The ability to control the alignment of molecules may have important purpose in stereodynamics [1], surface catalysis [2], trapping molecules [3], molecular focusing [4], and nanoscale design [5, 6]. Experimentally, several methods have been used to control the orientations of molecules [7, 8, 9, 10, 11]. For example, by turning on a picosecond laser pulse adiabatically, the pendular states—hybrid of field-free molecular eigenstates [12, 13, 14]—can be created. A femtosecond laser pulse, like impulsive excitation, is found to be able to generate a field-free orientation [15, 16].

Since entangled states are fundamental for quantum information processing [17, 18], many research works have been proposed to generate entanglement in quantum-optic and atomic systems [19, 20]. In this Letter we propose a novel way to generate entanglement between two coupled identical polar molecules separated in a distance of tens of nanometers. Both molecules are irradiated by ultra-short pulses of laser light. Our study shows the entanglement induced by the dipole interaction can be enhanced by controlling the inter-molecule distance and the field strength of laser pulse.

Consider now two identical polar molecules (separated by a distance of \(R\)). There exists dipole-dipole interaction between these two molecules. Ultrashort half-cycle laser pulses are applied to both molecules [21]. The Hamiltonian of the system can be written as

\[
H = \sum_{j=1,2} \frac{\hbar^2}{2I} L_j^2 + U_{dip} + H_i, 
\]

where \(L_j^2\) and \(\frac{\hbar^2}{2I} \) (= \(B\)) are the angular momentum operator and rotational constant, respectively. \(U_{dip} = [\vec{\mu}_1 \cdot \vec{\mu}_2 - 3 (\vec{\mu}_1 \cdot \vec{\varepsilon}_R)(\vec{\mu}_2 \cdot \vec{\varepsilon}_R)]/R^3\) is the dipole interaction between two molecules, where \(\vec{\mu}_1\) and \(\vec{\mu}_2\) are the dipole moments. For simplicity, the dipole moments of two molecules are assumed to be identical, i.e. \(\vec{\mu}_1 = \vec{\mu}_2 = \mu\). The field-molecule coupling can be expressed as \(H_i = -\mu E(t) \cos \theta \cos (\omega t) - \mu E'(t) \cos \theta' \cos (\omega t)\), where \(\theta\) and \(\theta'\) are the angles between the dipole moments and laser field. The laser profile is assumed to be Gaussian shape, i.e. \(E(t) = E_0 e^{-\frac{(t-t_0)^2}{\sigma^2}}\), where \(E_0\) is the field strength, \(t_0\) is the center of peak, and \(\sigma\) is the pulse duration. With these assumptions, the time-dependent Schrödinger equation can be solved by expanding the wave function in terms of a series of field-free spherical harmonic functions

\[
\Psi = \sum_{lml'm'} c_{lml'm'}(t) Y_{lm}(\theta, \phi) Y_{l'm'}(\theta', \phi'),
\]

where \((\theta, \phi)\) and \((\theta', \phi')\) are the coordinates of first and second molecule respectively. \(c_{lml'm'}(t)\) are the time-dependent coefficients corresponding to the quantum numbers \((l, m; l', m')\) and can be determined by solving the Schrödinger equations numerically. In above equation, total wavefunction has no spatial dependence since we keep inter-molecule separation \(R\) as a fixed parameter. One might argue that variation of \(R\) is inevitable because of the effects of laser fields or inter-molecule vibrations. However, recent experiments have shown that it is possible to resolve two individual molecules separated by tens of nanometers when they are hindered on a surface [22, 23]. In principle, the free orientation model can be easily generalized to hindered ones by replacing the spherical harmonic functions with hindered wavefunctions as shown in our previous work [24]. The essential physics discussed below should be similar.

The orientations \((\cos \theta)\) and \((\cos \theta')\) can be evaluated immediately after the coefficients \(c_{lml'm'}(t)\) are determined. The parameters for numerical calculations are based on NaI molecule whose dipole moment is 9.2 debyes and rotational constant is 0.12 cm\(^{-1}\) in the ground state. Other parameters are referred to Ref. [16]. The duration and frequency of the half-cycle pulse are set to 279 fs and 30 cm\(^{-1}\), respectively. The center of peak is 1200 fs and the initial condition is \(c_{0000}(t=0) = 1\). Fig. 1 shows the orientations of the first and second molecules after a single laser pulse is applied on both molecules. For \(R = 3 \times 10^{-8}\) m, the behavior of the first molecule is quite close to that of a free rotor [16]. This is not surprising because the dipole interaction is weak for this molecule separation. However, as two molecules get close enough (Fig. 1 (b)), both molecules orient disorderly, and the periodic behavior disappears. This is because the dipole interaction is increased as the distance between the molecules is decreased, and the energy exchange between two molecules becomes more frequently. The regular orientation caused by the laser pulse is inhibited by the mutual interaction.

The populations of some low-energy levels are shown in the lower panels of Fig. 1(a) and (b). The solid, dashed, and dotted lines represent the populations of...
the states $(1,0;0,0)$, $(1,0;1,0)$, and $(2,0;1,0)$, respectively. These states show different degrees of periodic behavior at different distances. However, the populations of some higher excited states, for example the $(3,0;1,0)$ state in the inset of Fig. 1(b), display different degrees of irregularity. This manifests a fact that the nonlinear effect, caused by the reduction of $R$, does not affect the regularity of the low-lying states, and the origin of the irregularity is caused by the higher excited states.

Consider now the molecules are irradiated by a series of laser pulses periodically. As shown in Fig. 2 (a), if the period of the applied periodically laser pulse $T$ is equal to $\hbar/B$, then both molecules behave disorderly no matter how the distance $R$ is varied. The chaotic behavior of the molecules can be ascribed to the well-known "kicked-rotor" problem. However, a series of regular-like orientations marked by dotted and dashed lines are present in Fig. 2 (b) if $T$ is equal to $\pi\hbar/B$. For a free rotor under a single kick, this interesting phenomenon comes from the situation as the magnitude of the orientation returns to its initial condition $\langle \cos \theta \rangle = 0$ after a certain period $T$ [10]. Therefore, for two molecules in weak interaction limit ($R = 3 \times 10^{-8}$ m), the wavepacket-like orientation is similar to that of a single free rotor under the same laser period. The difference is the suppression of the amplitudes at long time (dashed lines). It means that the dipole force can generate some accidental phases to perturb the regularity of the coupled system. The lower panel of Fig 2 (b) exhibits that the suppression of the regularity is quicker if the dipole force is stronger.

Let us now turn our attention to the entanglement generated in this system. The coupled molecules in fact can be expressed as a pure bipartite system

$$\ket{\Psi} = \sum_{lm; l'm'} c_{lm;l'm'}(t) \ket{Y_{lm}} \ket{Y_{l'm'}} ,$$

The partial density operator for the first molecule is given by

$$\rho_{\text{mol} 1} = \text{Tr}_{\text{mol} 2} \ket{\Psi}\bra{\Psi}.$$  

Following the procedure of Schmidt decomposition, the bases of molecule 1 is rotated to make the reduced density matrix $\rho_{\text{mol} 1}$ diagonal. The entangled state can then be represented by a biorthogonal expression with positive real coefficients as given by

$$\ket{\Psi} = \sum_{lm} \sqrt{\lambda_{lm}} \ket{Y_{lm}}_{\text{mol} 1} \ket{Y_{lm}}_{\text{mol} 2} ,$$

where $\lambda_{lm}$ is the eigenvalue corresponding to $\ket{Y_{lm}}_{\text{mol} 1} \ket{Y_{lm}}_{\text{mol} 2}$. The measure of entanglement
for the coupled molecules can be parametrized by the von Neumann entropy

\[ \text{Entropy} = - \sum_{lm} \lambda_{lm} \log \lambda_{lm}. \quad (6) \]

Fig. 3 shows the time-dependent entropy after one pulse passes through this system. For inter-distance \( R = 5 \times 10^{-8} \) m, the entropy increases slowly from zero. For \( R = 1.5 \times 10^{-8} \) m, on the contrary, the entropy grows rapidly with the increasing of time because the dipole force is stronger. Notes that the entropy only varies within a finite range at long time regime. This indicates that the system reaches a dynamic equilibrium state even though the dipole force is still present.

![Fig. 3: Time evolution of the entropy after applying single laser pulse for (a) \( R = 5 \times 10^{-8} \) m and (b) \( R = 1.5 \times 10^{-8} \) m. The field strength is set equal to \( 3 \times 10^7 \) V/m.](image)

Fig. 4 (a) illustrates the variations of the entropy with respect to different field strengths of the applied laser pulse as \( R \) is set equal to \( 1.5 \times 10^{-8} \) m. For the field strength \( E_0 = 1.5 \times 10^7 \) V/m, an irregular-like behavior of the entropy is obtained, and its value is not large enough for quantum information processing. However, Fig. 4 (b) shows that the degree of entanglement can be enhanced if one increases the field strength. This can be understood well by studying the relationship between the dipole interaction and the field strength. If the effect of dipole interaction overwhelms the laser field, most of the populations are distributed on the low-lying states. In this case, the entropy from Schmidt decomposition is certainly small as shown in Fig. 4 (a). On the other hand, if the field strength plays a dominant role, the distribution of molecular states covers a wider range and the entropy is enhanced in this limit.

A few remarks about the differences between present proposal and previous works on generating entangled states should be emphasized here. In our model, the rotational excited states instead of internal electronic states of the molecules are considered. Second, the laser frequency in our work is tuned far-away from resonance, while conventional creation of entanglement depends on the resonant driving pulses. This means our work provides a wider range to select the laser frequency to create entanglement. As for the effect of decoherence, our entanglement is formed by the excited rotational states, instead of the vibrational states. Therefore, the decoherence is dominated by photon emission even if the molecules are attached to the surface of a solid.

In conclusion, we have studied a system of two coupled polar molecules, irradiated by laser pulse. The chaotic behavior of the orientations comes from the populations in the excited states of higher mode numbers. The entangled states vary with the field strength of laser pulse. And more stable entangled state can be generated even though the coupled system has irregular orientations. This feature may be useful in quantum information processing.

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