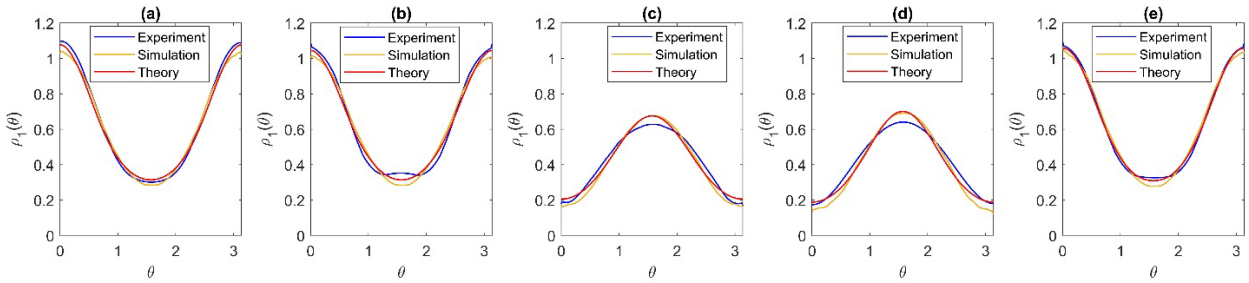
SUPPLEMENTARY NOTE 2. SUPPLEMENTARY FIGURES



Supplementary Figure 3. Experimental and simulated diffraction patterns. (a)-(e) are the experimental $\Delta I_{\mathrm{mol}}/I_{\mathrm{atom}}$ shown in figure 3 in main text . The corresponding simulated patterns are shown in (f)-(j).



Supplementary Figure 4. Retrieval of probability density of the ensemble from experimental data. (a) MPDF calculated from the experimental diffraction pattern at t=0. (b) The MPDF is converted into polar representation with angle as horizontal axis and distance between atom pairs as vertical axis. (c) The raw $g_{\mathrm{FI}}(\alpha)$ is calculated by integrating over the radial coordinate within the 1/e width of the peak using the data of atom pair FI, which is in the rectangle area of (b). The fitting of 4$^{\mathrm{th}}$ order polynomial is applied to the raw $g_{\mathrm{FI}}(\alpha)$ to remove the noise and artifact. $\rho_1(\theta)$ is the retrieved probability density of the ensemble.



Supplementary Figure 5. Angular distribution of the molecule ensemble retrieved from experimental (blue line) and simulated (orange line) diffraction patterns, and calculated from the wave packet (red line) directly, at five times (a) t=0 ps, (b)t= 166.8 ps, (c) t= 168.8 ps, (d) t= 335.5 ps, (e) t= 337.7 ps.

Reference

1. Zare, R.N., *Angular Momentum Understanding spatial aspects in chemistry and physics.* 1988: p. page 77-81.
2. Landau, L.D. and E.M. Lifshits, *Mechanics*. 2nd ed. Course of theoretical physics1969, Oxford ; New York: Pergamon Press. page 98 -100.
3. Rohatgi, V.K. and A.K.M.E. Saleh, *An Introduction to Probability and Statistics*2001: Wiley. page 133-135.
4. Seideman, T. and E. Hamilton, *Nonadiabatic alignment by intense pulses. Concepts, theory, and directions.* ADVANCES IN ATOMIC, MOLECULAR AND OPTICAL PHYSICS, 2006.
5. Blanco, M.A., M. Flórez, and M. Bermejo, *Evaluation of the rotation matrices in the basis of real spherical harmonics.* Journal of Molecular Structure: THEOCHEM, 1997. **419**(1-3): p. 19-27.