

Orientation of adsorbed dipolar molecules: A conical well model

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Orientation of single and two coupled polar molecules irradiated by a single laser pulse under a conical-well model is investigated theoretically. The orientation of a single hindered rotor shows a periodic behavior. In particular, the amplitude of the oscillation is sensitive to the degree of alternation of the laser field. Crossover from field-free to hindered rotation is observed by varying the hindering angle for different heights of conical wells. For a small hindering potential and angle, time-averaged orientation differs greatly from that for an infinite one. The orientation at a large hindering angle shows irregularlike behavior under strong dipole-dipole interaction. Entanglement induced by the dipole-dipole interaction is also calculated for the coupled-rotor system, in which the time-averaged entropy increases monotonically as the hindering angle is increased. The competition between the confinement effect and dipole interaction is found to dominate the behavior of the coupled-rotor system.

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Controlling the orientation of molecules has wide applications from stereodynamics to surface catalysis, molecular focusing, and nanoscale design.¹ The molecular alignment is responsible for the anisotropic polarizability induced by the nonresonant laser pulses. For adiabatic regime, the crucial characteristic is that the duration of the laser pulse is longer than the rotational period. The pendular states can be created adiabatically, and the molecular axis is aligned parallel to the direction of the field polarization. As the laser pulse is switched off, the molecule will go back to its initial condition and no longer be observed again.^{2,3} If the duration of the laser pulse is shorter than the rotational period, the alignment occurs periodically in time, i.e., the nonadiabatic regime.^{4,5} On the other hand, a field-free orientation can be generated by a femtosecond laser pulse.^{6,7} The dipole molecule will tend to orient by applying a highly asymmetrical pulse. It is found that a pronounced orientation can still persist after switching off of the pulse.

In addition to the rotation of a free rotor, the rotational motion of molecules adsorbed on a solid surface has attracted increasing interest. To understand the rotational behavior of adsorbed molecules, one can apply the UV laser beam along the surface direction to desorb the molecules. The rotational states can be determined by the quadrupole, which is a measure of the rotational alignment.⁸⁻¹⁰ On the theoretical side, an infinite-conical-well model has been proposed. It was found that the adsorbed molecule is only allowed to rotate within the well region.¹¹ In our earlier works, we have generalized the infinite-well model to a more realistic case of finite-conical well.^{12,13} It was found that there exists the avoided crossing between two adjacent rotational energies when varying the strength of the external field. Our theoretical calculation of the quadrupole moment based on the finite-conical-well model is in agreement with the experimental data.¹⁴

Recently, great attention has been focused on the coupled-rotor system since peculiar behaviors may occur in the presence of dipole-dipole interaction.¹⁵⁻¹⁷ For example, recent neutron scattering experiments on certain Hofmann clathrates have reported the temperature-dependent behavior of

the linewidths.¹⁸ A line broadening mechanism based on rotor-rotor coupling was proposed for the explanation of the widths.¹⁹ With the advances of nanotechnology, one can now investigate the quantum rotors which are mounted on the surfaces.^{20,21} From the laser spectroscopy, two individual fluorescent molecules separated by several nanometers can be resolved on the surface.²² The coherent interactions between the dipole moments associated with their optical transitions are found in the quantum optical measurements. The strong dipole-dipole coupling produces entangled subradiant and superradiant states in the two-molecule-system under laser radiation.

Even though the orientation of the free molecule is well studied, investigations on the rotation of the adsorbed molecule confined the surface potential are still lacking.²³ In the complex surface system, the adsorbed molecules are no longer isolated. Several studies have shown that interesting phenomena can occur due to the existence of dipole-dipole interaction. Besides, although the entangled behavior of two coupled rotors was also investigated recently, these works are limited in the model of kicked tops.^{24,25} However, the dynamical entanglement via the rotations of the adsorbed molecules remains mostly unexplored. In particular, a molecular system evolves from a nonentangled case to an entangled one. According to our previous study,¹⁷ it is found that the orientations of the coupled rotors relate closely to the entropy. This means that the orientations of the coupled rotors somehow reflect the entropy of the system and thus relates to the measurement of the entanglement. Since the measurement of the entanglement is one of the fundamental important issues in quantum information research, therefore, the study of the entanglement and its measurement is one of the interested problems. Moreover, from the experimental point of view, it is not clear how to keep two free rotors with a fixed distance. Therefore, this makes it more interesting to consider a more realistic system and discuss the corresponding entanglement dynamics.

In this paper, we first investigate the rotational motions of a polar diatomic molecule confined by a hindering conical well. After applying a single strong laser pulse, the hindered

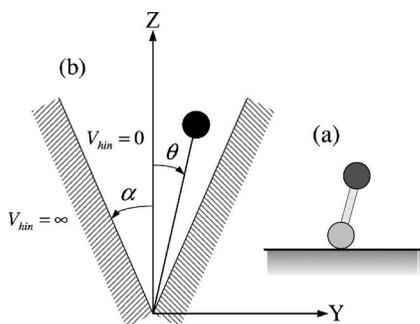


FIG. 1. (a) Schematic view of a single hindered rotor adsorbed on the surface. (b) The corresponding infinite-conical-well model.

rotor shows a periodic behavior. Different signatures between the finite-conical-well and infinite-conical-well model on orientations are pointed out. Besides, the amplitudes of the oscillations are varied by applying different widths of the pulse. Furthermore, we also consider two coupled identical polar molecules adsorbed on the surface with the dipole-dipole interaction and a simultaneously ultrashort laser pulse shined upon them. It is found that both the entanglement (the von Neumann entropy) and orientation show interesting behaviors.

Consider now a dipolar molecule (e.g., NaI) adsorbed on the surface. The rotation of the molecule is confined by the surface potential as shown in Fig. 1. An off-resonant laser field polarized in the z direction interacts with the hindered rotor. Because the laser frequency is much lower than the frequencies of the lowest vibrational and electronic transition, only the rotational excitations can occur in our model. The excitations can be viewed as two photon transitions between two different rotational states through a high intermediate virtual state.⁵ The Hamiltonian without the field-molecule interaction can be written as

$$H_0 = BJ^2 + V_{hin}(\theta, \phi), \quad (1)$$

where B and J^2 are the rotational constant and angular momentum. V_{hin} denotes the surface potential and confines the rotation of adsorbed molecule. For simplicity, the infinite-conical-well model $V_{hin}(\theta, \phi)$ is considered here. According to the previous studies, its dependence on ϕ is weaker than that on θ .^{26–28} We reasonably assume that the surface potential is independent of ϕ . Therefore, in the vertical adsorbed configuration, the surface potential can be written as¹¹

$$V_{hin}(\theta) = \begin{cases} 0, & 0 \leq \theta \leq \alpha \\ \infty, & \alpha < \theta \leq \pi \end{cases}, \quad (2)$$

where α is the hindering angle of the conical well.

The Hamiltonian concerning the field-molecule interaction can be written as

$$H_d = -\mu E(t) \cos \theta, \quad (3)$$

$$H_{ind} = -\frac{1}{2} E^2(t) [(\alpha_{\parallel} - \alpha_{\perp}) \cos^2 \theta + \alpha_{\perp}]. \quad (4)$$

The first term H_d describes a permanent dipole moment μ coupling with an external field, and θ is the angle

between the molecular axis and the field. In this work we choose a Gaussian pulse for our calculation, i.e., $E(t) = E_0 e^{-(t-t_0)^2/\sigma^2} \cos(2\pi\nu t)$, where E_0 is the field strength and ν is the laser frequency. The pulse is centered at the time t_0 , and σ is the pulse duration. The second term H_{ind} is a higher order interaction, in which the external field couples with the induced molecular polarization. The component of the polarizability $\alpha_{\parallel}(\alpha_{\perp})$ is parallel (perpendicular) to the molecular axis. According to our parameters, the field-dipole-moment interaction H_d is much greater than that of the field-induced-dipole-moment interaction H_{ind} in our model. This is because the strength of electric field used here is insufficient to enhance the higher order term. Actually the interaction H_{ind} can play an important role in the case of high strength of electric field.⁵ Therefore, the term (H_{ind}) can be neglected reasonably based on our parameters.

Before solving the time-dependent Schrödinger equation ($H_0 + H_d$), the eigenfunctions of the system [$H_0 = BJ^2 + V_{hin}(\theta)$] must be introduced first. Following Ref. 11, the eigenfunctions can be written as

$$\psi_{lm}(\theta, \phi) = \begin{cases} A_{lm} P_{\nu_{lm}}^{lm}(\cos \theta) \frac{\exp(im\phi)}{\sqrt{2\pi}}, & 0 \leq \theta \leq \alpha \\ 0, & \alpha < \theta \leq \pi \end{cases}, \quad (5)$$

where A_{lm} is the normalization constant and $P_{\nu_{lm}}^{lm}$ is the associated Legendre function of arbitrary order with the corresponding quantum number (l, m). In the above equations, the molecular rotational energy can be expressed as

$$\epsilon_{lm} = \nu_{lm}(\nu_{lm} + 1)B. \quad (6)$$

In order to determine ν_{lm} , one has to match the boundary condition

$$P_{\nu_{lm}}^{lm}(\cos \alpha) = 0. \quad (7)$$

To solve the time-dependent Schrödinger equation, the wave function is expressed in terms of a series of eigenfunctions

$$\Psi(t) = \sum_l c_{lm}(t) \psi_{lm}(\theta, \phi), \quad (8)$$

where $c_{lm}(t)$ is the time-dependent coefficient. The coefficient $c_{lm}(t)$ can be obtained from the different equations

$$i\hbar \dot{c}_{lm}(t) = c_{lm}(t) \epsilon_{lm} + \sum_{l'm'} c_{l'm'}(t) \langle \psi_{lm} | H_d | \psi_{l'm'} \rangle. \quad (9)$$

After determining the coefficients $c_{lm}(t)$, the orientation $\langle \cos \theta \rangle$ can be carried out immediately. We choose NaI as our model molecule, whose dipole moment $\mu = 9.2$ D and rotational constant $B = 0.12$ cm⁻¹. For simplicity (zero-temperature case), the rotor is assumed in the ground state initially, i.e., $c_{00}(t=0) = 1$. The field strength is 3×10^7 V/m and the laser frequency is about 9×10^{11} s⁻¹. The duration and center of the pulse are set equal to 279 and 1200 fs. The main feature is that the ratio in magnitude of the positive and negative peak value of this pulse is 5:1. Unless specified, the parameters of laser field are fixed throughout the paper.

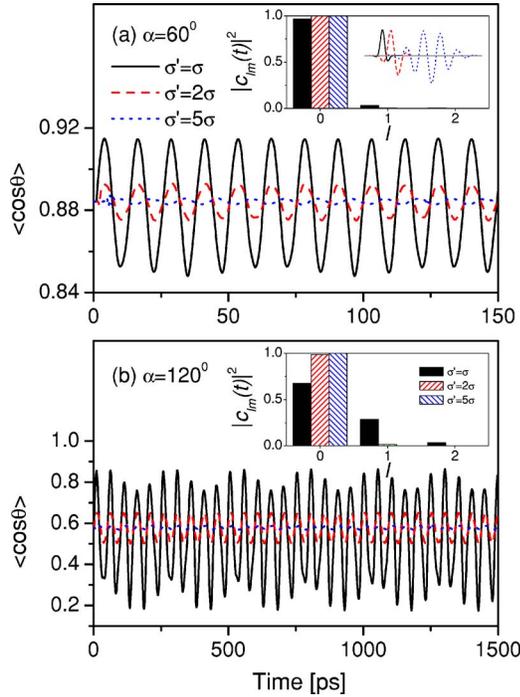


FIG. 2. (Color online) The orientation $\langle \cos \theta \rangle$ as a function of time for different hindering angle α and pulse duration σ' . The insets show the corresponding populations of the states ($l, m=0$) for (a) $\alpha=60^\circ$ and (b) $\alpha=120^\circ$, respectively. The corresponding laser fields are shown in the upper inset.

Figure 2 illustrates the orientation $\langle \cos \theta \rangle$ as a function of time for different hindering angles and pulse durations. In both cases, the orientations display periodiclike behavior. For the pulse duration ($\sigma' = \sigma$), the orientation of small hindering angle ($\alpha=60^\circ$) shows a relative large value but with small oscillatory amplitude, while for $\alpha=120^\circ$ a large oscillatory amplitude with multifrequency (insets of Fig. 2) is obtained. Obviously, such a difference comes from the quantum confinement effect. We further apply the laser pulses with different widths by tuning the duration and center. If the pulse duration increases, the amplitudes of the oscillations decrease and the orientations approach the initial value as shown in the insets. The reason is that the mean orientation is suppressed by the alternations of the electromagnetic field, i.e., the cancellation of negative and positive orientations.

To see more clearly the effect of the hindering potential, let us now consider the finite potential model

$$V_{hin}(\theta) = \begin{cases} 0, & 0 \leq \theta \leq \alpha \\ V_0, & \alpha < \theta \leq \pi \end{cases} \quad (10)$$

where V_0 is the height of well. Following Refs. 12–14, the rotational energy and eigenfunctions can be determined by matching appropriate boundary condition. Figure 3 shows the time-averaged orientation as a function of time for different hindering potentials. For infinite potential ($V_0=\infty$), the time-averaged orientation decreases monotonically from 1 to 0 as the hindering angle is increased. However, if the well is finite, the time-averaged orientation has a maximum point at certain angle. This means if the open angle α decreases fur-

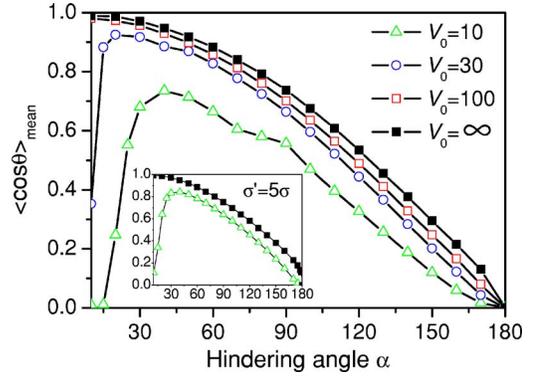


FIG. 3. (Color online) The mean orientation $\langle \cos \theta \rangle_{mean}$ as a function of hindering angle for fixed pulse duration ($\sigma' = \sigma$) and different conical-well potentials $V_0=10, 30, 100$. The inset shows the mean orientation $\langle \cos \theta \rangle_{mean}$ in the case of $V_0=10$ and ∞ by applying a pulse of $\sigma' = 5\sigma$. The potential V_0 is in units of the rotational constant B .

ther, the contribution from the penetrated wave function overwhelms the impenetrable one, rendering the decreasing of the time-averaged orientation. We also compare the case of $\sigma' = \sigma$ with that of $\sigma' = 5\sigma$ (inset of Fig. 3). It is found that, for larger duration $\sigma' = 5\sigma$, although the oscillatory amplitude is smaller (Fig. 2), the value of time-averaged orientation is larger comparing to the case of $\sigma' = \sigma$.

As we mentioned above, the spatial resolution of two individual molecules hindered on a surface in tens of nanometers is now possible.^{20–22} We further consider that two identical dipolar molecules (separated by a distance of R , R is in an order of magnitude of 10^{-8} m) confined by the hindering wells. The molecules are assumed to interact with each other via dipole-dipole interaction only. A polarized laser pulse is applied to interact with both molecules. The Hamiltonian of the coupled system can be written as

$$H_c = \sum_{j=1,2} H_{0,j} + U_{dip} + H_I, \quad (11)$$

where $H_{0,j}$ is the Hamiltonian of single hindered rotor without the laser-dipole interaction. The dipole interaction between two dipole moments μ_1 and μ_2 is

$$\begin{aligned} U_{dip} &= [\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \hat{e}_R)(\vec{\mu}_2 \cdot \hat{e}_R)]/R^3 \\ &= \mu_1 \mu_2 (\sin \theta_1 \cos \phi_1 \sin \theta_2 \cos \phi_2 + \cos \theta_1 \cos \theta_2 \\ &\quad - 2 \sin \theta_1 \sin \phi_1 \sin \theta_2 \sin \phi_2)/R^3, \end{aligned} \quad (12)$$

where $\hat{e}_R (= \vec{R}/R)$ is assumed to be in the y direction, and (θ_1, ϕ_1) and (θ_2, ϕ_2) are the coordinates of first and second molecule, respectively. For simplicity, we assume the dipole moments of two molecules are identical, i.e., $\mu_1 = \mu_2 = \mu$. One might argue that the higher order terms may also contribute to the results. According to previous study,¹⁵ the next higher order term is about the order of r^3/R^4 with bond length r . If one compares the dipole-dipole interaction, $[O(r^2/R^3)]$, with the next higher order effect [the bond length $r=2.7 \text{ \AA}$ (Ref. 29) and separation $R=15 \text{ nm}$], it is found that the contribution from the next higher-order term is only 2%

of the dipole-dipole interaction. Therefore, it is reasonable to include only the dipole interaction in our model. The field-molecule coupling H_I can then be expressed as

$$H_I = -\mu E(t) \cos \theta_1 \cos(\omega t) - \mu E(t) \cos \theta_2 \cos(\omega t), \quad (13)$$

where θ_1 and θ_2 are the angles between dipole moments and laser field. In the above equations, the time-dependent Schrödinger equation can be solved by expanding the wave function in terms of a series of eigenfunctions

$$\Psi_c = \sum_{l_1 m_1 l_2 m_2} c_{l_1 m_1 l_2 m_2}(t) \psi_{l_1 m_1}(\theta_1, \phi_1) \psi_{l_2 m_2}(\theta_2, \phi_2), \quad (14)$$

where (θ_1, ϕ_1) and (θ_2, ϕ_2) are the coordinates for two molecules. $c_{l_1 m_1 l_2 m_2}(t)$ are the time-dependent coefficients corresponding to the quantum numbers $(l_1, m_1; l_2, m_2)$, and can be determined by solving Schrödinger equations numerically. The initial state is set as $\psi_{00}\psi_{00}$ [$c_{0000}(t=0)=1$].

In addition to the orientation, one can also analyze the entanglement induced by the dipole interaction. The wave function of the coupled molecules can be expressed as a pure bipartite system [a compact form of Eq. (14)]: $|\Psi_c\rangle = \sum_{l_1 m_1 l_2 m_2} c_{l_1 m_1 l_2 m_2}(t) |\psi_{l_1 m_1}\rangle |\psi_{l_2 m_2}\rangle$. The reduced density operator for the first molecule is defined as

$$\rho_{\text{mol } 1} = \text{Tr}_{\text{mol } 2} |\Psi_c\rangle \langle \Psi_c|. \quad (15)$$

To obtain the entanglement of entropy, the bases of molecule 1 is transformed to make the reduced density matrix $\rho_{\text{mol } 1}$ to be diagonal. The entangled state can be represented by a biorthogonal expression with positive real coefficients λ_{lm} . The degree of entanglement for the coupled molecules can be measured by von Neumann entropy^{30,31}

$$\text{Entropy} = - \sum_{lm} \lambda_{lm} \log_n \lambda_{lm}. \quad (16)$$

Figure 4 shows the entropy and orientation evolves with time for fixed angle $\alpha=120^\circ$ and interdistance $R=1.5 \times 10^{-8}$ m. Because of the presence of the laser pulse, contributions to the energy exchange between two molecules come from many excited states, resulting in an irregularlike behavior of the entropy shown in Fig. 4(a). Further analysis of the dynamics gives the fact that the entropy grows monotonically from zero to a certain finite value. This is because the laser pulse dominates at the initial stage. The strength of the laser pulse is much larger than that of the dipole-dipole interaction. In addition, the duration is much shorter than the characteristic time of the dipole interaction. After the laser pulse, populations to the (rotational) excited states are formed (inset). The nonlinear dipole interaction then initiates the exchange process between the states until certain “dynamical equilibrium” is reached. One can conclude that the nonlinear variations of populations confirm the feature shown in the inset. Moreover, the orientations of the coupled molecules are also displayed in Fig. 4(b). Compared to the single molecule case, the irregular behavior is certainly from the nonlinear dipole interaction.

Figure 5 shows the time-averaged entropy for different hindering angles. As the hindering angle increases, the time-

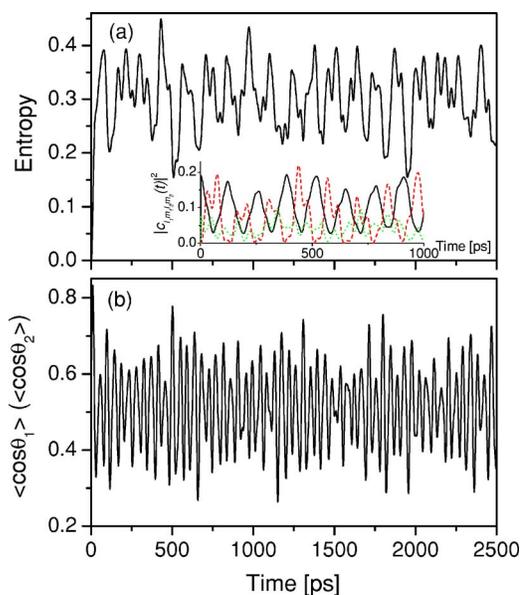


FIG. 4. (Color online) The entropy (a) and orientations $\langle \cos \theta_1 \rangle$ ($\langle \cos \theta_2 \rangle$) (b) in an infinite conical well for a fixed angle $\alpha=120^\circ$ and interdistance $R=1.5 \times 10^{-8}$ m. The inset shows the populations $(|c_{l_1 m_1 l_2 m_2}(t)|^2)$ irregularly oscillate with time, corresponding to the quantum number $(l_1, m_1; l_2, m_2) = (1, 0; 0, 0)$ (black solid curve), $(1, 1; 0, 0)$ (red dashed curve), and $(1, 0; 1, 0)$ (green dotted curve), respectively. Although we only focus on several excited states here, the populations of most states similarly remain irregular behavior.

averaged entropy increases monotonically. This is because for larger angles more excited states can be obtained under the same strength of the laser pulse, resulting in larger entropy. Note that the magnitude of orientation is high as the hindering angle is set equal to 30° (inset of Fig. 5). This again verifies that the narrow potential restricts the motion of the hindered rotor. In this case, the dipole interaction is suppressed, causing the regularlike behavior of the orientation. On the contrary, more excitations are populated such that the orientation oscillates with irregularity at $\alpha=150^\circ$.

A few remarks about the experimental verifications of our model should be addressed here. According to our previous

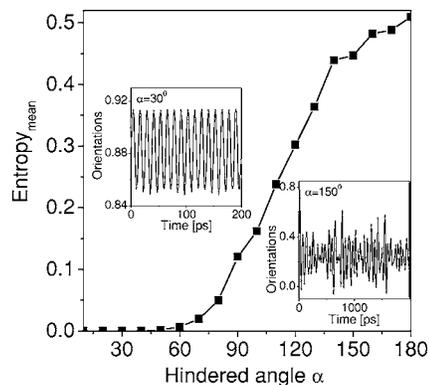


FIG. 5. The time-averaged entropy as a function of the hindered angle in the infinite conical well. The insets show the orientations of two molecules for hindered angles $\alpha=30^\circ$ and $\alpha=150^\circ$, respectively. The intermolecule separation is $R=1.5 \times 10^{-8}$ m.

study¹⁷ and this work, it is found that the orientations of the coupled rotors relate closely to the entropy. This indicates that the orientations of the coupled rotors somehow reflect the entropy of the system. For the measurement of orientation many experiments have been performed. For example, the Coulomb explosion of the molecules using intense femtosecond probe laser pulses and a time-of-flight mass spectrometer.³²⁻³⁴ The degree of orientation is determined by the measurement of fragment ions. Under proper arrangements, the orientation of hindered rotors can also be measured by similar technologies. This may provide some indication of the entanglement.

In summary, we have studied the dynamics of the adsorbed polar molecules under the irradiation of a single laser pulse. It is found that the orientation of a single hindered

rotor shows a periodic behavior. In particular, the amplitude of oscillation is sensitive to the degree of alternation of the laser field. On the other hand, the orientation of the coupled rotors shows irregular behavior because of the dipole-dipole interaction. Comparisons between the infinite-well and finite-well models are made, and the differences are both shown explicitly in the orientations and entanglement of entropy. These findings contribute to the essential physics of coupled rotors and may be useful in the field of surface science.

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