Analyzing laser-induced alignment of weakly-bound molecular aggregates

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The rotational and torsional dynamics of the prototypical floppy indole(H2O) molecular cluster was theoretically and computationally analyzed. The time-dependent Schrödinger equation was solved for a reduced-dimensionality description of the cluster, taking into account overall rotations and the internal rotation of the water moiety. Based on our results, it became clear that coupling between the internal and the overall rotations are small, and that for typical field strengths in alignment and mixed-field orientation experiments the rigid rotor approximation can be employed to describe the investigated dynamics. Furthermore, the parameter space over which this is valid and its boundaries where the coupling of the internal and overall rotation can no longer be neglected were explored.

I. INTRODUCTION

Biological function is strongly shaped by the intricate interaction of the molecules with their aqueous environment. Unraveling the underlying (bio)molecule-water solvation interactions as well as their relevance for chemical dynamics promises a detailed understanding of their contributions to function. Approaching this through studies of the elementary chemical processes as intrinsic properties in well-defined molecular aggregates enables the definition of fundamental building blocks as a dynamical basis of intermolecular solute-solvent interactions and their chemical dynamics. This rationalizes the longstanding history of detailed studies of molecule-solvent clusters in the gas phase [11,2].

Novel imaging techniques with highest spatiotemporal resolution, such as ultrafast x-ray [3,4] or electron diffraction [5,6], photoelectron imaging [7,9], and laser-induced electron diffraction [10] will provide a new level of detail to these investigations and promise to allow for the recording of molecular movies of the dynamical interactions. The applicability of these imaging methods to complex molecular systems relies on the preparation of pure samples [11,12] and benefits tremendously from fixing the molecules in space [11,13–15], i.e., to align or orient them [16–19]. Recently, some of us have demonstrated the preparation of pure beams of the prototypical indole-water dimer cluster as well as its laser alignment [20,22].

However, it is not clear in how far the very floppy structure of weakly bound molecular clusters modifies or hinders the control techniques, especially regarding alignment with strong laser fields. It is well understood that internal rotation, or torsions, and overall rotation are coupled [22] and that internal rotations can also be controlled with the same strong laser fields [23]. So far, experimental and theoretical studies were limited to highly symmetric molecular systems [24,28], e.g., with C16 symmetry, such as biphenyl. It is a priori not clear how these effects will transfer to complex “real world” (bio)molecules and their complexes.

Here, we set out to analyze the laser alignment, and the corresponding influence of internal rotations to the overall rotational dynamics, of molecule-solvent systems, which, generally, have lower symmetries and asymmetric shapes of the constituents. Specifically, we start these investigations with a theoretical analysis of the laser alignment of the prototypical indole-water dimer systems [29,32], which we treat as a semi-rigid rotor with an additional one-dimensional internal rotation coordinate corresponding to the rotation of the water moiety about its b-axis; see Fig. 1.

We utilize a reduced-mode variational approach based on the general-molecule variational approach [33–35] combined with a general treatment of electric fields [36].

II. THEORY AND COMPUTATIONAL SETUP

The model structure of indole(H2O) that is employed in this work is schematically shown in Fig. 1. The water molecule is attached to the planar indole frame via a hydrogen bond where the oxygen atom of the water molecule lies in the indole planer. We treat the indole(H2O) cluster as a floppy molecule with the water molecule undergoing an internal rotation. The angle of internal rotation \( \tau \) is defined as the dihedral angle between the indole and the water planes, see Fig. 1, with \( \tau = 90^\circ \) in the equilibrium configuration [29]. We keep all other vibrational coordinates fixed at their equilibrium values along the minimum energy path (MEP) of the internal rotation. The MEP is determined by optimizing the structural parameters of indole(H2O) complex at different values of the \( \tau \) coordinate between 0° and 360°.

We assume the Born-Oppenheimer approximation and consider four degrees of freedom, three Euler angles (\( \phi, \theta, \))
\( \chi \) describing the overall rotation of the system and the angle \( \tau \) associated with the internal rotation of the water molecule. The field-free Hamiltonian of the system is

\[
H_0 = \frac{1}{2} \sum_{\alpha,\beta=x,y,z} \hat{J}_\alpha G^\text{rot}_{\alpha\beta}(\tau) \hat{J}_\beta + \frac{1}{2} p_\tau G^\text{rot}_{\text{tor}}(\tau) p_\tau + V(\tau),
\]

where \( \hat{J}_\alpha \) are components of the rotational angular momentum operator in the molecule-fixed frame and \( p_\tau = -i\hbar \partial / \partial \tau \). The kinetic energy matrices \( G^\text{rot}(\tau) \) and \( G^\text{rot}_{\alpha\beta}(\tau) \) are associated with the internal torsional and overall rotational motions, \( G^\text{rot}_{\text{tor}}(\tau) \) describes coupling between the two motions, and \( V \) is the potential energy function. The elements of the kinetic energy matrices are calculated as functions of the torsional coordinate \( \tau \) following the generalized procedure from TROVE \cite{35, 37}.

The kinetic energy matrices and potential energy function in \cite{2} were built along the MEP. The geometry optimizations were carried out using the density-fitted second-order Møller-Plesset perturbation theory DF-MP2 in the frozen-core approximation, in conjunction with the augmented correlation-consistent basis set aug-cc-pVTZ \cite{38, 39}. For the density fitting approximation we utilized the JKFIT \cite{40} and MP2FIT \cite{41} auxiliary basis sets specifically matched to aug-cc-pVTZ. All electronic structure calculations were carried out using Psi4 \cite{42}.

The \textit{ab initio} potential energy surface (PES) is represented by an analytical function by fitting the expression

\[
V(\tau) = \sum_{n=0}^{2} V_{2n} \cos(2n\tau) \, .
\]

The PES is depicted in Fig. 2(a) and the coefficients are \( V_0 = -101.950 \text{ cm}^{-1} \), \( V_2 = 106.006 \text{ cm}^{-1} \) and \( V_4 = -3.58143 \text{ cm}^{-1} \), in good agreement with the experimental value for this motion of \( V_2 = 99 \text{ cm}^{-1} \) \cite{29}. The structural parameters are represented by similar analytical functions; see the Supplemental Material \cite{43} for the \textit{ab initio} results of the EDM and polarizability, the analytical expressions and coefficients for the internal coordinates, EDM and polarizability, as well as the symmetry properties of indole(H\textsubscript{2}O) in the presence of external electric fields \cite{13}.

Our analysis is restricted to a non-resonant linearly-polarized laser ac electric field combined with a parallel weak dc electric field. The interaction of the polarizability with the weak dc field is neglected. In addition, we can average over the rapid oscillations of the non-resonant ac field and the interaction of the electric dipole moment with the laser field vanishes. The interaction of the molecule with the external electric fields then reads

\[
H_{\text{int}}(t) = -\mu(\tau) \cdot E_{\text{stat}} - \frac{1}{4} E_{\text{laser}}(t) \alpha(\tau) E_{\text{laser}}(t) \, ,
\]

where \( E_{\text{stat}} \) is the static electric field and \( E_{\text{laser}}(t) \) is the envelope of the laser electric field. The electric dipole moment (EDM) \( \mu(\tau) \) and the polarizability tensor \( \alpha(\tau) \) of indole(H\textsubscript{2}O) are calculated along the minimum energy path created by varying the \( \tau \) coordinate. They are represented by analytical functions similar to the ones used for the PES, see Supplemental Material \cite{13}. The polarization axis of the laser is chosen as the Z-axis of the
laboratory fixed frame (LFF). The molecule fixed frame \((x, y, z)\) is defined by the principle axes of polarizability at the equilibrium configuration so that the diagonal elements fulfill \(\alpha_{xx} < \alpha_{yy} < \alpha_{zz}\).

To study the rotational dynamics of indole\((\text{H}_2\text{O})\), we solve the time-dependent Schrödinger equation (TDSE) for the full Hamiltonian

\[
H(t) = H_0 + H_{\text{int}}(t),
\]

using the short interative Lanczos method \cite{44, 45} for the time-propagation and a basis set expansion for the spatial coordinates using the eigenstates of the field-free Hamiltonian \cite{2}. The field-free eigenbasis is calculated variationally in several steps. First, the pure rotational and torsional basis functions, \(\Psi_{i}^{\text{rot}}(\phi, \theta, \chi)\) and \(\Psi_{j}^{\text{tor}}(\tau)\), are constructed by diagonalizing the respective parts of the field-free Hamiltonian \cite{2}. In this step, we use Wang states \cite{16}, i.e., symmetrized combinations of symmetric-top functions, as a basis set for the rotational coordinates. For the torsional coordinates, we use sine and cosine functions \(\phi_{n}^{\text{even}}(\tau) = \cos(n\tau)/\sqrt{\pi}\) and \(\phi_{n}^{\text{odd}}(\tau) = \sin(n\tau)/\sqrt{\pi}\), \(n > 0\) and \(\phi_{0}^{\text{even}}(\tau) = 1/\sqrt{2\pi}\) to preserve the even and odd symmetry of states. The matrix elements of the full Hamiltonian \cite{41} are then set up in the product basis \(\Psi_{i}^{\text{rot}}(\phi, \theta, \chi)\Psi_{j}^{\text{tor}}(\tau)\) and transformed to the eigenbasis of the complete field-free Hamiltonian \cite{2} following the generalized approach developed in richmol \cite{39}.

To analyze the importance of the internal motion of the water molecule, we compare our results to calculations using the rigid rotor approximation \cite{17}, i.e., considering only the three degrees of freedom of the overall rotation in \cite{2}. For the rigid rotor calculations, we use the structural parameters, EDM and polarizability tensor at the equilibrium configuration, i.e., \(\tau = 90^\circ\).

### III. RESULTS AND DISCUSSION

In this section, we analyze the overall rotational and torsional dynamics of indole\((\text{H}_2\text{O})\). We solve the TDSE using the field-free ground state as the initial state of the time-propagation, i.e., \(T = 0\) K. For the laser pulse, we consider a Gaussian envelope \(E_{\text{total}}(t) = \bar{E}E_0 \exp(-4\ln2t^2/\bar{\tau}^2_{\text{FWHM}})\) with \(E_0 = 2.74 \times 10^7\) V/cm and \(\bar{\tau}_{\text{FWHM}} = 1\) ns. The parallel static electric field is increased to a field strength of \(E_{\text{total}} = 600\) V/cm slowly enough to ensure adiabatic behavior before the laser field is applied. We analyze the alignment and mixed-field orientation dynamics of indole\((\text{H}_2\text{O})\), quantified by the expectation values \(\langle \cos^2\theta \rangle\) and \(\langle \cos\theta \rangle\), respectively, as well as the torsional alignment \(\langle \cos^2\tau \rangle\).

**Fig. 3 (a) and (b)** show the time evolution of the alignment and orientation of the ground state of indole\((\text{H}_2\text{O})\) obtained using the non-rigid rotational-torsional Hamiltonian (blue lines) as well as the results using the rigid rotor approximation (red lines). As the laser field strength rises, the most polarizable axis (MPA) becomes strongly aligned along the polarization axis of the laser, reaching \(\langle \cos^2\theta \rangle = 0.98\) at the peak intensity. For both, the rigid and the non-rigid models, we observe a typical mixed-field orientation dynamics that has previously been described for other linear and asymmetric top molecules \cite{48–51}. Due to the presence of the static electric field, the orientation increases as laser-aligned pendular states are formed and increasingly coupled with increasing laser field strength. The orientation at the peak intensity, \(\langle \cos\theta \rangle = 0.82\), is lower than the value obtained in the adiabatic description, \(\langle \cos\theta \rangle = 0.99\), indicating a non-adiabatic dynamics, i.e., several field-dressed eigenstates of the instantaneous Hamiltonian \cite{4} contribute to the time-dependent wave function \cite{17, 52, 53}.
We point out that the results obtained for the rigid and non-rigid descriptions are practically indentical, which shows that the indole(H₂O) cluster can be treated as a rigid molecule for moderate electric field strengths that are typically employed in molecular alignment and mixed-field orientation experiments. To understand why the internal rotation of the water molecule does not influence the overall rotational dynamics, we look at the coupling between the internal and overall rotations and the resulting rotation-torsional energy levels. In the field-free case, the coupling of the two motions is described by the Coriolis-type coupling and the dependence of the kinetic energy matrix $G_{\alpha\beta}^{rot}(\tau)$ on the torsional angle $\tau$ in [2]. Since this field-free coupling is very small [29], the eigenstates of the Hamiltonian [2] are approximately described by the product states $\Psi_{\phi,\chi}^{tor}(\phi, \theta, \chi)\Psi_{m}^{rot}(\tau)$, and the energy levels are given by the sum of the pure rotational and torsional energies, even for large values of the quantum number $J$. Due to tunneling, each torsional level splits into two sublevels, denoted by $\sigma = 0, 1$ in Fig. 2 (a). The energy difference between two consecutive torsional states is three orders of magnitude larger than the energy gaps between pure rotational states. As a result, the rotation-torsion energy levels are distributed as bands of rotational states for each torsional sublevel, see Fig. 2 (b).

In the presence of an external electric field, the internal and overall rotations are additionally coupled due to the dependence of the EDM and the polarizability on the torsional angle, see [3], which is weak for indole(H₂O). Thus, for the ac and dc field strengths considered here, the field-induced coupling between the torsional ground and first excited state $\langle \Psi_{\phi,\chi}^{tor} | H_{int} | \Psi_{m}^{rot} \rangle$, where $v = 0, 1$ indicates the torsional ground and excited state, respectively, is small ($< 1 \text{ cm}^{-1}$) compared to the energy gap $\Delta E \approx 98 \text{ cm}^{-1}$ between these torsional levels. Due to the symmetry of the EDM and the polarizability, the two sublevels $\sigma = 0, 1$ of a torsional state are not coupled by the external electric fields, see Section IV in the Supplemental Material [43]. As a consequence, the field-dressed rotational-torsional wavepacket is dominated by the torsional ground state. The torsional alignment shown in Fig. 3 (c) (blue lines) thus remains constant with $\langle \cos^2 \tau \rangle = 0.126$. To achieve a field-induced coupling that is strong enough to overcome the energy gap between the torsional ground and first excited state, laser field strengths larger than $E_0 \approx 10^3 \text{ V/cm}$, i.e., intensities $I_{\text{control}} > 10^{13} \text{ W/cm}^2$, would be necessary. Such fields would, however, affect the electronic structure and induce ionization of indole(H₂O) and are generally not used to control the rotational dynamics of these clusters [22].

In the following, we investigate for which regimes of field-free and field-induced couplings the rigid rotor approximation can still be applied to describe the rotational dynamics. To obtain a large field-induced coupling, stronger external ac and dc electric fields could be applied or the dependence of the EDM and the polarizability on the torsional angle $\tau$ could be, artificially, increased. We begin by studying a molecular cluster that has a modified polarizability $\tilde{\alpha}(\tau)$ and is otherwise identical to indole(H₂O). Since the interaction with the weak static electric field is much weaker than the one with the laser field, we do not modify the EDM. We set $\tilde{\alpha}_{pq}(\tau)$ including only terms with $n \leq 1$ and with the coefficients listed in Table V in the Supplemental Material [43]. The coefficients $\tilde{\alpha}_{pq}^{(2)}$ are chosen to be 200 times larger than the largest ones obtained from fits to the ab initio results. The chosen $\tilde{\alpha}_{pq}^{(2)}$ satisfy $\tilde{\alpha}(\tau = 90°) = \alpha(\tau = 90°)$. This polarizability increases the field-induced coupling by a similar magnitude as increasing the laser field strength by a factor of $\sqrt{200}$. We carry out an additional rigid rotor calculation using the structural parameters and EDM at the equilibrium configuration, but the expectation values $\langle \tilde{\alpha}_{pq} \rangle = \langle \Psi_{\phi,\chi}^{tor} | \tilde{\alpha}_{pq}(\tau) | \Psi_{\phi,\chi}^{tor} \rangle$ in the torsional ground state as these values differ significantly from $\tilde{\alpha}_{pq}(\tau = 90°)$. We point out that the expectation value of the modified polarizability is not diagonal in the chosen MFF, i.e., the MPA of the modified polarizability is not parallel to the MFF $z$-axis.

The results for this enhanced-response molecular system are depicted in Fig. 3 for the non-rigid (black lines) and rigid rotor cases (green lines). At lower laser field strengths, the alignment does not differ from the results obtained using the rigid-rotor approximation. Close to the peak intensity, the alignment starts to decrease and reaches a value of $\langle \cos^2 \theta \rangle = 0.965$, slightly smaller than the rigid rotor result $\langle \cos^2 \theta \rangle = 0.972$. Simultaneously, the orientation starts to differ slightly from the rigid rotor result, reaching a smaller value at the peak intensity. Regarding the torsional alignment, we observe an increase of $\langle \cos^2 \tau \rangle$ with increasing laser field strength, due to the contribution of excited torsional states, in particular the second excited state $\sigma = 2, \tau = 0$. The reason for this is that due to the symmetry of the polarizability, the coupling between the field-free rotation-torsional states with different torsional symmetry is small [23, 24], see the Supplemental Material [43]. The difference between the non-rigid and the rigid rotor description can be understood in terms of the effective polarizability $\langle \Psi_{\phi,\chi}^{rot} | \tilde{\alpha}(\tau) | \Psi_{\phi,\chi}^{rot} \rangle$ of the torsional states. For weak laser fields, excited torsional states are not involved in the dynamics. As a consequence, the alignment and orientation evolve in a similar way as for the rigid indole(H₂O). The torsional ground state wave function is localized around $\tau = 90°$ yielding a polarizability with small off-diagonal elements $\tilde{\alpha}_{13}(\tau = 90°) = 5.2 \text{ a.u.}$. At stronger laser fields, the contributions of excited torsional states modify the polarizability, with $\tilde{\alpha}_{13}(\tau = 90°) = 23.5 \text{ a.u.}$ at the peak intensity. As a result, a different molecular axis is aligned compared to the rigid rotor case, and $\langle \cos^2 \theta \rangle$ decreases. In addition to the change in the MPA, the anisotropy of the polarizability increases with increasing laser field strength. The alignment of the MPA $\langle \cos^2 \theta_{\text{MPA}} \rangle$, where $\theta_{\text{MPA}}$ is the angle between the MPA and the LFF $z$-axis, is thus larger at the peak intensity than for the rigid rotor case. As a result of the change in the MPA, the orientation $\langle \cos \theta \rangle$...
Additionally modifying the EDM in an analogous way results in different effective dipole moments (µ) and a correspondingly changed degree of orientation compared to the rigid-rotor result. However, since the interaction of the dc electric field with the dipole moment is comparably weak, no additional excitation of torsional states occurs. Increasing the laser field strength by the corresponding factor of \( \sqrt{200} \) does not have the same impact on the rotational dynamics as the modified polarizability. While a stronger laser field leads to contributions of excited torsional states, the expectation value of the polarizability in these excited states does not differ much from the one in the torsional ground state. Thus, no significant change of the MPA or polarizability anisotropy occurs. Calculations performed for a laser field strength of \( E_0 = 3 \times 10^8 \) V/cm and \( E_{\text{stat}} = 0 \) show a small increase in \( \langle \cos^2 \tau \rangle \) during the laser pulse, but no difference in the overall alignment \( \langle \cos^2 \theta \rangle \) between the rigid and non-rigid descriptions. Increasing the laser field strength further was computationally too expensive.

In addition to analyzing the impact of a strong field-induced coupling, we investigate the influence of the barrier height. This affects the torsional energy level structure \( \omega \) and may thus alter the field-dressed coupling necessary to achieve an excitation of the torsion in the presence of external fields. To this end, we use a modified torsional potential \( V(\tau) = V_0(\cos(2\tau) - 1) \) with a very small barrier height \( V_0 = 1.0 \) cm\(^{-1} \). Using the same field parameters as in Fig. 3 and the \textit{ab initio} polarizability, we observe an overall rotational dynamics that is very similar to the dynamics obtained using the \textit{ab initio} torsional potential. The reason for this is that by lowering the barrier height the energy gap between the torsional ground and second excited level is only decreased to \( \Delta E \approx 55 \) cm\(^{-1} \), which is still large compared to the coupling induced by the external electric fields. Finally, we consider molecules with an internal rotor that has a smaller rotational constant. For a modified molecular system increasing the laser field strength further was computationally too expensive.

We investigate the rotational dynamics of a floppy molecule in combined laser and static electric fields. Our work is focused on the prototypical indole(H\(_2\)O) cluster where the attached water molecule undergoes an internal rotation. The molecular structure, electric dipole moment and polarizability are calculated with \textit{ab initio} methods. We solve the time-dependent Schrödinger equation for a moderate laser field strength and a weak dc electric field taking into account four degrees of freedom for the internal and overall rotation. We compare the obtained alignment and orientation dynamics to results computed within the rigid rotor approximation. We demonstrate that indole(H\(_2\)O) can be treated as a rigid molecule in typical alignment and mixed-field orientation experiments. This conclusion is rationalized by the weak field-free and field-induced couplings of the internal and overall motions compared to the respective energy spacings. We explore regimes of laser-field strengths for which the internal rotation of the water moiety can no longer be neglected. However, such strong laser pulses, \( I_{\text{control}} > 10^{13} \) W/cm\(^2\), are not likely to be used in alignment experiments as they would result in electronic excitation and ionization. Let us remark that even at a rotational temperature of \( T = 0 \) K, both torsional sublevels \( \sigma = 0, 1 \) of the rotational ground state would be populated in a molecular beam according to their nuclear spin statistical weights. However, as the rotational and torsional dynamics of these two sublevels in the presence of the ac and dc fields do not differ significantly, our analysis of the \( \sigma = 0 \) sublevel provides a good description of the overall rotational dynamics in the external fields.

We analyze the influence of a larger field-induced coupling on the overall and internal rotational dynamics by using artificially modified electric dipole moment and polarizability with a two orders of magnitude stronger dependence on the torsional angle. We find a decrease of the overall alignment and orientation close to the peak intensity due to an effective change in the MPA in the excited torsional state. In addition, we observe an increase of the torsional alignment with increasing laser field strength caused by the contributions of excited torsional states. In contrast, for unmodified indole(H\(_2\)O), a constant torsional alignment is found.

Based on these results for indole(H\(_2\)O), we conclude that similar molecular clusters can also be treated as rigid molecules. This conclusion can also be extended to other floppy molecular systems provided their dipole moment and polarizability depends only weakly on the internal motion and their rotational and torsional energy levels are approximately given by the sum of pure rotational and torsional energies with large gaps between consecutive torsional levels. For molecules with a small torsional barrier or a smaller internal rotational constant, \( e.g. \), for previously studied biphenyl-type molecules, a weaker field induced coupling may be necessary to achieve contributions of excited torsional states to the field-dressed dynam-
ics. However, the rigid rotor approximation can still be employed for moderate laser fields strengths. This is different than for previously studied biphenyl-type molecules, with their axis of internal rotation parallel to a principle axis of inertia and their MPA not modified by the torsion, which results in a qualitatively different coupled rotational and torsional dynamics than for generic low-symmetry molecular clusters, such as indole(H$_2$O). To achieve an accurate description of the rotational dynamics for molecules with small energy gaps between the torsional ground and excited states, the coupling of the internal and overall rotations cannot be neglected. Furthermore, for impulsive alignment even the small coupling between the internal and overall rotation in indole(H$_2$O) becomes important on longer, e.g., nanosecond, timescales.

The variational approach applied in this work allows to extend our study to include multiple internal modes in a multi-dimensional PES and to study their effect on the field-dressed rotational dynamics, which will be investigated in the future.

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