Entanglement of two coupled molecules

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Entangled states of two coupled polar molecules controlled by laser pulses are studied theoretically. Schmidt decomposition is used to measure the degree of entanglement. By varying the pulse shape of the applied laser, transition from regular to chaotic behavior may occur. This quantum feature is due to the inference of different phases. Moreover, the entanglement is also found to be enhanced by increasing the strength of the laser pulses.

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The control of the molecular alignment and orientation may be important in stereodynamics, trapping molecules, molecular focusing, surface catalysis, and nanoscale design. The alignment is due to the anisotropic polarizability induced by nonresonant pulses. The pendular states— hybrid of field-free molecular eigenstates —can be created by turning on a picosecond laser pulse adiabatically. For polar molecules, a femtosecond laser pulse is able to generate a field-free orientation. The molecule remains oriented after turn off the pulse. Experimentally, several methods concerning the femtosecond photodissociation spectroscopy and the ion imaging have been employed to measure the rotation of molecules.

Recently, many researches have been focused to generate entanglement in quantum-optic and atomic systems because entangled states are fundamental in quantum information processing. For molecular systems, most works are focused on the implementations of quantum computation. In general, the qubits are encoded by the vibrational (rotational) modes of the molecules. In order to realize the quantum logic gates experimentally, the optimal control theory is usually applied to design the suitable laser pulses. Recently, coupled-rotor- model attracts much interest also because some physical properties such as dielectric response may display peculiar behaviors in the presence of dipole-dipole interaction. However, studies on the entanglement of coupled molecules under strong laser fields are still lack until now. In this rapid communication, a novel method to create entanglement between two coupled identical polar molecules separated in a distance of $R$. The molecule system is irradiated by a series of ultrashort half-cycle laser pulses. The Hamiltonian of the system can be written as

$$H = \sum_{j=1,2} \frac{\hbar^2}{2I} L_j^2 + U_{dip} + H_{f-m},$$

where $L_j^2$ and $\hbar^2/2I$ are the angular momentum operator and rotational constant, respectively. $U_{dip}$ is the dipole interaction between two molecules:

$$U_{dip} = \frac{[\vec{\mu}_1 \cdot \vec{\mu}_2 - 3 (\vec{\mu}_1 \cdot \vec{e}_R) (\vec{\mu}_2 \cdot \vec{e}_R)]}{R^3},$$

where $\vec{\mu}_1$ and $\vec{\mu}_2$ are the dipole moments. The dipole moments of two molecules are assumed, for simplicity, to be identical, i.e. $\mu_1 = \mu_2 = \mu$. The field-molecule coupling $H_{f-m}$ can thus be expressed as

$$H_{f-m} = -\sum_{i=1,2} \mu E(t) \cos \theta_i \cos (\omega t),$$

where $\theta_1$ and $\theta_2$ are angles between dipole moments and laser field. The laser profile is assumed in Gaussian shape, i.e. $E(t) = E_0 \exp \left(-\frac{(t-t_0)^2}{2\sigma^2}\right)$, where $E_0$ is the field strength, $t_0$ is the center of peak and $\sigma$ is the pulse duration. The time-dependent Schrödinger equation can be solved by expanding the wave function $\Psi$ in terms of a series of field-free spherical harmonic functions $Y_{lm}(\theta, \phi)$ as

$$\Psi = \sum_{l_1 m_1 l_2 m_2} c_{l_1 m_1 l_2 m_2} (t) Y_{l_1 m_1} (\theta_1, \phi_1) Y_{l_2 m_2} (\theta_2, \phi_2),$$

where $(\theta_1, \phi_1)$ and $(\theta_2, \phi_2)$ are the coordinates of first and second molecule respectively. The time-dependent coefficients $c_{l_1 m_1 l_2 m_2} (t)$ corresponding to the quantum numbers $(l_1, m_1; l_2, m_2)$ can be determined by solving the Schrödinger equations numerically. In the above equation, the inter-molecule separation $R$ is assumed to be fixed so that the total wavefunction has no spatial dependence. The variation of $R$ might be inevitable due to the influence of laser fields or inter-molecule vibrations. However, recent experiments exhibited that the spacial resolution in tens of nanometers for two individual molecules hindered on a surface is actually possible. The
free orientation model can be easily generalized to hindered ones, in principle, by replacing the spherical harmonic functions with hindered wavefunctions as shown in our previous work [24]. Thus, the essential physics discussed here should be realistic.

We now focus our attention on the entanglement generated in this system. The coupled molecules can be expressed as a pure bipartite system as \( |\Psi\rangle = \sum_{l,m} c_{lm} |Y_{lm}\rangle_1 |Y_{lm}\rangle_2 \). The reduced density operator for the first molecule is defined as

\[
\rho_{mol 1} = Tr_{mol 2} |\Psi\rangle \langle \Psi|.
\]

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

\[
|\Psi\rangle = \sum_{lm} \sqrt{\lambda_{lm}} |Y_{lm}\rangle_{mol 1} |Y_{lm}\rangle_{mol 2},
\]

where \( \lambda_{lm} \) is the eigenvalue corresponding to \( |Y_{lm}\rangle_{mol 1} |Y_{lm}\rangle_{mol 2} \). The measure of entanglement for the coupled molecules can be parametrized by von Neumann entropy

\[
\text{Entropy} = -\sum_{lm} \lambda_{lm} \log \lambda_{lm}.
\]

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. The duration and frequency of the half-cycle pulse are set to 279 fs and 30 cm\(^{-1}\), respectively. The center of the peak is 1200 fs and the initial condition is set as \( c_{\mu000} (t = 0) = 1 \). The ratio of the magnitude of positive peak and that of negative peak of the pulse is 5 : 1. Fig. 1 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 to almost finite value of 0.4. 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 systems reaches a dynamic equilibrium state even though the dipole force is still present. In the insets, the orientations \( \langle \cos \theta_1 \rangle \) and \( \langle \cos \theta_2 \rangle \), which can be evaluated immediately after the coefficients \( c_{l,m_1m_2} (t) \) are determined, also reflect the effect of the dipole interaction. For \( R = 5 \times 10^{-8} \) m, the behavior of both molecules is quite close to that of a free rotor \( \hbar \), in which the rotational period is close to \( \pi \hbar / B \). As the two molecules get close enough (the inset of 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.

FIG. 1: 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 insets in (a) and (b) represent the orientations of two molecules at different distances. The field strength is set equal to \( 3 \times 10^7 \) V/m.

Fig. 2 illustrates the time evolution of the entropy with different ratios in magnitude of the positive and negative peak value of the laser pulse as \( R \) is set equal to \( 1.5 \times 10^{-8} \) m. For the case of ratio 9 : 1, an irregular-like behavior is still obtained, but its time-averaged value is 0.51, which is larger than the averaged one (0.43) in Fig. 1. If the ratio is set equal to 1 : 1, the entanglement shows a nearly periodic behavior with small averaged entropy. This result is very similar to the case of no laser limit. This implies that the entanglement depends sensitively on the shape of the laser pulse. The positive and negative parts of the laser pulse seem to interfere with each other. Moreover, the dipole force only establishes a periodic-like entropy.

The distributions of the first ten contributive eigenvalues \( \lambda_{\mu} \) to the entropy at short and long time regimes are shown in the insets of Fig. 2. In the case of 9 : 1 ratio, the eigenvalue \( \lambda_1 \) dominates the contributions at short time regime \( t = 50 \) ps. However, the dominant contributions are distributed to several values as \( t = 2000 \) ps regime. This means in long time limit the system is in some sort of dynamic equilibrium, and entropy saturates to certain value. On the contrary, \( \lambda_1 \) always dominates the contributions for either short or long time regime in the case of symmetrical laser shape as shown on the lower
FIG. 2: Time evolution of the entropy after applying single laser pulse for different ratios in magnitudes of the positive and negative peak value of the laser pulse. The graphs show the irregular (periodic) behavior for ratio 9 : 1 (1 : 1). The inset : the first ten contributive eigenvalues $\lambda_i$ at short time ($t = 50$ ps) and long time ($t = 2000$ ps). The field strength and inter-molecule separation are $E_0 = 3 \times 10^7$ V/m and $R = 1.5 \times 10^{-8}$ m.

Inset of Fig. 2. From statistical point of view, this somehow explains the suppressed and regular behaviors of the entanglement (entropy).

Fig. 3 shows the time evolutions of the populations of the eigenstates for different ratio of pulse shapes. For 1 : 1 ratio, the energy level (0, 0; 0, 0) is mostly populated as shown in the lower panel of Fig. 3. Like the ground state, the populations of the higher levels (the inset of Fig. 3) also show the periodic behavior. The reason is attributed to the symmetrical shape of the laser so that the populations of the higher levels are almost contributed by the dipole interaction. In this case, the magnitudes of the higher level populations are rather small such that the periodic evolution of the entropy is obtained. On the other hand, for 9 : 1 ratio the populations of the higher states represent different degrees of irregularity as shown in the upper panel of Fig. 3. This is because a single laser pulse can generate high populations in the excited states $|l_1, m_1; l_2, m_2\rangle$. Energy transfer by means of (mediated) dipole interaction generates the irregular evolutions of the higher excited states, which result in a randomly time-varying entropy.

By adjusting the laser parameters, one can vary the degrees of the entanglement. Fig. 4 illustrates the time evolution of the entropy for fixed inter-molecule separation $R = 1.5 \times 10^{-8}$ m and laser ratio 5 : 1 for a doubling of the laser field strength ($E_0 = 6 \times 10^7$ V/m). As can be seen, an irregular-like behavior of the entropy is obtained, and its averaged value is larger in comparison with Fig. 1(b). This can be understood well by studying the relationship between the dipolar interaction and the field strength. If the effect of laser field overwhelms the dipole interaction, the populations are distributed to a wider range. Since most of the populations are also distributed more averagely in this case, the entropy from Schmidt decomposition is certainly larger. Another way to control the degree of entanglement in this system is to change the positive and negative ratios of the laser pulse. Inset of Fig. 4 shows the time-averaged entropy with respect to different ratios. We find that the entropy is more enhanced as the ratio is larger. This means that the high asymmetric shape of laser pulse can generate a larger entropy at the same field strength.

A few remarks about the differences between our model and previous works on generating entangled states should be addressed here. In our model, we consider the rotational excited states instead of internal electronic states of the molecules. Second, the laser frequency in our work is tuned as possible as 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 generate 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 the entanglement of two coupled polar molecules irradiated by an ultra-short laser pulse. Schmidt decomposition is used to generated the time evolution of the entropy. The degree of the entanglement is analyzed by varying the inter-molecule distance, symmetry of the laser shape, and field strength. Its dependence on the controlled parameters may be useful for the quantum information processing.

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