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Citation: The Journal of Chemical Physics **148**, 101103 (2018); doi: 10.1063/1.5023645
View online: https://doi.org/10.1063/1.5023645
View Table of Contents: http://aip.scitation.org/toc/jcp/148/10
Published by the American Institute of Physics

THE JOURNAL OF CHEMICAL PHYSICS **148**, 101103 (2018)

Communication: Strong laser alignment of solvent-solute aggregates in the gas-phase

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(Received 26 January 2018; accepted 27 February 2018; published online 12 March 2018)

Strong quasi-adiabatic laser alignment of the indole-water-dimer clusters, an amino-acid chromophore bound to a single water molecule through a hydrogen bond, was experimentally realized. The alignment was visualized through ion and electron imaging following strong-field ionization. Molecular-frame photoelectron angular distributions showed a clear suppression of the electron yield in the plane of the ionizing laser's polarization, which was analyzed as strong alignment of the molecular cluster with $\langle\cos^2\theta_{2D}\rangle \geq 0.9$. *Published by AIP Publishing.* https://doi.org/10.1063/1.5023645

INTRODUCTION

The properties of atoms and molecules are strongly dependent on their environment. The photochemical pathways and functions of biological chromophores are, for instance, strongly affected by hydrogen-bond interactions with the surrounding protein and solvent environment.[1–3] Hydrogen bonds in general are of universal importance in chemistry and biochemistry, and it is of great interest to bridge the gap between single isolated molecules and molecules in solvation.

Indole is the chromophore of the amino acid tryptophan, and indole-water corresponds to a model system of a chromophore "solvated" by a single water molecule. Indole's intrinsic properties have been widely studied.[4–6] Also the influence of water solvation on indole has been discussed extensively since it has a strong influence on its electronic properties.[7] This includes the energetic of the lowest electronically excited states, which interchange their order with the addition of water and other polar molecules.[8] Its emission properties are regularly used in fluorescence studies of proteins, where spectral shifts are directly related to the chromophores' environment.[9] The indole-water dimer has a well-defined structure,[10–12] in which water is hydrogen bonded to the N–H moiety of the pyrrole-unit. The indole-water binding energy was determined to be 0.2 eV.[13]

The rotational motion of molecules can be controlled by the torque exerted on their dipole moment that is induced by the interaction of the molecule's polarizability with external electric fields. Intense laser light, providing electric-ac-field intensities on the order of 1 TW/cm^2 and above, can strongly align, and in consequence spatially fix, one or two molecular axes to the laboratory frame.[14] These aligned molecules serve as ideal samples, e.g., to image the structure and dynamics of complex molecules directly in the molecular frame. This includes time-resolved dynamics studies using molecular-frame photoelectron angular distributions (MFPADs)[15] or photoelectron holography.[16,17] In addition, as most chemical reactivity depends on the relative orientation of the reactants, aligned molecules are well suited to study steric effects in chemical reactions. Further applications of aligned molecules range from attosecond-light-pulse and high-harmonic generation[18] over ultrafast electron or x-ray diffraction[19–22] to quantum information processing.[23] Time-resolved diffractive-imaging experiments are of utmost interest for the recording of the so-called molecular movies, which is also especially interesting for large and complex molecules. The contrast in these experiments can be greatly increased if the molecules are fixed in space, e.g., strongly aligned, typically when $\langle\cos^2\theta_{2D}\rangle > 0.9$.[19,24] Strong molecular alignment in combination with tomographic approaches to observe three-dimensional diffraction volumes has the potential to retrieve the bond angles of complex molecules.[25] The structural dynamics of the indole-water system could be extracted from ultrafast electron or x-ray-diffraction experiments[21,26] on the controlled system.

Strong alignment was achieved for linear, symmetric top, and asymmetric top molecules in the adiabatic,[27] intermediate,[28,29] and impulsive regimes.[30,31] Especially the combination with rotational-state selection[32,33] has improved the achievable control dramatically, the recorded degree of alignment reaching values as high as $\langle\cos^2\theta_{2D}\rangle > 0.97$.[34] For the imaging of complex chemical dynamics, it is highly desirable to extend the range of directionally controlled molecular systems to molecular aggregates with weak intermolecular interactions, such as hydrogen bonded solvent-solute clusters. These systems also serve as tests for the possibilities to laser-align large biomolecules without deterioration of the secondary structure.[24,35] Besides the generation

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of weak rotational coherences, corresponding to very weak alignment, in spectroscopic investigations of hydrogen bonded clusters and even very weakly bound molecule-rare-gas clusters,[11,36–38] so far no alignment for such systems has been reported.

Here, we report strong three-dimensional laser alignment of the prototypical indole-water dimer cluster. This enables for the molecular-frame imaging (*vide supra*) of such complex, floppy, composite molecular systems. More specifically, we present experimental results, concerning the long-pulse quasi-adiabatic alignment of the spatially separated indole-water cluster and its strong-field-ionization (SFI) molecular-frame photoelectron angular distributions (MFPADs).

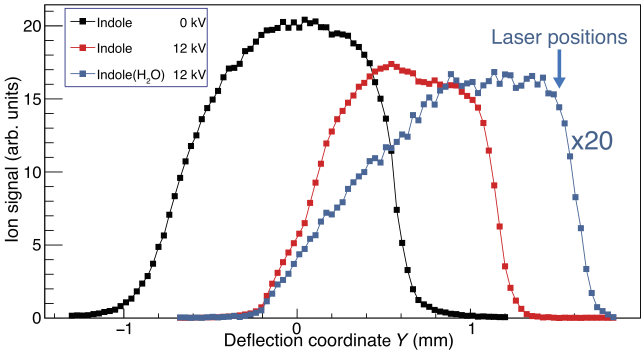

FIG. 1. Molecular-beam and deflection profiles of indole and indole-water.

EXPERIMENTAL SETUP

The experimental setup was described elsewhere.[28] In brief, a pulsed molecular beam was provided by expanding a few millibar of indole and a trace of water seeded in 80 bars of helium through an Even-Lavie valve[39] operated at a temperature of 110 °C and at a repetition rate of 100 Hz, limited by pumping speed. Due to three-body collisions in the early phase of the expansion, $(\text{indole})_m(H_2O)_n$ clusters were formed. Using the electrostatic deflector, the molecular beam was dispersed according to the species' and quantum states' dipole-moment-to-mass ratio.[32,33,40]

The indole-water clusters were 3D aligned by a moderately intense ($I_{\text{control}} \approx 10^{11}$ W/cm^2), 485 ps long laser pulse inside a velocity map imaging (VMI) spectrometer. The rise time in intensity (10%–90%) was 100 ps.[29] The laser pulse was elliptically polarized with an aspect ratio of 3:1 in intensity, with the major axis along the laboratory Z axis. The angular confinement was probed through strong-field multiple ionization by a linearly polarized, 30 fs laser pulse ($I_{\text{probe}} = 3\cdot10^{14}$ W/cm^2), resulting in Coulomb explosion of the cluster. The resulting ions were velocity mapped onto a position sensitive detector. The alignment and probe laser pulses were provided by an amplified femtosecond laser system.[28] The probe pulses had pulse energies of 200 μJ and a beam waist of $\omega_0 = 24$ μm. The alignment laser pulses had energies controlled between 0 and 7 mJ and a beam waist of $\omega_0 = 30$ μm. The alignment laser itself did not ionize the molecules.

For the MFPAD experiments, a circularly polarized 30 fs probe pulse centered at 800 nm with a peak intensity of $I_{\text{probe}} = 1.3\cdot10^{14}$ W/cm^2 was used, which places the ionization process close to the tunneling regime with a Keldysh parameter of $\gamma = 0.7$. The circular polarization ensures that no recollisions of the electrons with the parent ions occur. Under these conditions, the cluster undergoes only single ionization, as confirmed by ion time-of-flight mass spectrometry.

RESULTS

Figure 1 shows the measured horizontally integrated column density profiles of the undeflected and deflected molecular beam as a function of the vertical laser position; for further details, see Ref. 33. The profiles were measured *via* strong-field ionization of the clusters and molecules in a velocity map imaging spectrometer. The individual profiles were obtained by gating the detector on the specific parent ion masses. The undeflected molecular beam column density profile, which has the same shape for all species, is shown as a black line, whereas the deflected molecular beam column density profiles for indole and indole-water are plotted in red and blue, respectively. The indole-water profile is multiplied by a factor of 20 with respect to the undeflected and deflected indole signal, which reflects the relative amount of this dimer formed in the supersonic expansion. A clear separation of indole and indole-water clusters was observed.[40] From the various species present in the beam, the indole-water cluster possesses the largest dipole moment ($\mu = 4.4$ D)[12] and the largest dipole-moment-to-mass ratio and, therefore, was deflected significantly more than the indole ($\mu = 1.96$ D) and water ($\mu = 1.86$ D) monomers.[40,41] Similarly, higher order clusters $(\text{indole})_m(H_2O)_n$ ($m > 1 \vee n > 1$) were deflected significantly less. Thus, a pure sample of indole-water is obtained, and the blue arrow marks the vertical position in the molecular beam where the alignment and MFPAD measurements were performed.

The 2D momentum image for H_3O^+ ions for the alignment-field-free case is shown in Fig. 2(b). Clearly visible are two, a slow and a fast, ionic channels, assigned to the two Coulomb explosion channels $C_8H_7N(H_2O) \rightarrow C_8H_6N^+ + H_3O^+$ and $C_8H_7N(H_2O) \rightarrow C_8H_6N^{++} + H_3O^+$. The central part of the image was cut due to the presence of the background signal in this region. The observed distribution is circularly symmetric, as expected for the case of an isotropic sample and the probe-laser polarization linear and perpendicular to the detector plane. Figure 2(c) shows the corresponding ion distribution when the molecules were 3D aligned by the elliptically polarized control laser with its major axis perpendicular to the detector plane. The pairs of red and cyan circles indicate the velocity ranges that were used to extract the degree of alignment for the two channels. This H_3O^+ distribution was fairly directional and provided the direct evidence of the alignment of the indole-water clusters at the time of ionization. The mean of the momentum distribution of the H_3O^+ fragments was located in the molecular plane of the indole moiety due to the planarity of the indole-water cluster. Measuring its transverse momentum distribution, therefore, directly linked the molecular plane of the indole moiety to the laboratory frame.

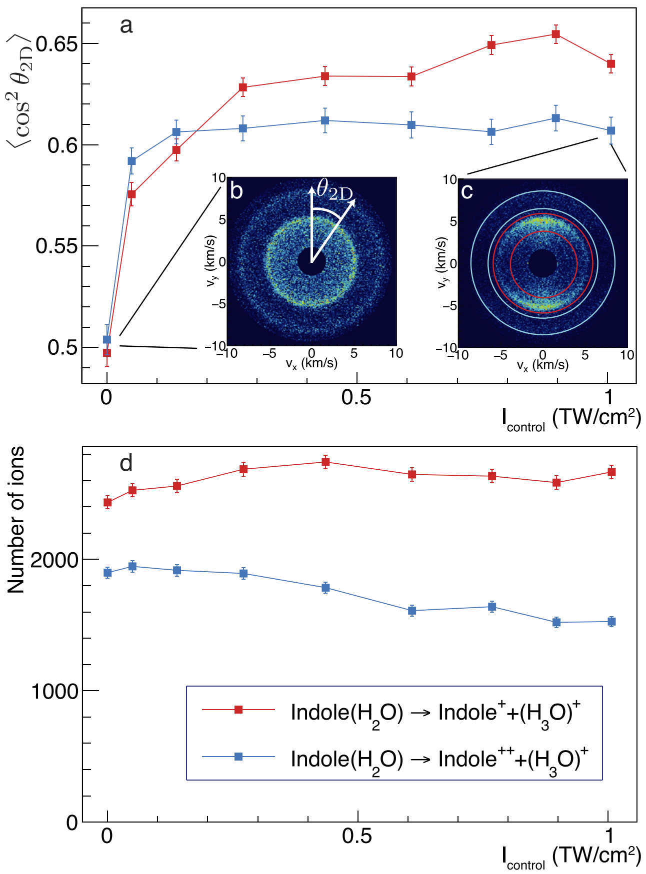

FIG. 2. (a) Observed degree of alignment of H_3O^+ as a function of the control laser peak intensity for the fragmentation channels with singly (red) and doubly (cyan) charged indole fragments. The angle θ_{2D} is defined in (b). Velocity maps (b) without alignment laser and (c) with alignment laser at a peak intensity of 1 TW/cm^2. Pairs of circles indicate the corresponding velocity cuts for the two channels. (d) Number of ions for the singly (red) and doubly (cyan) indole-charge separation channel inside the velocity selected areas.

Figure 2(a) shows the experimentally derived degree of alignment $\langle\cos^2\theta_{2D}\rangle$[42] as a function of the peak intensity of the alignment pulse for the slow, $C_8H_7N(H_2O) \rightarrow C_8H_6N^+ + H_3O^+$, and fast, $C_8H_7N(H_2O) \rightarrow C_8H_6N^{++} + H_3O^+$, channels in red and cyan, respectively. Without alignment laser, a degree of alignment $\langle\cos^2\theta_{2D}\rangle = 0.5$ was observed. With increasing laser intensity, the degree of alignment increased. It saturated for both channels at relatively moderate intensities.

Figure 2(d) shows the integrated number of H_3O^+ ions for the two channels within the corresponding velocity cuts as a function of the alignment laser peak intensity. For the singly charged-indole fragmentation channel, the number of ions increased with the peak laser intensity is observed. In contrast, it decreased for the doubly charged-indole fragmentation channel.

Figure 3(a) shows a sketch of the MFPAD measurements. Indole-water clusters were aligned to the YZ-plane, as described above and singly ionized by a circularly polarized probe laser, indicated by the red spiral. The emitted electrons are accelerated by the combined static electric field in the spectrometer and the laser field and were projected onto a position sensitive detector. Figure 3(b) shows the recorded MFPAD of the aligned indole-water clusters. The electron emission is suppressed along the vertical direction, clearly seen as dips in the corresponding angular distributions. The maximum in the off-the-nodal-plane angle in the electron emission[43] occurs at an angle $\Omega = 22°$ with respect to the YZ-plane.

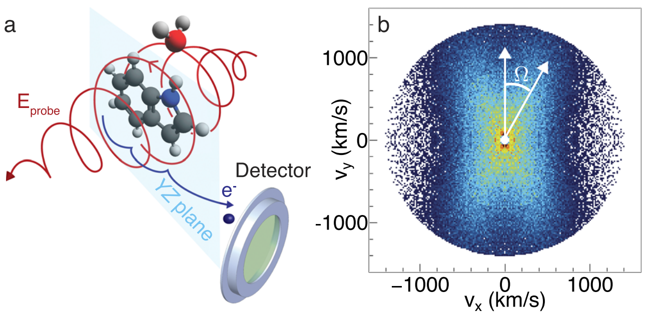

FIG. 3. (a) Schematic of the experimental setup showing the indole-water cluster aligned to the YZ plane (cyan). The circularly polarized probe laser is indicated by the red spiral. (b) Experimentally observed MFPAD of indole-water.

DISCUSSION

Indole-water has a longest classical-rotation period of 484 ps. The control laser pulse duration of 485 ps with a rising edge of about 100 ps places the alignment dynamics of the cluster into the intermediate regime between the impulsive and adiabatic alignment.[29] Different from observations for rotational-ground-state-selected carbonyl sulfide (OCS), no oscillations in the degree of alignment as a function of the delay between control-laser and probe-laser pulses are observed. While for every initial rotational state an oscillatory behavior in the degree of alignment should be induced, these effects are averaged out due to the different phases of these oscillations for different initial states and the large number of initial rotational states present in the deflected part of the beam for larger molecules.[32]

The observed power dependence of the degree of alignment for both channels in Fig. 2(a) is similar to the typical dependence observed for a cold molecular beam.[34] The degree of alignment increases strongly with increasing control laser power until it reaches a plateau at relatively low control laser intensities. It differs from experiments with good indicators for the degree of alignment in the actual degree of alignment of the plateau, which is given by $\langle\cos^2\theta_{2D}\rangle = 0.64$ and $\langle\cos^2\theta_{2D}\rangle = 0.61$ for the singly and doubly charged fragmentation channels, respectively. For a strongly aligned sample with good axial recoil, a limit of $\langle\cos^2\theta_{2D}\rangle > 0.95$ is typically observed. On the other hand, a slow increase in the degree of alignment is usually observed as a function of the peak intensity of the alignment laser for a warm molecular beam.[44] In that case, the degree of alignment does not reach the plateau region for laser intensities in the order of 1 TW/cm^2. Therefore, the saturation behavior observed here is attributed to the strong alignment of cold molecules and the poor representation of this alignment is attributed to non-axial recoil in the molecular frame, likely due to complex, possibly slow, chemical dynamics of the formation of H_3O^+.

Knowledge of the in-plane momentum distribution of the H_3O^+ fragments in the molecular frame would, in addition, allow us to determine the three-dimensional degree of alignment and orientation of the cluster by measuring the three-dimensional momentum vector. However, this is not trivial as this dynamics in the molecular frame is unknown and an analysis through complex quantum-chemical computations is beyond the scope of this publication. Moreover, as the measured degree of alignment was saturated at a degree of alignment of $\langle\cos^2\theta_{2D}\rangle = 0.64$, the directionality of this probe process is also not expected to be highly directional inside the molecular plane of the indole moiety. On the other hand, three-dimensional alignment is routinely obtained for a control-laser-pulse ellipticity of 3:1 if the one-dimensional alignment is strong.[45,46]

The strong degree of planar alignment is supported by the recorded MFPADs, which contain information on the relative dipole moments, polarizabilities, molecular orbitals involved in the ionization, and laser-field-dependent ionization potentials.[43,47] The local minimum of electrons along the vertical direction results from the suppression of electron emission in the nodal plane of the highest-occupied molecular orbitals (HOMO and HOMO-1).[43] Instead, due to the symmetry of these π orbitals, the emission occurs off the nodal plane in the molecular frame. The suppression manifests itself by a dip along the vertical axis of the measured MFPAD since the nodal plane of the molecule is strongly fixed to the laboratory frame (YZ plane). This feature appears typically if the molecules are strongly aligned with a degree of alignment $\langle\cos^2\theta_{2D}\rangle \geq 0.9$. The measured opening angle $\Omega = 22° \pm 2°$ is in good agreement with the theoretical value of $\Omega_{\text{theo}} = 20°$ obtained within the extended strong-field ionization model,[43] using a computed ionization potential of the cluster of $I_p = 7.71$ eV (MP2/6-311G**). Rotating the major axis of the ellipse of the control-laser polarization with respect to the detector allowed us to retrieve the three-dimensional MFPAD of indole-water by tomographic reconstruction methods, similar to previous work for napthalene.[48] Preliminary analysis of these data further confirms this argument.

The limit of the measured degree of alignment for the slow channel is higher than for the fast channel. This is surprising as the velocity for the doubly charged indole channel is faster and thus better axial recoil is expected. We attribute this behavior to a change in the branching ratios of both channels as a function of the peak intensity of the alignment laser. The faster channel is suppressed in the strong field compared to the slow channel; see Fig. 2(d). This signal decrease might be attributed to the symmetry plane of the involved orbitals, which leads to a reduced ionization probability when the molecular frame is fixed to the laboratory frame (*vide supra*). For the most-strongly aligned molecules, situated and probed at the peak of the alignment laser intensity distribution, multiple ionization is suppressed and H_3O^+ is preferentially observed in the slow channel. This leads to a faster saturation effect in the measured degree of alignment for the doubly charged indole channel as a function of the laser intensity. The degree of alignment for the singly charged channel is still slightly increasing due to the increase in the degree of alignment.

One could speculate that the cluster might be destroyed by the control laser itself. A possible neutral destruction mechanism would lead to a reduction of the H_3O^+ Coulomb explosion channels, as the pulse duration of the control laser is relatively long compared to a typical dissociation time scale. However, the constant number of H_3O^+ fragments for the whole range of control-laser intensities indicates that the clusters are not destroyed by the alignment laser. This is consistent with a small probability expected for a transition of a bound state to the continuum wavefunction, which leads to a highly inefficient direct fragmentation of the cluster in the electronic ground state by the absorption of a single photon at the wavelength of the alignment laser. In addition, while electronically excited states of indole-water could break the cluster by a charge transfer in the $A''(\pi\sigma^*)$ state,[7] the three-photon-transition probability to populate these states by the alignment laser is very small.[49] Moreover, the laser-induced Stark effect, which is on the order of a few meV for the alignment laser intensity, is not relevant for breaking the intermolecular hydrogen bond in the cluster, which is bound by 0.2 eV.

CONCLUSIONS

The hydrogen-bound indole-water clusters were strongly quasi-adiabatically aligned by moderately strong elliptically polarized laser pulses. Alignment was observed in velocity-map images of H_3O^+ fragments, albeit only a weak degree of alignment, $\langle\cos^2\theta_{2D}\rangle = 0.64$, could be deduced, which is attributed to non-axial recoil. Much stronger alignment, $\langle\cos^2\theta_{2D}\rangle \geq 0.9$, was deduced from a clearly visible nodal plane in the molecular-frame photoelectron angular distributions. This strong control opens up possibilities to study the photo-induced ultrafast chemical dynamics around the intermolecular hydrogen bond[50] through the imaging of half-collisions in the molecular frame, which could provide unprecedented details on these intermolecular interactions.

The current results highlight that the determination of molecular axes through fragment recoil leads not always to the correct determination of the degree of alignment in the laboratory frame. Reconstructing the MFPADs from the recoil frame distribution is, therefore, not possible for such systems. Our findings underline the advantage of active laser alignment, in which the laser polarization fixes the molecular frame to the principal axes of polarizability. However, a possible influence of the alignment laser on the investigated dynamics has to be considered. Field-free-alignment with shaped laser pulses could provide the best solution, but in that approach it is difficult to achieve strong alignment for asymmetric tops, and we are currently exploring novel schemes for complex molecules.

ACKNOWLEDGMENTS

Besides DESY, this work has been supported by the *Deutsche Forschungsgemeinschaft* (DFG) through the excellence cluster "The Hamburg Center for Ultrafast Imaging–Structure, Dynamics and Control of Matter at the Atomic Scale" (CUI, No. EXC1074) and the priority program 1840 "Quantum Dynamics in Tailored Intense Fields" (QUTIF, KU1527/3), by the European Research Council through the Consolidator Grant COMOTION (ERC-Küpper-614507), and by the Helmholtz Association “Initiative and Networking Fund.”

[1] I. Tatischeff, R. Klein, T. Zemb, and M. Duquesne, “Solvent interactions with the indole chromophore,” Chem. Phys. Lett. **54**, 394–398 (1978).

[2] P. Song and F.-C. Ma, “Intermolecular hydrogen-bonding effects on photophysics and photochemistry,” Int. Rev. Phys. Chem. **32**, 589–609 (2013).

[3] D. A. Horke, H. M. Watts, A. D. Smith, E. Jager, E. Springate, O. Alexander, C. Cacho, R. T. Chapman, and R. S. Minns, “Hydrogen bonds in excited state proton transfer,” Phys. Rev. Lett. **117**, 163002 (2016).

[4] G. Berden, W. L. Meerts, and E. Jalviste, “Rotationally resolved ultraviolet spectroscopy of indole, indazole, and benzimidazole: Inertial axis reorientation in the $S_1(^1L_b) \leftarrow S_0$ transitions,” J. Chem. Phys. **103**, 9596–9606 (1995).

[5] J. Küpper, D. W. Pratt, L. Meerts, C. Brand, J. Tatchen, and M. Schmitt, “Vibronic coupling in indole. II. Experimental investigation of the ^1L_a–^1L_b interaction using rotationally resolved electronic spectroscopy,” Phys. Chem. Chem. Phys. **12**, 4980–4988 (2010).

[6] R. Livingstone, O. Schalk, A. E. Boguslavskiy, G. Wu, L. T. Bergendahl, A. Stolow, M. J. Paterson, and D. Townsend, “Following the excited state relaxation dynamics of indole and 5-hydroxyindole using time-resolved photoelectron spectroscopy,” J. Chem. Phys. **135**, 194307 (2011).

[7] A. L. Sobolewski and W. Domcke, “Photoinduced charge separation in indole–water clusters,” Chem. Phys. Lett. **329**, 130–137 (2000).

[8] H. Lami and N. Glasser, “Indole solvatochromism revisited,” J. Chem. Phys. **84**, 597–604 (1986).

[9] J. T. Vivian and P. R. Callis, “Mechanisms of tryptophan fluorescence shifts in proteins,” Biophys. J. **80**, 2093–2109 (2001).

[10] T. M. Korter, D. W. Pratt, and J. Küpper, “Indole-H_2O in the gas phase. Structures, barriers to internal motion, and $S_1 \leftarrow S_0$ transition moment orientation. Solvent reorganization in the electronically excited state,” J. Phys. Chem. A **102**, 7211–7216 (1998).

[11] S. Blanco, J. C. Lopez, J. L. Alonso, P. Ottaviani, and W. Caminati, “Pure rotational spectrum and model calculations of indole-water,” J. Chem. Phys. **119**, 880–886 (2003).

[12] C. Kang, T. M. Korter, and D. W. Pratt, “Experimental measurement of the induced dipole moment of an isolated molecule in its ground and electronically excited states: Indole and indole–H_2O,” J. Chem. Phys. **122**, 174301 (2005).

[13] M. Mons, I. Dimicoli, B. Tardivel, F. Piuzzi, V. Brenner, and P. Millié, “Site dependence of the binding energy of water to indole: Microscopic approach to the side chain hydration of tryptophan,” J. Phys. Chem. A **103**, 9958–9965 (1999).

[14] H. Stapelfeldt and T. Seideman, “Colloquium: Aligning molecules with strong laser pulses,” Rev. Mod. Phys. **75**, 543–557 (2003).

[15] J. Hansen, H. Stapelfeldt, D. Dimitrovski, M. Abu-Samha, C. Martiny, and L. Madsen, “Time-resolved photoelectron angular distributions from strong-field ionization of rotating naphthalene molecules,” Phys. Rev. Lett. **106**, 073001 (2011).

[16] F. Krasniqi, B. Najjari, L. Strüder, D. Rolles, A. Voitkiv, and J. Ullrich, “Imaging molecules from within: Ultrafast angström-scale structure determination of molecules via photoelectron holography using free-electron lasers,” Phys. Rev. A **81**, 033411 (2010).

[17] A. Landers, T. Weber, I. Ali, A. Cassimi, M. Hattass, O. Jagutzki, A. Nauert, T. Osipov, A. Staudte, M. H. Prior, H. Schmidt-Böcking, C. L. Cocke, and R. Dörner, “Photoelectron diffraction mapping: Molecules illuminated from within,” Phys. Rev. Lett. **87**, 013002 (2001).

[18] R. Velotta, N. Hay, M. B. Mason, M. Castillejo, and J. P. Marangos, “High-order harmonic generation in aligned molecules,” Phys. Rev. Lett. **87**, 183901 (2001).

[19] F. Filsinger, G. Meijer, H. Stapelfeldt, H. Chapman, and J. Küpper, “State- and conformer-selected beams of aligned and oriented molecules for ultrafast diffraction studies,” Phys. Chem. Chem. Phys. **13**, 2076–2087 (2011); e-print arXiv:1009.0871 [physics].

[20] C. J. Hensley, J. Yang, and M. Centurion, “Imaging of isolated molecules with ultrafast electron pulses,” Phys. Rev. Lett. **109**, 133202 (2012).

[21] J. Küpper, S. Stern, L. Holmegaard, F. Filsinger, A. Rouzée, A. Rudenko, P. Johnsson, A. V. Martin, M. Adolph, A. Aquila, S. Bajt, A. Barty, C. Bostedt, J. Bozek, C. Caleman, R. Coffee, N. Coppola, T. Delmas, S. Epp, B. Erk, L. Foucar, T. Gorkhover, L. Gumprecht, A. Hartmann, R. Hartmann, G. Hauser, P. Holl, A. Hömke, N. Kimmel, F. Krasniqi, K.-U. Kühnel, J. Maurer, M. Messerschmidt, R. Moshammer, C. Reich, B. Rudek, R. Santra, I. Schlichting, C. Schmidt, S. Schorb, J. Schulz, H. Soltau, J. C. H. Spence, D. Starodub, L. Strüder, J. Thøgersen, M. J. J. Vrakking, G. Weidenspointner, T. A. White, C. Wunderer, G. Meijer, J. Ullrich, H. Stapelfeldt, D. Rolles, and H. N. Chapman, “X-ray diffraction from isolated and strongly aligned gas-phase molecules with a free-electron laser,” Phys. Rev. Lett. **112**, 083002 (2014); e-print arXiv:1307.4577 [physics].

[22] J. Yang, M. Guehr, X. Shen, R. Li, T. Vecchione, R. Coffee, J. Corbett, A. Fry, N. Hartmann, C. Hast, K. Hegazy, K. Jobe, I. Makasyuk, J. Robinson, M. S. Robinson, S. Vetter, S. Weathersby, C. Yoneda, X. Wang, and M. Centurion, “Diffractive imaging of coherent nuclear motion in isolated molecules,” Phys. Rev. Lett. **117**, 153002 (2016).

[23] E. A. Shapiro, I. Khavkine, M. Spanner, and M. Y. Ivanov, “Strong-field molecular alignment for quantum logic and quantum control,” Phys. Rev. A **67**, 013406 (2003).

[24] A. Barty, J. Küpper, and H. N. Chapman, “Molecular imaging using x-ray free-electron lasers,” Annu. Rev. Phys. Chem. **64**, 415–435 (2013).

[25] E. Wolf, “Three-dimensional structure determination of semi-transparent objects from holographic data,” Opt. Commun. **1**, 153–156 (1969).

[26] S. T. Park, A. Gahlmann, Y. He, J. S. Feenstra, and A. H. Zewail, “Ultrafast electron diffraction reveals dark structures of the biological chromophore indole,” Angew. Chem., Int. Ed. **47**, 9496–9499 (2008).

[27] J. J. Larsen, H. Sakai, C. P. Safvan, I. Wendt-Larsen, and H. Stapelfeldt, “Aligning molecules with intense nonresonant laser fields,” J. Chem. Phys. **111**, 7774 (1999).

[28] S. Trippel, T. Mullins, N. L. M. Müller, J. S. Kienitz, K. Długołęcki, and J. Küpper, “Strongly aligned and oriented molecular samples at a kHz repetition rate,” Mol. Phys. **111**, 1738 (2013); e-print arXiv:1301.1826 [physics].

[29] S. Trippel, T. Mullins, N. L. M. Müller, J. S. Kienitz, J. J. Omiste, H. Stapelfeldt, R. González-Férez, and J. Küpper, “Strongly driven quantum pendulum of the carbonyl sulfide molecule,” Phys. Rev. A **89**, 051401(R) (2014); e-print arXiv:1401.6897 [quant-ph].

[30] F. Rosca-Pruna and M. J. J. Vrakking, “Experimental observation of revival structures in picosecond laser-induced alignment of I_2,” Phys. Rev. Lett. **87**, 153902 (2001).

[31] An adiabatic response of the system to the laser field is provided if the time scales of the laser pulse are longer than the rotational period of the molecule. The impulsive regime is achieved if the pulse duration of the laser is much shorter than the rotational period of the molecule.

[32] F. Filsinger, J. Küpper, G. Meijer, L. Holmegaard, J. H. Nielsen, I. Nevo, J. L. Hansen, and H. Stapelfeldt, “Quantum-state selection, alignment, and orientation of large molecules using static electric and laser fields,” J. Chem. Phys. **131**, 064309 (2009); e-print arXiv:0903.5413 [physics].

[33] Y.-P. Chang, D. A. Horke, S. Trippel, and J. Küpper, “Spatially-controlled complex molecules and their applications,” Int. Rev. Phys. Chem. **34**, 557–590 (2015); e-print arXiv:1505.05632 [physics].

[34] L. Holmegaard, J. H. Nielsen, I. Nevo, H. Stapelfeldt, F. Filsinger, J. Küpper, and G. Meijer, “Laser-induced alignment and orientation of quantum-state-selected large molecules,” Phys. Rev. Lett. **102**, 023001 (2009); e-print arXiv:0810.2307 [physics].

[35] J. C. H. Spence and R. B. Doak, “Single molecule diffraction,” Phys. Rev. Lett. **92**, 198102 (2004).

[36] L. L. Connell, S. M. Ohline, P. W. Joireman, T. C. Corcoran, and P. M. Felker, “Rotational coherence spectroscopy of 1-naphthol-(water)$_2$ clusters: Structural evidence for a cyclic hydrogen-bonded trimer,” J. Chem. Phys. **94**, 4668 (1991).

[37] C. Riehn, “High-resolution pump-probe rotational coherence spectroscopy–rotational constants and structure of ground and electronically excited states of large molecular systems,” Chem. Phys. **283**, 297–329 (2002).

[38] G. Galinis, C. Cacho, R. T. Chapman, A. M. Ellis, M. Lewerenz, L. G. Mendoza Luna, R. S. Minns, M. Mladenović, A. Rouzée, E. Springate, I. C. E. Turcu, M. J. Watkins, and K. von Haeften, “Probing the structure and dynamics of molecular clusters using rotational wave packets,” Phys. Rev. Lett. **113**, 043004 (2014); e-print arXiv:1402.5401 [physics.atm-clus].

[39] U. Even, J. Jortner, D. Noy, N. Lavie, and N. Cossart-Magos, “Cooling of large molecules below 1 K and He clusters formation,” J. Chem. Phys. **112**, 8068–8071 (2000).

[40] S. Trippel, Y.-P. Chang, S. Stern, T. Mullins, L. Holmegaard, and J. Küpper, “Spatial separation of state- and size-selected neutral clusters,” Phys. Rev. A **86**, 033202 (2012); e-print arXiv:1208.4935 [physics].

[41] D. A. Horke, Y.-P. Chang, K. Długołęcki, and J. Küpper, “Separating para and ortho water,” Angew. Chem., Int. Ed. **53**, 11965–11968 (2014); e-print arXiv:1407.2056 [physics] .

[42] The two-dimensional degree of alignment is defined as $\langle\cos^2\theta_{2\mathrm{D}}\rangle = \int_0^{\pi}\int_0^{r_{\max}}\cos^2(\theta_{2\mathrm{D}})f(\theta_{2\mathrm{D}},r_{2D})\,dr_{2D}d\theta_{2\mathrm{D}}$. $f(\theta_{2\mathrm{D}},\ r_{2\mathrm{D}})$. The degree of alignment is extracted from the raw data by accepting only ion events in the integrals with transverse velocities within the specific velocity regions depicted in Fig. 2(a).

[43] L. Holmegaard, J. L. Hansen, L. Kalhøj, S. L. Kragh, H. Stapelfeldt, F. Filsinger, J. Küpper, G. Meijer, D. Dimitrovski, M. Abu-samha, C. P. J. Martiny, and L. B. Madsen, "Photoelectron angular distributions from strong-field ionization of oriented molecules," Nat. Phys. **6**, 428 (2010); e-print arXiv:1003.4634 [physics].

[44] V. Kumarappan, C. Z. Bisgaard, S. S. Viftrup, L. Holmegaard, and H. Stapelfeldt, "Role of rotational temperature in adiabatic molecular alignment," J. Chem. Phys. **125**, 194309 (2006).

[45] J. J. Larsen, K. Hald, N. Bjerre, H. Stapelfeldt, and T. Seideman, "Three dimensional alignment of molecules using elliptically polarized laser fields," Phys. Rev. Lett. **85**, 2470–2473 (2000).

[46] I. Nevo, L. Holmegaard, J. H. Nielsen, J. L. Hansen, H. Stapelfeldt, F. Filsinger, G. Meijer, and J. Küpper, "Laser-induced 3D alignment and orientation of quantum state-selected molecules," Phys. Chem. Chem. Phys. **11**, 9912–9918 (2009); e-print arXiv:0906.2971 [physics].

[47] T. Kjeldsen, C. Bisgaard, L. Madsen, and H. Stapelfeldt, "Influence of molecular symmetry on strong-field ionization: Studies on ethylene, benzene, fluorobenzene, and chlorofluorobenzene," Phys. Rev. A **71**, 013418 (2005).

[48] J. Maurer, D. Dimitrovski, L. Christensen, L. B. Madsen, and H. Stapelfeldt, "Molecular-frame 3D photoelectron momentum distributions by tomographic reconstruction," Phys. Rev. Lett. **109**, 123001 (2012).

[49] H. Lippert, V. Stert, L. Hesse, C. P. Schulz, I. V. Hertel, and W. Radloff, "Ultrafast photoinduced processes in indole–water clusters," Chem. Phys. Lett. **376**, 40–48 (2003).

[50] A. Peralta Conde, V. Ovejas, R. Montero, and F. Castaño, "Influence of solvation on the indole photophysics: Ultrafast dynamics of indole–water clusters," Chem. Phys. **530**, 25 (2012).