PHYSICAL REVIEW A **88**, 012504 (2013)

Intramolecular energy transfer, entanglement, and decoherence in molecular systems

Liangjun Zhai (翟良君) and Yujun Zheng (郑雨军)*
School of Physics, Shandong University, Jinan 250100, China

(Received 3 November 2012; published 8 July 2013)

The intramolecular energy transfer, dynamical entanglement of vibrations, and decoherence process in triatomic molecular systems are studied. The benchmark molecules of H_2S, NO_2, and O_3 are sampled to investigate the intramolecular energy transfer and dynamical entanglement of stretching-stretching vibrational modes in triatomic molecular systems by restricting the bending vibration to its ground state. The comparative study is applied to explore the dynamical differences of initial local-mode and normal-mode characteristic states. Also, the decoherence process of the stretching-stretching qubits system caused by the bending vibration is discussed.

DOI: 10.1103/PhysRevA.88.012504 PACS number(s): 33.20.Tp, 03.65.Ud

I. INTRODUCTION

The advent of quantum computation and quantum information has led to the study of quantum computation based on molecular vibrations [1]. The concept of quantum computation based on molecular vibrations employs vibrational states of molecules to represent the qubit. The shaped femtosecond laser pulse in the IR regime can be adopted to implement quantum logic operation [1–3]. One of the challenges of realizing quantum computation is how to utilize entanglement. Considering the achievements in quantum computation based on molecular vibrations, studies of dynamical entanglement in realistic molecular systems are becoming more and more interesting [2–7]. Undoubtedly, the intramolecular vibrational energy redistribution (IVR) has great influence on the entanglement between different vibrational modes [8]. Since IVR has been demonstrated to be controllable [9], the relationship between dynamical entanglement and energy transfer is thus interesting in studies of intramolecular dynamics.

One of the basic requirements of quantum computation is to utilize coherence, the decoherence of qubits is an important issue in the practical realization of quantum computation. Decoherence is often caused by unavoidable coupling with the environment. For a multipartite quantum system, decoherence leads to degradation of entanglement and, in certain cases, entanglement sudden death [10,11]. For the molecular vibrational qubits, the decoherence resources may come from collisions with other molecules and the intramolecular anharmonic resonances with the remaining vibrational modes, rotational freedom, and electronic freedom [12]. Regarding molecules in the gas phase, the number of collisions can be kept low. The studies on the intramolecular decoherence and robustness of entanglement against the remaining modes are thus important in selecting suitable molecules to apply quantum computation [8].

The Lie algebraic model of molecules has been proven to be an effective model in describing vibrations in polyatomic molecules [13,14]. The Lie algebraic model has a simple form in description, and the anharmonicity of each mode and resonances between different modes can be introduced automatically by the matrix elements of operators [15]. Because of these advantages, the algebraic method has extensive applications, including the vibrational spectra, potential energy surface, and dynamical entanglement [5,6,13–19]. In the present work, the U(4) algebraic model of triatomic molecule is adopted. Based on this model, the stretching and bending vibrations are well described. With bending vibration restricted to its ground state, we investigate intramolecular energy transfer and bipartite entanglement between two stretching vibrational modes and the entanglement dynamics in different types of molecules (that is, the normal or local-mode molecules). We study the decoherence process caused by the bending vibration and the robustness of entanglement against the bending vibration under the assumption of the stretching-stretching vibration as a bipartite qubits system. This study will help us to control the entanglement and decoherence, since the success of quantum computation will depend on one's theoretical understanding and experimental control of quantum entanglement and decoherence.

The organization of this paper is as follows. In Sec. II, the U(4) algebraic Hamiltonian for symmetrical bent triatomic molecules is reviewed. In Sec. III, the dynamical properties of stretching-stretching entanglement are studied by employing linear entropy, and the relationship between dynamical entanglement and energy transfer is also studied in this section. Decoherence of the stretching-stretching qubits and robustness of stretching-stretching entanglement against the bending vibration are considered in Sec. IV. A brief summary is presented in Sec. V.

II. THEORETICAL FRAMEWORK

In this section we show the theoretical framework of the U(4) algebraic model of molecules. The dynamical group of triatomic molecules is $U_1(4) \otimes U_2(4)$ (we denote the left bond of triatomic molecules as bond 1, and the right bond as bond 2), and the dynamical symmetric chains are written as [14]

$$\begin{aligned} &U_1(4) \otimes U_2(4) \supset U_{12}(4) \supset O_{12}(4),\\ &U_1(4) \otimes U_2(4) \supset O_1(4) \otimes O_2(4) \supset O_{12}(4). \end{aligned} \tag{1}$$

The local basis is characterized by

$$|[N_1][N_2](\omega_1,0)(\omega_2,0)(\tau_1,\tau_2)\rangle, \tag{2}$$

where $[N_i]$ labels the total symmetric representation of $U_i(4)$ $(i = 1,2)$, $(\omega_i,0)$ labels the symmetric representation of $O_i(4)$ $(i = 1,2)$, and (τ_1,τ_2) denotes the irreducible

---

*Corresponding author: yzheng@sdu.edu.cn representation of $O_{12}(4)$. From the theory of Lie group [14,20], $[N_i]$ corresponds to the Young tableau since it denotes the representations of $U_i(4)$. Physically, N_i characterizes the total number of bosons in bond i. This means that the dimension of bond i, for the Fock state in Hilbert space, is $N_i + 1$. Correspondingly, the values of ω_i are taken as

$$\omega_i = \begin{cases} N_i, N_i - 2, \ldots, 1, & \text{if } N_i \text{ is odd;} \\ N_i, N_i - 2, \ldots, 0, & \text{if } N_i \text{ is even.} \end{cases} \tag{3}$$

The quantum Hamiltonian is expressed as [14]

$$\mathcal{H} = A_1 C_1 + A_2 C_2 + A_{12} C_{12}^{(1)} + A'_{12} C_{12}^{(2)} + \lambda M_{12}, \tag{4}$$

where A_1, A_2, A_{12}, A'_{12}, and λ are the expansion coefficients which can be determined by fitting spectroscopic data ($A_1 = A_2$ for symmetric triatomic molecule). The magnitude of A_i determines the anharmonicity of each mode, and λ denotes the coupling strength between vibrational modes. C_1 and C_2 are Casimir operators of groups $O_1(4)$ and $O_2(4)$, respectively; $C_{12}^{(1)}$ and $C_{12}^{(2)}$ are two Casimir operators of $O_{12}(4)$ representing the bending vibrations; M_{12} is the Majorana operator representing the coupling between two bonds.

By denoting the quantum numbers of stretching vibration in the two bonds as v_1 and v_2, and the quantum numbers of bending and rotation as v_b and κ, the relations between $(\omega_1, \omega_2, \tau_1, \tau_2)$ and (v_1, v_b, v_2, κ) are as follows [14]:

$$\begin{aligned} v_1 &= \tfrac{1}{2}(N_1 - \omega_1), \quad v_2 = \tfrac{1}{2}(N_2 - \omega_2), \\ v_b &= \tfrac{1}{2}(\omega_1 + \omega_2 - \tau_1 - \tau_2), \quad \kappa = \tau_2. \end{aligned} \tag{5}$$

The matrix elements of invariants in the local basis, after considering Eq. (5), are given by [14,20]

$$\begin{aligned} \langle C_1 \rangle &= (N_1 - 2v_1)(N_1 - 2v_1 + 2), \\ \langle C_2 \rangle &= (N_2 - 2v_2)(N_2 - 2v_2 + 2), \\ \left\langle C_{12}^{(1)} \right\rangle &= (N_{12} - 2v - \kappa)(N_{12} - 2v - \kappa + 2) + \kappa^2, \\ \left\langle C_{12}^{(2)} \right\rangle &= (N_{12} - 2v - \kappa)\kappa, \end{aligned} \tag{6}$$

where $v = v_1 + v_b + v_2$, $N_{12} = N_1 + N_2$. The Majorana operator is not diagonal in the basis (2), and its matrix elements in the basis (2) can be calculated by employing the Wigner-Eckart theorem [14,20]. The diagonal and the nondiagonal elements of M_{12} are given via

$$\begin{aligned} &\langle N_1 N_2 \omega_1 \omega_2 (\tau_1, \tau_2) | M_{12} | N_1 N_2 \omega_1 \omega_2 (\tau_1, \tau_2) \rangle \\ &\quad = \frac{3}{4} N_1 N_2 - \frac{1}{4} \{ \tau_1 (\tau_1 + \tau_2 + 2) - \omega_1 (\omega_1 + 2) \\ &\qquad - \omega_2 (\omega_2 + 2) \} - \frac{(N_1 + 2)(N_2 + 2)}{16 \omega_1 (\omega_1 + 2) \omega_2 (\omega_2 + 2)} \\ &\qquad \times [\omega_1(\omega_1 + 2) + \omega_2(\omega_2 + 2) - (\tau_1 + \tau_2)(\tau_1 + \tau_2 + 2)] \\ &\qquad \times [\omega_1(\omega_1 + 2) + \omega_2(\omega_2 + 2) - (\tau_1 - \tau_2)(\tau_1 - \tau_2 + 2)], \end{aligned} \tag{7}$$

and

$$\begin{aligned} &\langle N_1 N_2 \omega'_1 \omega'_2 (\tau_1, \tau_2) | M_{12} | N_1 N_2 \omega_1 \omega_2 (\tau_1, \tau_2) \rangle \\ &\quad = (-1)^{\tau_1 + 1} (\omega'_1 + 1)(\omega'_2 + 1) \left\{ \begin{matrix} \frac{\omega_1}{2} & \frac{\omega_2}{2} & \frac{\tau_1 - \tau_2}{2} \\ \frac{\omega'_1}{2} & \frac{\omega'_2}{2} & 1 \end{matrix} \right\} \\ &\quad \times \left\{ \begin{matrix} \frac{\omega_1}{2} & \frac{\omega_2}{2} & \frac{\tau_1 + \tau_2}{2} \\ \frac{\omega'_1}{2} & \frac{\omega'_2}{2} & 1 \end{matrix} \right\} \langle N_1 \omega'_1 || \hat{D}_1 || N_1 \omega_1 \rangle \\ &\quad \times \langle N_2 \omega'_2 || \hat{D}_2 || N_2 \omega_2 \rangle \delta_{\omega'_1, \omega_1 \pm 2} \delta_{\omega'_1, \omega_1 \pm 2}, \end{aligned} \tag{8}$$

where $\{\cdots\}$ is the Wigner $6 - j$ symbol. The matrix elements of $\langle N\omega' || \hat{D} || N\omega \rangle$ are given as

$$\langle N\omega' || \hat{D} || N\omega \rangle = \begin{cases} \frac{N+2}{2} & \omega' = \omega, \\ \frac{1}{2}\sqrt{\frac{(N-\omega+2)(N+\omega+2)(\omega+1)}{\omega-1}} & \omega' = \omega - 2, \\ \frac{1}{2}\sqrt{\frac{(N-\omega)(N+\omega+4)(\omega+1)}{\omega+3}} & \omega' = \omega + 2. \end{cases} \tag{9}$$

The transition from the local limit to the normal limit is well described by the locality parameter [14]. Based on the U(4) algebraic model, the locality parameter ξ is defined as

$$\xi = \frac{2}{\pi} \left| \arctan \left(\frac{8\lambda_{12}}{A_i + A_{12}} \right) \right|. \tag{10}$$

For the local-mode molecules, the locality parameter ξ is near to 0; for normal-mode molecules, the locality parameter $\xi \to 1$.

The evolution of the system is given by

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}\mathcal{H}t} |\psi(0)\rangle, \tag{11}$$

where $|\psi(0)\rangle$ is the initial state of the system. All the dynamical information of the system can be obtained from the time-dependent quantum state $|\psi(t)\rangle$. We define the density matrix of molecular system $\rho(t)$ as

$$\rho(t) = |\psi(t)\rangle\langle\psi(t)|. \tag{12}$$

In the previous study, the Hamiltonian (4) was employed to describe the (ro-)vibrational spectra and dynamics of triatomic molecules [21,22]. We here consider three triatomic molecules: H_2S (local-mode molecule), NO_2 (normal-mode molecule), and O_3 (normal-mode molecule). The expansion coefficients A_1, A_2, A_{12}, A'_{12}, and λ of these molecules in the Hamiltonian of Eq. (4) have been obtained by fitting their vibrational spectra. The coefficients, taken from Refs. [16–18], and the locality parameters are listed in Table I.

The quantum number of κ denotes the rotation of triatomic molecules. Physically, if the rotational motion of molecules can be separated from the molecular vibrational motion, the quantum number of κ would have no influence on the dynamics of entanglement. However, this motion is usually not separated from the vibrational motion. If this happens, the rotational motion will lead to the decoherence of vibrations. Also, molecular rotational transitions in excited vibrational states are generally very weak, and the molecular rotational constants are slightly vibrationally dependent [23]; in the

TABLE I. The parameters of molecules: H_2S, NO_2, and O_3. $i = 1$ and 2 are the two bonds in molecules. A_i, A_{12}, λ are in cm^{-1}.

Molecule	N_i	A_i	A_{12}	λ	ξ
H_2S	40	−13.57	−2.14	0.458	0.14
NO_2	115	−1.9052	0.0055	−0.6369	0.7728
O_3	70	−11.6522	2.9914	−3.0782	0.7847

following numerical simulations, the rotational motion of triatomic molecules is neglected.

III. STRETCHING-STRETCHING ENTANGLEMENT AND ENERGY TRANSFER: THE CASE OF THE GROUND STATE OF BENDING VIBRATION

In this section, the dynamics of entanglement and energy transfer between two stretching modes are considered, and the bending vibration is restricted to its ground state. Several measures of quantum bipartite entanglement are introduced, such as entanglement of formation, entanglement of distillation, von Neumann entropy, concurrence, and negativity [24–30]. These different definitions of entanglement are used to characterize entanglement in different manners. Here, linear entropy is employed to measure the entanglement of vibrations in triatomic molecules.

The linear entropy S_l is defined as follows [30]:

$$S_l = 1 - \mathrm{Tr}[\rho_{s1}(t)]^2, \tag{13}$$

where $\rho_{s1}(t)$ denotes the reduced-density matrix of stretching vibrational mode in bond 1, and Tr means the trace over the square of $\rho_{s1}(t)$. $\rho_{s1}(t)$ is obtained by tracing over the stretching vibrational mode in bond 2

$$\rho_{s1}(t) = \mathrm{Tr}_2 \rho_{ss}(t), \tag{14}$$

where $\rho_{ss}(t) = |\psi_{ss}(t)\rangle\langle\psi_{ss}(t)|$ is density matrix of two stretching vibrational modes, and $|\psi_{ss}(t)\rangle$ is the stretching vibrational states of the molecules. For the case of the bending vibration restricted to its ground state, $\rho_{ss}(t)$ will keep its purity during the vibration if $\rho_{ss}(t)$ is prepared in a pure state.

Physically, the entropy can be interpreted as a measurement of the disorder of the subsystem. Linear entropy is usually used to measure the deviations of the states of the system from the pure state, and it is also the measurement of the decoherence process of the subsystem [31].

We here define the stretching Hamiltonian of bond i as

$$\mathcal{H}_i = A_i C_i, \tag{15}$$

where C_i $(i = 1,2)$ is the Casimir operator of bond i. The stretching energy of bond i is therefore written as

$$E_i(t) = \mathrm{Tr}[\rho(t)\mathcal{H}_i]. \tag{16}$$

We consider S_l and energy transfer for the initial states of the product of Fock states. This initial state can be written as [32]

$$|\psi_{ss}(0)\rangle = |N_1,v_1\rangle \otimes |N_2,N_s - v_1\rangle \equiv |v_1,N_s - v_1\rangle, \tag{17}$$

where N_s is the total quantum number of two stretching bonds, namely, $N_s = v_1 + v_2$. Since the product Fock state has a clear meaning in the quantum computation, dynamical behaviors of S_l are important for quantum computation.

S_l and $E_{1(2)}$ for H_2S with initial states $|0,1\rangle$ and $|1,1\rangle$ are plotted in Fig. 1. The evolutions of S_l and $E_{1(2)}$ for both states of $|0,1\rangle$ and $|1,1\rangle$ display periodicity nicely. For the state $|0,1\rangle$, the period of E_1 or E_2 is twice of S_l, and the maximum value of entanglement appears when the energies of the bonds are close to each other. For $|1,1\rangle$, the period of S_l is the same with the period of $E_{1(2)}$ (E_1 is identical with E_2), and S_l is anticorrelated with $E_{1(2)}$. For the normal-mode molecules, similar behaviors of $E_{1(2)}$ and S_l for these two states are also found. S_l of NO_2 and O_3 for the initial states $|0,1\rangle$ and $|1,1\rangle$ are plotted in Fig. 2.

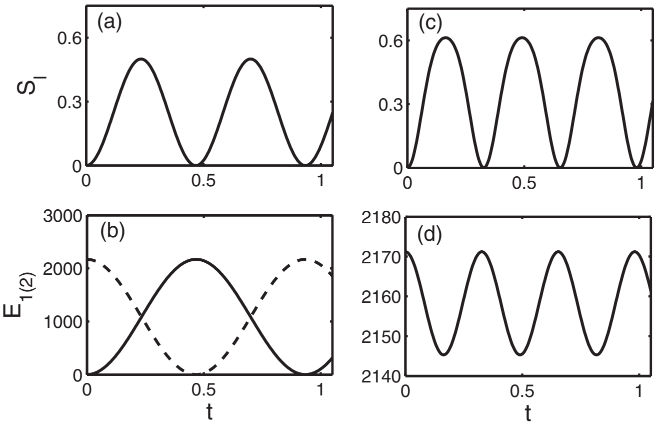

FIG. 1. S_l [panels (a) and (c)], E_1 [solid lines in (b) and (d)], and E_2 [dashed lines in (b)] as a function of time t for H_2S for two product Fock states: $|0,1\rangle$ [(a) and (b)] and $|1,1\rangle$ [(c) and (d)]. In (d), E_1 and E_2 are the same. t is in ps, and $E_{1(2)}$ is in cm^{-1}.

It shows that the period of S_l of the normal-mode molecules is much shorter than that of local-mode molecules. If we take the ground vibrational state $|0\rangle$ and first excited state $|1\rangle$ of one stretching vibrational mode to represent a qubit, the other stretching vibrational modes can be thought of as the environment, which causes the decoherence. Since S_l is also the measurement of the decoherence, the long period of the local-mode molecules indicates that the states of the local-mode molecules are more stable than the states of the normal-mode molecules. The stability of states is particularly important in quantum computation [33], since it can strongly influence the quantum computation fidelity. In this sense, the local-mode molecules are more suitable to accomplishing quantum computation. For both of the initial low-level states, entanglement is closely related to the energies of two bonds, which demonstrates that entanglement is controllable by controlling the energy transfer between vibrational modes.

A local-mode characteristic state corresponds to the state of high excitation in one bond but low excitation in the other one. Because of the energy gap of local-mode doublets, the energy transfer of the local-mode characteristic states in

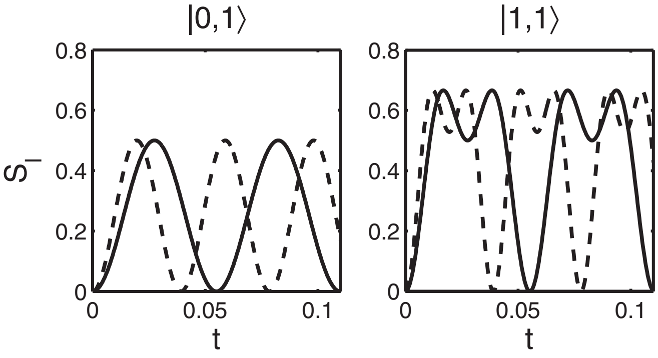

FIG. 2. S_l for the initial state $|0,1\rangle$ and $|1,1\rangle$ of NO_2 (solid lines) and O_3 (dashed lines). t is in ps.

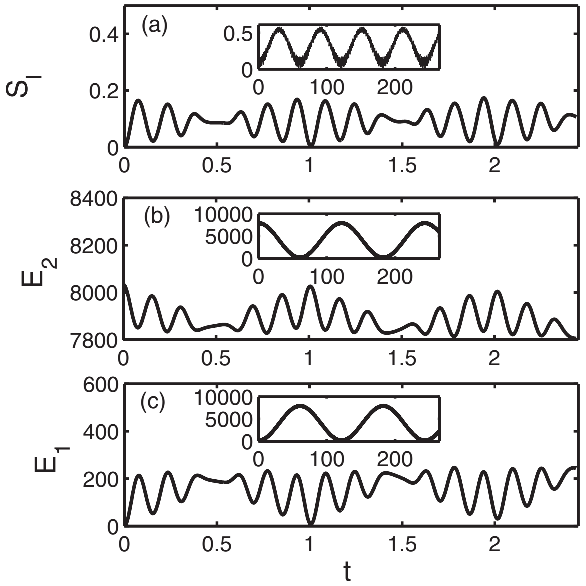

FIG. 3. S_l (a), E_2 (b), and E_1 (c) in early times for the initial state $|0,4\rangle$ of H_2S. The long-time evolutions of S_l, E_1, and E_2 are plotted in the insets of each panel. t is in ps and $E_{1(2)}$ is in cm^{-1}.

the local-mode molecules is slower than that of the normal-mode characteristic states [34]. To illustrate the dynamical properties, we sample the Fock state $|0,4\rangle$ of H_2S as the initial state. In Fig. 3, S_l and $E_{1(2)}$ are plotted. We can find that the period of S_l is synchronic with E_1 or E_2 in early time evolution. E_2 is much higher than E_1, and both of them fluctuate with small amplitude around their equilibrium values. Correspondingly, S_l vibrates in "packets" periodically with low level of entanglement. However, for the long time scale, S_l is shown as the sine wave with a long-time period. The long beat of S_l means the entanglement of the local-mode characteristic states can live for a long time, and it could be the carrier of quantum information. Additionally, the correspondence between S_l and $E_{1(2)}$ is similar to that of $|0,1\rangle$, and the clear correspondence means the entanglement of the local-mode characteristic states of H_2S is controllable by controlling energy transfer [35,36].

As shown in Fig. 3, the linear entropy S_l of the local-mode molecule H_2S has periodical properties for the local initial state. We attribute these properties to the periodical properties of the Fock states in Fock space [5]. For the case of initial Fock states, the probabilities $P^{(v)}(t)$ of Fock states $|v,N_s-v\rangle$ ($v=0,1,\ldots,N_s$) have periodicity with the time evolution. This leads to the periodicity of linear entropy and energy transfer in molecular bonds. This periodicity of distribution, however, becomes complicated when the locality parameters ξ of the molecules increase.

However, for the normal-mode characteristic initial state, the probabilities $P^{(v)}(t)$ of Fock states $|v,N_s-v\rangle$ have no periodicity in the evolution. This means that the linear entropy S_l and energy transfer vary irregularly for the normal-mode characteristic initial state $|v,N_s-v\rangle$ ($v\simeq N_s-v$). To comparatively study the properties of entanglement and energy transfer between the bonds of the initial local-mode and normal-mode characteristic states, we show the relation of linear entropy S_l and energy transfer $\Delta E=(E_1-E_2)/E_0$ [E_0 is the bending vibrational energy of the ground bending vibrational state $|0,1^0,0\rangle$. The expression $\Delta E=(E_1-E_2)/E_0$ means that we scale ΔE using E_0 of the corresponding molecule] in the space of $S_l\sim\Delta E$ (hereafter we note it as the "$S_l\sim\Delta E$ section"). The $S_l\sim\Delta E$ section represents the periodicity of linear entropy S_l and energy transfer ΔE with vividly picture.

Practically, we expect to find dynamical entanglement of normal-mode characteristic state by building an initial state with (around) equal initial excitation in both bonds [namely, $v_1\simeq N_s-v_1$ in Eq. (17)]. As an example, the two types of Fock states: the normal-mode characteristic state $|2,3\rangle$ and the local-mode characteristic state of $|0,5\rangle$ with the same N_s of the sampled molecules are selected.

For the local-mode molecule H_2S, the $S_l\sim\Delta E$ section, under the local-mode characteristic initial Fock state $|0,5\rangle$, presents the shape of an inverse V since linear entropy S_l and energy transfer ΔE are periodical with the time evolution. However, for the molecules of NO_2 and O_3, whose locality parameter ξ becomes bigger, the periodical properties of linear entropies S_l and energy transfer ΔE (and $E_{1(2)}$) become complicated. This leads to the area of the $S_l\sim\Delta E$ section becoming bigger, and the inverse-V shape of the $S_l\sim\Delta E$ section becoming wider. This is shown in the left column of Fig. 4.

As noted above, the linear entropy S_l and energy transfer vary irregularly for the initial Fock state $|2,3\rangle$, therefore, their corresponding $S_l\sim\Delta E$ sections show different behaviors

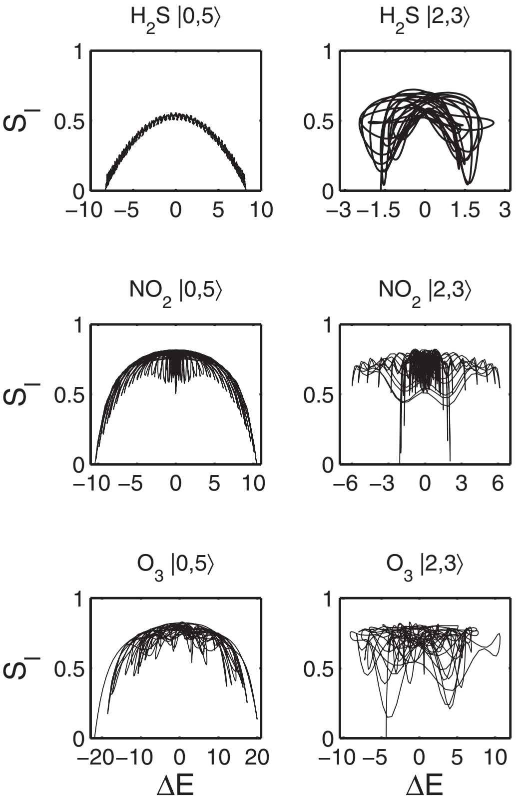

FIG. 4. $S_l\sim\Delta E$ section. The initial states are $|0,5\rangle$ (left column) and $|2,3\rangle$ (right column) for H_2S (top), NO_2 (middle), and O_3 (bottom). $\Delta E=(E_1-E_2)/E_0$.

with local-mode characteristic states as shown in the right column of Fig. 4. Although the $S_l \sim \Delta E$ sections show the irregularity in this case, the sections of the local-mode molecules and normal-mode molecules have different behaviors: for the local-mode molecule, such as the H_2S molecule, the $S_l \sim \Delta E$ section shows a round symmetry about $\Delta E = 0$. This round symmetry goes away as the locality parameter ξ increases as shown in the right column of Fig. 4. Also, the $S_l \sim \Delta E$ section spreads over a wider area with the increase of the locality parameter ξ (namely, from local-mode molecule to normal-mode molecule, as shown from top to bottom in the right column of Fig. 4).

IV. INFLUENCE OF BENDING VIBRATION ON THE STRETCHING-STRETCHING QUBITS

In this section, we consider the influence of bending vibrations on the stretching-stretching qubits. We study the decoherence process and the robustness of the entanglement of the stretching-stretching qubits. In our numerical simulations, the stretching vibrations in two bonds are assumed as a bipartite qubit system: the ground state and first excited state of each mode are selected to represent the qubits. For this case, the bending vibration of the triatomic molecules is considered as the resource of decoherence.

The initial state is taken as

$$|\psi(0)\rangle = |\psi_{ss}(0)\rangle \otimes \left|v_b^{\kappa}\right\rangle, \tag{18}$$

where $\psi_{ss}(0)\rangle$ is the initial vibrational state of two bonds, and $|v_b^{\kappa}\rangle$ is the initial state of bending motion of the molecule with rotation. As noted above, we assume $\kappa = 0$ in the following numerical simulations since we neglect the molecular rotation motion.

A. Decoherence of the stretching-stretching qubits

When the whole system is prepared in the pure state, it will maintain this pure state during evolution, but not for the subsystem. We measure the decoherence of the stretching-stretching system by its loss of purity. Purity is defined as [37]

$$p = \mathrm{Tr}[\rho_{ss}(t)^2], \tag{19}$$

where $\rho_{ss}(t)$ is the density matrix of two stretching vibrational modes. Purity varies from 1 for pure state to $1/D_s$ for the completely mixed state (D_s is the Hilbert space dimension of the subsystem). Also, p has a relation with the entanglement between the stretching-stretching and bending vibrations.

For these three molecules, the decoherence processes are considered for the initial states $|\psi_{ss}(0)\rangle = |0,1\rangle$, $|1,1\rangle$, $|0,0\rangle + |1,1\rangle$, and $|0,1\rangle + |1,0\rangle$ (the normalization constant is neglected) for different bending states. The results of the loss of purity p are plotted in Fig. 5.

Except for the initial entangled state $|0,0\rangle + |1,1\rangle$, the purity for the other three states fluctuate regularly with high value of purity, which indicates that the influence of the bending vibration on the decoherence of stretching-stretching qubits is not obvious. By comparing the behaviors of purity of the three molecules, it is shown that the generation of decoherence of the normal-mode molecules is much faster than that of the local-mode molecules. We find that the state of stretching-stretching qubits can recover to pure (purification) with stable periods for the states of $|0,1\rangle$, $|1,1\rangle$, and $|0,1\rangle + |1,0\rangle$.

Also, our more numerical calculation shows that the higher the excitation of bending vibrations, the more obvious the decoherence of molecular stretching-stretching (the details of our calculations is not shown here). The purification time, however, is not changed. Based on this property, the purification time could be thought of as one character quantity,

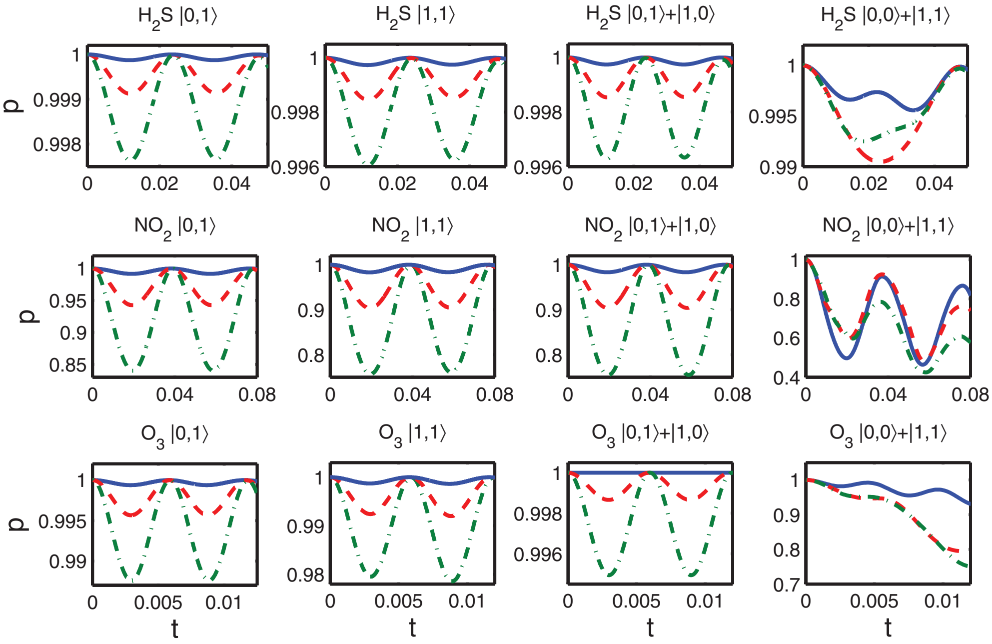

FIG. 5. (Color online) Purity of the stretching-stretching qubits system for three molecules: H_2S, NO_2, and O_3. Different initial excitation in bending vibration is labeled using blue solid lines ($v_b = 0$), red dashed lines ($v_b = 1$), and green dash-dotted lines ($v_b = 2$). t is in ps.

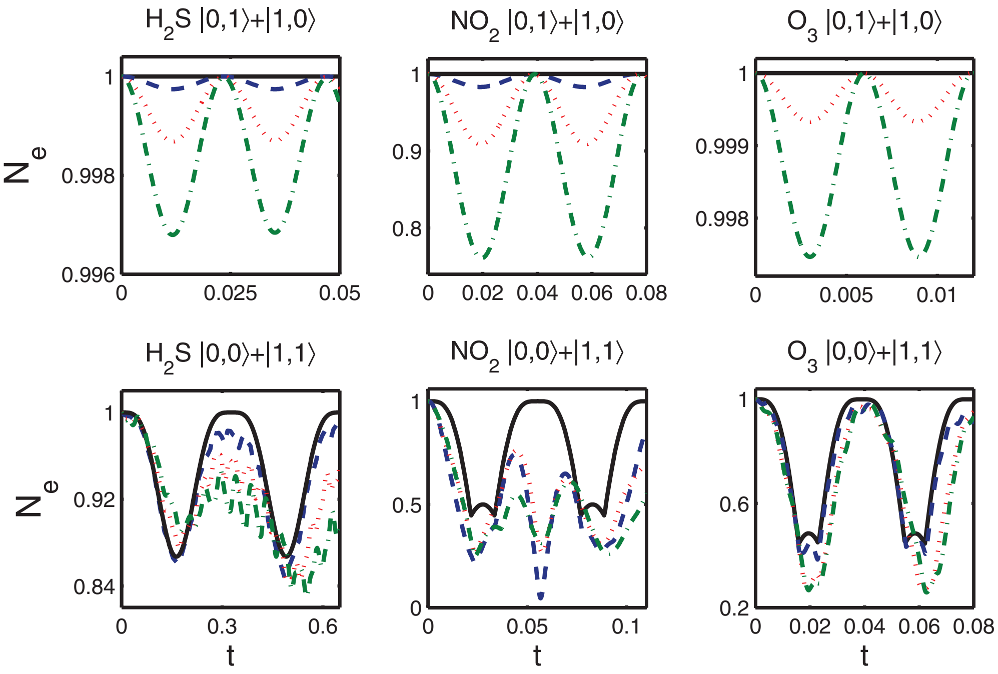

FIG. 6. (Color online) Negativity of the stretching-stretching qubit system for three molecules. Negativity with bending restricted to its ground state is labeled using black lines. Different initial excitation in bending vibration is labeled using dashed blue lines ($v_b = 0$), dotted red lines ($v_b = 1$), and dash-dotted green lines ($v_b = 2$). t is in ps.

and it may have important implications in quantum computing, such as the design of quantum logic operation.

However, for the state $|0,0\rangle + |1,1\rangle$, the evolution of purity is not periodic and exhibits more obvious decoherence than the other states. We have examined this for long-time evolution of this state. The results represent that purity shows the periodical behavior on long-time scale, but the purification time goes to infinity.

B. Robustness of entanglement of stretching-stretching qubits against bending vibration

In this section, we investigate the entanglement between two stretching vibrational modes when the initial states of the stretching-stretching qubits are the entangled states. As examples, we consider the initial states: $|0,1\rangle + |1,0\rangle$ and $|0,0\rangle + |1,1\rangle$. Since the stretching-stretching density is in a mixed state, we use negativity to represent the entanglement between two stretching vibrational modes. The negativity of $\rho_{\mathrm{ss}}(t)$ is defined by [29]

$$\mathcal{N}_e(t) = 2\max(0, -\mu_{\min}), \tag{20}$$

where $\mu_{\min}$ is the minimum value of the eigenvalues of the partial transpose of ρ_{ss}, and the partial transpose is given by

$$\rho_{\mathrm{ss}\,i\alpha,j\beta}^{T_2}(t) = \rho_{\mathrm{ss}\,i\beta,j\alpha}(t), \tag{21}$$

where T_2 is representing the partial transpose for the second subsystem.

In Fig. 6, the negativities for these three molecules are plotted. The bending vibration is initially prepared in ground and two excited states.

For the initial state $|0,1\rangle + |1,0\rangle$, when bending vibration is restricted to its ground state, energy will not exchange between bonds, and the negativity keeps its maximum value during vibration. But when the bending vibration is released, energy can transfer between bonds with the help of bending vibration. Correspondingly, the entanglement will change with energy. As shown in Fig. 6, the negativity shows the periodic behavior, similar with purity in Fig. 5. A stable period of entanglement recovering back to its maximum value is found, and the period is not affected by the different excitation of the bending vibration. It should be noted that for O_3, the negativity also maintains the maximum value when $v_b = 0$. The decay time of entanglement of the local-mode molecule is much longer than the normal-mode molecules, which indicates the robustness of the stretching-stretching entanglement of the local-mode molecule is better than that of the normal-mode molecule.

For the initial state $|0,0\rangle + |1,1\rangle$, energy can exchange between bonds when bending vibration is restricted and the evolution of negativity shows nice periodicity. But when the bending is released, as shown in Fig. 6, the dynamical behavior of the negativity becomes irregular. For the normal-mode molecules, entanglement decreases at a faster rate.

V. CONCLUSION

In this paper, we discuss the intramolecular energy transfer, entanglement between two stretching vibrational modes, and the decoherence process of the stretching-stretching qubit system caused by the bending vibration in the triatomic molecules. We here select the local-mode molecule H_2S and normal-mode molecules NO_2 and O_3 as the models to investigate the dynamical difference between different types of molecules.

When the bending vibration is restricted, we studied the dynamical properties of entanglement between two stretching vibrational modes and the correlations with the intramolecular energy transfer. The results show that the generation of entanglement is closely related to the energy transfer of the low excited states. Some issues of entanglement generation are considered in Refs. [38,39]. Because IVR has a role in the molecular process, many experimental techniques to examine IVR have developed, such as dispersed fluorescence, molecular beam techniques, and the transient absorption spectroscopy [40–42]. Also, the experimental realization of a common paradigm for quantum entanglement has already been established [43]. As a result, the relationship between dynamical entanglement and intramolecular energy transfer can be tested using modern experimental methods. It should be noted that there exists difficulty in creating the entangled states in molecular quantum computing; for example, in some cases unexpected states could be introduced [44]. The close relation between dynamical entanglement and energy transfer could be helpful in generating entangled states. The maximum entangled states can be obtained by controlling the energy distribution. Moreover, we have also found that entanglement of local-mode characteristic states of the local-mode molecule can survive for a long time. Since the preparation of local-mode characteristic states has been studied theoretically, it will be possible to prepare the long-lived entangled states in molecular systems using the methods of direct vibrational excitation, such as Franck-Condon pumping via an electronic excitation, and two-step pumping [42,45].

For the bipartite qubit system of two stretching modes, we find that when the system is in the initial states of $|0,1\rangle$, $|1,1\rangle$, and $|0,1\rangle + |1,0\rangle$, the influence from bending is not obvious, which indicates that the two stretching vibrations would be suitable to construct the qubits. But, for some special initial states, the decoherence process and decay of entanglement are significant. In practice, to minimize the effects of decoherence in the molecular systems, the method of dynamical control of the coupling between vibrational modes of interest and remaining vibrational modes has been proposed [46]. And recently it has been suggested that the quantum logic operation can be tailored by considering the influence from the remaining rovibrational modes [47]. Therefore, the dynamical features of purity and entanglement of the interested vibrations, such as the stable time of entanglement recovering to its maximum value and purification time, can be used in the process of designing quantum logic operations and dynamical control of entanglement.

The comparison of the decoherence process and the robustness of entanglement against the bending vibration shows that the purity and entanglement of stretching-stretching vibrations are more stable for local-mode molecules than normal-mode molecules. In this sense, as a candidate system with potential applications in quantum computations, the local-mode molecules with low-value locality parameters could be a wise choice.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation of China (Grants No. 91021009 and No. 10874102).

[1] R. de Vivie-Riedle and U. Troppmann, Chem. Rev. **107**, 5082 (2007).

[2] C. M. Tesch and R. de Vivie-Riedle, Phys. Rev. Lett. **89**, 157901 (2002).

[3] T. Cheng and A. Brown, J. Chem. Phys. **124**, 034111 (2006).

[4] L. K. McKemmish, R. H. McKenzie, N. S. Hush, and J. R. Reimers, J. Chem. Phys. **135**, 244110 (2011).

[5] Y. Liu, Y. Zheng, W. Ren, and S. Ding, Phys. Rev. A **78**, 032523 (2008).

[6] X. W. Hou, J. H. Chen, and Z. Q. Ma, Phys. Rev. A **74**, 062513 (2006).

[7] X. W. Hou, J. Huang, and M. F. Wan, Phys. Rev. A **85**, 044501 (2012).

[8] K. Mishima and K. Yamashita, Int. J. Quantum Chem. **109**, 1827 (2009).

[9] M. Shapiro and P. Brumer, *Principles of the Quantum Control of Molecular Processes* (Wiley, New York, 2003).

[10] W. H. Zurek, arXiv:quant-ph/0306072.

[11] T. Yu and J. H. Eberly, Science **323**, 598 (2009).

[12] H. Fujisaki, Phys. Rev. A **70**, 012313 (2004).

[13] O. S. van Roosmalen, F. Iachello, R. D. Levine, and A. E. L. Dieperink, J. Chem. Phys. **79**, 2515 (1983).

[14] F. Iachello and R. D. Levine, *Algebraic Theory of Molecules* (Oxford University Press, New York, 1995).

[15] F. Iachello and S. Oss, Eur. Phys. J. D **19**, 307 (2002).

[16] S. Ding and Y. Zheng, J. Chem. Phys. **111**, 4466 (1999).

[17] Y. Zheng and S. Ding, Int. J. Quantum Chem. **108**, 1059 (2008).

[18] Y. Zheng and S. Ding, Phys. Rev. A **64**, 032720 (2001).

[19] H. Feng, Y. Liu, Y. Zheng, S. Ding, and W. Ren, Phys. Rev. A **75**, 063417 (2007).

[20] B. G. Wybourne, *Classical Groups for Physicists* (Wiley, New York, 1974).

[21] Y. Zheng and S. Ding, Chem. Phys. **255**, 217 (2000).

[22] Y. Zheng and S. Ding, Phys. Lett. A **256**, 197 (1999).

[23] J. M. Hollas, *Modern Spectroscopy* (Wiley, New York, 1996).

[24] S. Hill and W. K. Wootters, Phys. Rev. Lett. **78**, 5022 (1997).

[25] O. Osenda and P. Serra, Phys. Rev. A **75**, 042331 (2007).

[26] V. S. Malinovsky and I. R. Sola, Phys. Rev. Lett. **96**, 050502 (2006).

[27] C. H. Bennett, D. P. DiVincenzo, J. A. Smolin, and W. K. Wootters, Phys. Rev. A **54**, 3824 (1996).

[28] V. Vedral, M. B. Plenio, M. A. Rippin, and P. L. Knight, Phys. Rev. Lett. **78**, 2275 (1997).

[29] B. Kraus, J. I. Cirac, S. Karnas, and M. Lewenstein, Phys. Rev. A **61**, 062302 (2000).

[30] S. Bose and V. Vedral, Phys. Rev. A **61**, 040101 (2000).

[31] K. Furuya, M. C. Nemes, and G. Q. Pellegrino, Phys. Rev. Lett. **80**, 5524 (1998).

[32] M. O. Scully and M. S. Zubairy, *Quantum Optics*, 1st ed. (Cambridge University Press, Cambridge, England, 1997).

[33] K. Mishima and K. Yamashita, Chem. Phys. **367**, 63 (2010).

[34] J. S. Hutchinson, E. L. Sibert, III, and J. T. Hynes, J. Chem. Phys. **81**, 1314 (1984).

[35] M. Gruebele, Theo. Chem. Acc. **109**, 53 (2007).

[36] D. Weidinger and M. Gruebele, Mol. Phys. **105**, 1999 (2007).
[37] J. N. Bandyopadhyay, Europhys. Lett. **85**, 50006 (2009).
[38] P. A. Miller and S. Sarkar, Phys. Rev. E **60**, 1542 (1999).
[39] H. Fujisaki, T. Miyadera, and A. Yanaka, Phys. Rev. E **67**, 066201 (2003).
[40] D. Boyall and K. L. Reid, Chem. Soc. Rev. **26**, 223 (1997).
[41] R. S. von Benten and B. Abel, Chem. Phys. **378**, 19 (2010).
[42] D. J. Nesbitt and R. W. Field, J. Phys. Chem. **100**, 12735 (1996).
[43] S. Chaudhury, A. Smith, B. E. Anderson, S. Ghose, and P. S. Jessen, Nature **461**, 768 (2009).
[44] K. Mishima, K. Shioya, and K. Yamashita, Chem. Phys. Lett. **442**, 58 (2007).
[45] T. A. Holme and J. S. Hutchinson, Chem. Phys. Lett. **124**, 181 (1986).
[46] G. Kurizki, A. G. Kofman, D. Petrosyan, and T. Opatrný, J. Opt. B: Quantum Semiclass. Opt. **4**, S294 (2002).
[47] M. Schroder and A. Brown, J. Chem. Phys. **131**, 034101 (2009).