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## Entropy, energy and negativity in Fermi-resonance coupled states of substituted methanes

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### Abstract

Several measures of entanglement have attracted considerable interest in the relationship of a measure of entanglement with other quantities. The dynamics of entropy, energy and negativity is studied for Fermi-resonance coupled vibrations in substituted methanes with three kinds of initial mixed states, which are the mixed density matrices of binomial states, thermal states and squeezed states on two vibrational modes, respectively. It is demonstrated that for mixed binomial states and mixed thermal states with small magnitudes the entropies of the stretch and the bend are anti-correlated in the same oscillatory frequency, so do the energies for each kind of state with small magnitudes, whereas the entropies exhibit positive correlations with the corresponding energies. Furthermore, for small magnitudes quantum mutual entropy is positively correlated with the interacting energy. Analytic forms of entropies and energies are provided with initial conditions in which they are stationary, and the agreement between analytic and numerical simulations is satisfactory. The dynamical entanglement measured by negativity is examined for those states and conditions. It is shown that negativity displays a sudden death for mixed binomial states and mixed thermal states with small magnitudes, and the time-averaged negativity has the minimal value under the conditions of stationary entropies and energies. Moreover, negativity is positively correlated with the mutual entropy and the interacting energy just for mixed squeezed states with small magnitudes. Those are useful for molecular quantum information processing and dynamical entanglement.

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## 1. Introduction

In recent years, quantum entropy has been studied extensively due to its central role in quantum information theory [1]. In a typical scenario, the partial entropy of a bipartite system has been discussed in various subjects such as in two-mode Bose–Einstein condensates [2–5] and two stretching vibrations in small polyatomic molecules [6]. One of the important properties in the former cases [2–5] is that the model parameter can be varied for many behaviors of the von Neumann entropy or the linear entropy. Hence, the maximal entropy can be achieved with nonlinear interactions [5]. It is shown that the von Neumann entropy can be taken as an indicator of normal-to-local transitions in molecular vibrations [6]. Those studies [2–6] concentrate on the linear entropy and the von Neumann entropy for a pure state in an integrable quantum system with 1:1 resonance coupling between two modes.

In the present work we will investigate not only the entropy of an individual subsystem but also the entropy correlations between the two subsystems for three kinds of mixed states in an important spectroscopic Hamiltonian based on experimental spectra of substituted methanes, where the bending and the stretching modes are coupled by 2:1 Fermi-resonance. This resonance was named after Fermi [7] since he initially introduced it for the description of an anomalous infrared spectrum of CO<sub>2</sub>, in which the symmetric CO stretching mode is strongly interacted with the first overtone of the O–C–O bending mode. Fermi-resonances are nowadays playing a remarkable role in the understanding of complex experimental situations [8–12] as well as in the mechanism of intramolecular vibrational energy redistribution [13]. In addition, the targeted energy transfer by Fermi-resonance or harmonic resonance in a pure theoretical model for two nonlinear oscillators has been studied in classical and quantum mechanics [14], where analytic conditions for complete energy exchange are explicated for an initial pure state. Here we study the energy of each vibrational mode and the correlations between entropy and energy for mixed states in substituted methanes.

On the other hand, there are various measures of entanglement in the literature. Negativity based on the Peres–Horodecki criterion [15] is an entanglement monotone [16], and it serves as an upper bound of quantum teleportation capacity [16]. The physical meaning of negativity is, however, not transparent in general for its abstract mathematical definition. Recent attention has been paid to the relationship of negativity with other quantities [17, 18, 20–23]. The analytical expression of maximal entanglement versus entropy shows that the forms of maximally entangled mixed states can change discontinuously at a specific value of von Neumann entropy for mixed states in two-qubit systems [17]. A relationship between negativity and uncertainty products has been constructed for asymmetric two-mode Gaussian states [18]. For a mixed state in qudits the entanglement of formation [19] is anti-correlated with the participation ratio defined by  $1/\text{Tr}(\rho^2)$  for a density matrix  $\rho$ , whereas it is strongly correlated with negativity [20]. A comparative study of the relative entropy and negativity for two-qubit pure and mixed states demonstrates that there are mixed states exhibiting the relative entropy for a given negativity in some range higher than for pure states [21]. The entanglement dynamics of a mixed state has been discussed for other models [22, 23]. It is shown that some factors including entanglement, classical correlations and entropy affect the time evolution of mixed states in a bipartite two-level system with two spins in magnetic fields [23]. It is thus of interest to explore the dynamics of negativity and its correlations with entropy and energy for mixed states in substituted methanes from experimental spectra.

This paper is organized as follows. Section 2 presents the Hamiltonian for anharmonic vibrations based on experimental spectra of substituted methanes. Section 3 is devoted to calculating the von Neumann entropy and the energy of the stretching (bending) mode for three kinds of initial mixed states. Thereby the dynamical correlations among entropies and

**Table 1.** Fit parameters ( $\text{cm}^{-1}$ ) in the spectroscopic Hamiltonian.

	$\omega_s$	$\omega_b$	$X_{ss}$	$X_{bb}$	$X_{sb}$	$K_{sbb}$
CHD <sub>3</sub>	3047.04	1293.35	-55.91	-4.49	-22.12	-25.84
CH(CF <sub>3</sub> ) <sub>3</sub>	3042.8	1356.4	-56.9	-0.32	-14.0	-65.5
CHCl <sub>3</sub>	3093.8	1235.6	-63.7	-15.6	-21.2	-71.1
CHF <sub>3</sub>	3079.8	1377.8	-61.7	-6.5	-28.6	-106.1

energies are discussed, and quantum mutual entropy is calculated as well. Initial conditions for stationary entropies and energies are obtained analytically. Section 4 studies the dynamical entanglement measured by negativity and its correlation with entropy and energy. The conclusion with discussions is given in section 5.

## 2. Hamiltonian

An effective and yet simple Hamiltonian has been proposed for the understanding of all of the major bands with a considerable insight into the nature of the stretch-bend vibrations in substituted methanes, that is, CHD<sub>3</sub>, CH(CF<sub>3</sub>)<sub>3</sub>, CHCl<sub>3</sub> and CHF<sub>3</sub>. The Hamiltonian has the following form [8–11]:

$$H = H_0(v_s, v_b) + K_{sbb}(a_s^\dagger a_b a_b + a_s a_b^\dagger a_b^\dagger), \quad (1)$$

where  $H_0(v_s, v_b) = \omega_s(v_s + \frac{1}{2}) + \omega_b(v_b + 1) + X_{ss}(v_s + \frac{1}{2})^2 + X_{bb}(v_b + 1)^2 + X_{sb}(v_s + \frac{1}{2})(v_b + 1)$  is the diagonal Hamiltonian, the last term in equation (1) is the non-diagonal Hamiltonian,  $v_{s(b)}$  is the quantum number on the stretching (bending) mode, indices  $s$  and  $b$  stand for the degree of freedom on stretching and bending vibrations, respectively,  $a_i$  and  $a_i^\dagger$  ( $i = s, b$ ) are the annihilation and creation operators on mode  $i$ ,  $\omega_i$  are the so-called zeroth-order vibrational frequencies (harmonic parameters),  $X_{ss}$ ,  $X_{bb}$ ,  $X_{sb}$  and  $K_{sbb}$  are the anharmonic parameters and  $K_{sbb}$  describes the Fermi-resonance interaction between the stretch and the bend. Fermi-resonance couples the CH-stretching and bending states that have fairly similar energies such as  $|v_s, v_b = 0\rangle$ ,  $|v_s - 1, 2\rangle$ ,  $|v_s - 2, 4\rangle$ ,  $\dots$  because the bending fundamental is about half the wave number of the stretching fundamental in those molecules. The values of the parameters obtained in the least squares fit to the spectra of CHD<sub>3</sub> [8], CH(CF<sub>3</sub>)<sub>3</sub> [9], CHCl<sub>3</sub> [10] and CHF<sub>3</sub> [11] are reproduced in table 1 for convenience. It is seen that anharmonic interactions ( $X_{ss}$ ,  $X_{bb}$ ,  $X_{sb}$  and  $K_{sbb}$ ) are important for highly excited vibrations in these molecules. According to the values of  $K_{sbb}$ , one can regard Fermi coupling as weak in CHD<sub>3</sub> and strong in CHF<sub>3</sub>. Using those parameters, Xiao and Kellman have analyzed the phase space structure and the catastrophe map classification of vibrational spectra [24]. The extension of equation (1) to include all vibrational modes becomes a useful model for the description of the highly excited vibrational spectra of polyatomic molecules [25]. Details for theories of molecules are referred to [26]. In the next section we consider the dynamical correlation between entropy and energy for various initial states in these molecules.

## 3. Entropy and energy

In order to examine the dynamics of entropy and energy correlations between the stretching and bending modes of substituted methanes, we choose the following three kinds of initial mixed

states: mixed binomial states (MBSs), mixed thermal states (MTSs) and mixed squeezed states (MSSs). The mixed density matrices of initial states in full system is taken to be

$$\rho_{sb}(0) = \rho_s(0) \otimes \rho_b(0), \quad (2)$$

where  $\rho_i(0) = \sum_{v_i=0} P_A(v_i, \bar{v}_i) |v_i\rangle \langle v_i|$  is the initial density matrix of mode  $i$ . The subscript  $A = B, T$  and  $S$  respectively represent binomial states, thermal states and squeezed states on mode  $i$  with the coefficients being [27]

$$P_B(v_i, \bar{v}_i) = \frac{N_i!}{(N_i - v_i)! v_i!} q_i^{v_i} (1 - q_i)^{N_i - v_i}, \quad (3)$$

$$P_T(v_i, \bar{v}_i) = \frac{1}{1 + \bar{v}_i} \left[ \frac{\bar{v}_i}{1 + \bar{v}_i} \right]^{v_i}, \quad (4)$$

$$P_S(v_i, \bar{v}_i) = \begin{cases} \frac{v_i!}{[(v_i/2)!]^2 \cosh r} \left[ \frac{\tanh r}{2} \right]^{v_i}, & v_i \text{ even,} \\ 0, & v_i \text{ odd,} \end{cases} \quad (5)$$

where  $N_i = \frac{\bar{v}_i}{q_i}$ ,  $0 < q_i < 1$ ,  $r = \text{arcsinh} \sqrt{\bar{v}_i}$  and  $\bar{v}_i$  is the average quantum number on the mode  $i$  that will be taken as a parameter in what follows. In the simulation of entropy and energy dynamics we cut the set of Fock states that consists of the corresponding distribution at some  $v_i$  with  $\sum_{v_i=0}^{v_i} P_A(v_i, \bar{v}_i) \simeq 1$ . The obtained results are further tested by adding more Fock states to that distribution to see whether they are changed. It should be remarked that those states can be realizable in experiments since the hybrid of field-free molecular eigenstates [28] is created by turning on a picosecond laser pulse adiabatically.

We are interested in the entropy of the mode  $i$  given by the von Neumann entropy [29]

$$S_{s(b)}(t) = -\text{Tr}[\rho_{s(b)}(t) \ln \rho_{s(b)}(t)], \quad (6)$$

where  $\rho_{s(b)}(t) = \text{Tr}_{b(s)} \rho_{sb}(t)$  is the reduced-density matrix. The purity of mode  $s(b)$  is given by  $\text{Tr} \rho_{s(b)}^2(t)$ . Thus, an increase in the von Neumann entropy is parallel to a decrease in purity. The entropy of mode  $s(b)$  can be described in terms of the linear entropy

$$s_{s(b)}(t) = 1 - \text{Tr} \rho_{s(b)}^2(t). \quad (7)$$

Both entropies have the same trend for a bipartite system [30] so that the results of the von Neumann entropy are presented below. Nevertheless, it is much easier to obtain the linear entropy analytically in some cases. The full density matrix governed by equation (1) evolves in time with the Liouville equation:

$$\dot{\rho}_{sb}(t) = -i[H, \rho_{sb}(t)]. \quad (8)$$

For the energy of a subsystem we consider the mean value of the relevant restriction of the free Hamiltonian:

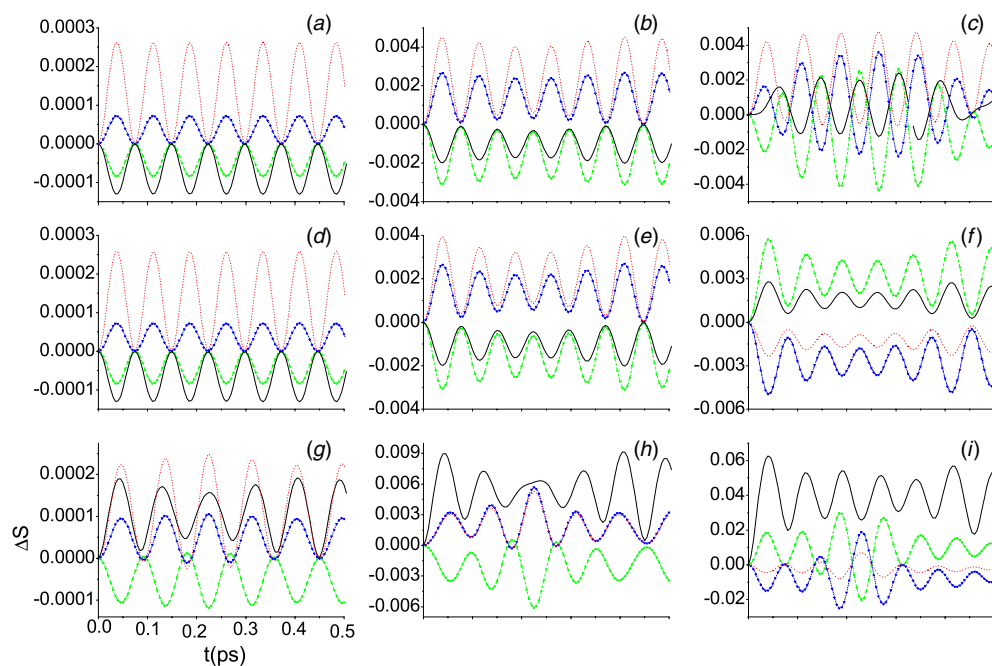
$$E_{s(b)}(t) = \text{Tr}[\rho_{sb}(t) H_{s(b)}], \quad (9)$$

where

$$H_s = \omega_s \left( v_s + \frac{1}{2} \right) + X_{ss} \left( v_s + \frac{1}{2} \right)^2, \quad (10)$$

$$H_b = \omega_b (v_b + 1) + X_{bb} (v_b + 1)^2. \quad (11)$$

Figure 1 shows the changes ( $\Delta S = S(t) - S(0)$ ) of the stretching and bending subsystem entropies for CHD<sub>3</sub> in these states with magnitudes  $(\bar{v}_s, \bar{v}_b)$  taken to be (0.003, 0.001), (0.1, 0.1) and (0.2, 0.9), as examples, where the value of  $q$ ,  $q = q_s = q_b$  for simplicity, in the



**Figure 1.** Entropy changes ( $\Delta S = S(t) - S(0)$ ) of the stretch (solid line) and the bend (dotted line) and energy changes ( $\Delta E = E(t) - E(0)$ ) divided by  $800 \text{ cm}^{-1}$  of the stretch (dashed line with  $\circ$ ) and the bend (short dashed line with  $\nabla$ ) in  $\text{CHD}_3$  for MBSs (a), (b) and (c), MTSs (d), (e) and (f) and MSSs (g), (h) and (i) with magnitudes  $(\bar{v}_s, \bar{v}_b) = (0.003, 0.001)$  (a), (d) and (g),  $(0.1, 0.1)$  (b), (e) and (h) and  $(0.2, 0.9)$  (c), (f) and (i), where the value of  $q$  in MBSs is set to  $0.001$  (a),  $0.02$  (b) and  $0.1$  (c).

binomial states is set to be  $0.001$ ,  $0.02$  and  $0.1$ , respectively. The changes ( $\Delta E = E(t) - E(0)$ ) of subsystem energies divided by  $800 \text{ cm}^{-1}$  are plotted in figure 1 for comparison. Similar figures for  $\text{CH}(\text{CF}_3)_3$ ,  $\text{CHCl}_3$  and  $\text{CHF}_3$  are available upon request. For small magnitudes  $(\bar{v}_s, \bar{v}_b) = (0.003, 0.001)$ , the evolution of entropies and energies is regular with a nice periodicity that will be analytically explained in what follows. As the magnitudes increase, the maximal entropy or energy increases and the fluctuation of entropies and energies becomes more irregular. That agrees with the result of the partial entropy observed in other models [4–6, 22]. Here we would like to discuss figure 1 in detail and mention the key difference in entropy and energy among these molecules.

We analyze the correlations of entropies. Two qualitatively different correlations are found in figure 1. The first type of correlation is a case where both quantities go up and down together, and the second type of correlation is a case where they are anti-correlated, that is, one quantity increases with time while another decreases or vice versa. It is clearly shown that for MBSs and MTSs with small magnitudes  $(\bar{v}_s, \bar{v}_b) = (0.003, 0.001)$  both entropies are anti-correlated in the same oscillatory frequency, which can be interpreted in terms of the following analytic form for the linear entropy:

$$s_s(t) = -2y_1(z_1 - z_2)[\cos(\Omega_1 t) - 1], \quad (12)$$

$$s_b(t) = 2y_1(z_3 - z_4)[\cos(\Omega_1 t) - 1], \quad (13)$$

where  $y_1 = a_1[p(0, 2) - p(1, 0)]$  with  $a_1 = \frac{K_{sbb}^2}{\Omega_1^2}$  and  $p(v_s, v_b) = P_A(v_s, \bar{v}_s)P_A(v_b, \bar{v}_b)$ ,  $\Omega_1^2 = [H_0(0, 2) - H_0(1, 0)]^2 + 2K_{sbb}^2$ ,  $z_1 = p(0, 0) + p(0, 1) + a_1p(1, 0) + b_1p(0, 2)$ ,  $z_2 = (1 + a_1)p(0, 2) + a_2p(2, 0) + b_1p(1, 0) + b_2p(1, 2)$ ,  $z_3 = p(0, 0) + a_1p(0, 2) + a_2p(1, 2) + b_1p(1, 0) + b_2p(2, 0)$ , and  $z_4 = p(2, 2) + a_1p(1, 0) + a_2p(2, 0) + b_1p(0, 2) + b_2p(1, 2)$  with  $a_2 = \frac{2K_{sbb}^2}{\Omega_2^2}$ ,  $b_1 = \frac{[H_0(0, 2) - H_0(1, 0)]^2 + \Omega_1^2}{2\Omega_1^2}$  and  $b_2 = \frac{[H_0(1, 2) - H_0(2, 0)]^2 + \Omega_2^2}{2\Omega_2^2}$  with  $\Omega_2^2 = [H_0(1, 2) - H_0(2, 0)]^2 + 4K_{sbb}^2$ . With those formulas it is easy to find out that the period ( $2\pi/\Omega_1$ ) of entropic oscillations is determined by molecular intrinsic properties, that is, the difference in energies  $H_0(0, 2) - H_0(1, 0)$  and the Fermi parameter  $K_{sbb}$ , while the oscillatory amplitude is governed by molecular intrinsic properties as well as initial conditions  $p(v_s, v_b)$ . Using the parameters in table 1, we know that the period of entropic oscillations in  $\text{CH}(\text{CH}_3)_3$  is the longest while that in  $\text{CHCl}_3$  is the shortest with the amplitude being the largest in  $\text{CHF}_3$  and the smallest in  $\text{CHD}_3$ . In addition, the amplitude of the entropic oscillation in the stretching mode is smaller than that in the bending mode in these molecules. The entropic evolutions are quite similar for both states since the difference in  $p(v_s, v_b)$  between MBSs and MTSs is very small. The anti-correlation remains with the increasing of the magnitudes  $\bar{v}_s$  and  $\bar{v}_b$ , as shown in figures 1(b) and (e). When the magnitudes increase further, anti-correlation or positive correlation between both entropies occurs in an irregular manner (see figure 1(c) as an example). That is because equations (12) and (13) are based on a simplified model with a few states. For large magnitudes more states are needed for the corresponding distribution  $\sum P_A(v_i, \bar{v}_i) \simeq 1$ .

For MSSs with small magnitudes  $(\bar{v}_s, \bar{v}_b) = (0.003, 0.001)$  in figure 1(g), the correlation of entropies is dominantly positive with different oscillatory frequency. In this case the entropy of the stretching mode is still given by equation (12) while that of the bending mode is

$$s_b(t) = 2y_2(z_3 - z_4)[\cos(\Omega_2 t) - 1], \quad (14)$$

where  $y_2 = a_2[p(1, 2) - p(2, 0)]$ . Both entropies of equations (12) and (14) are dominantly anti-correlated, suggesting that the entropy correlation strongly depends on the initial states. It should be mentioned that the entropy correlation is of importance for the description of critical phenomena [31].

We discuss the correlations of energies. For three kinds of mixed states with small magnitudes  $(\bar{v}_s, \bar{v}_b) = (0.003, 0.001)$  both energies are given by

$$E_s(t) = -y_1(\omega_s + X_{ss})[\cos(\Omega_1 t) - 1], \quad (15)$$

$$E_b(t) = y_1(2\omega_b + 4X_{bb})[\cos(\Omega_1 t) - 1], \quad (16)$$

for MBSs and MTSs, and

$$E_s(t) = -y_2(\omega_s + 3X_{ss})[\cos(\Omega_2 t) - 1], \quad (17)$$

$$E_b(t) = y_2(2\omega_b + 4X_{bb})[\cos(\Omega_2 t) - 1], \quad (18)$$

for MSSs, where initial energies have been removed. The analytic forms of equations (15)–(18) clearly show that both energies are anti-correlated in the same frequency for three kinds of mixed states with the oscillatory amplitude being the largest in  $\text{CHF}_3$ . The amplitude of energy oscillation in the stretching mode is larger than that in the bending. As the magnitudes increase, anti-correlation between both energies is dominant with the amplitude of fluctuations. That is due to the reason mentioned above. It should be pointed out that in small magnitudes  $(\bar{v}_s, \bar{v}_b) = (0.003, 0.001)$  numerical simulations have also been compared with the analytic calculations of entropies and energies, and the agreement is essentially perfect.

We study the correlation between entropies and energies. For the considered states most entropies of the stretching (bending) mode are positively correlated with the corresponding energies. The smaller the magnitudes in MBSs and MTSs, the more distinct such correlations, shown in figures 1(a) and (d). However, for MSSs with a small magnitudes the entropy of the stretching mode is dominantly anti-correlated with the energy, as shown in figures 1(g) and (h). It is noted that the entropy and the energy of the bending mode have almost the same behavior of evolution in figure 1(h). Those imply that the correlations between the entropy and energy strongly depend on an initial state and a subsystem. That is helpful to understand information and energy transfer in molecules and other models [14, 30, 32].

In order to quantitatively study the entropy correlations, we compute quantum mutual entropy, also called the correlation index, which indicates the entropy shared between two modes. It should be remarked that in classical information theory the mutual entropy is an important quantity to analyze the communication processes and physical transformations. Similarly, the quantum mutual entropy is of importance in quantum information processing [30, 33] as well as in the study of the physics in general many-body systems [31]. Quantum mutual entropy is defined by [33]

$$S_m = S_s + S_b - S_{sb}, \quad (19)$$

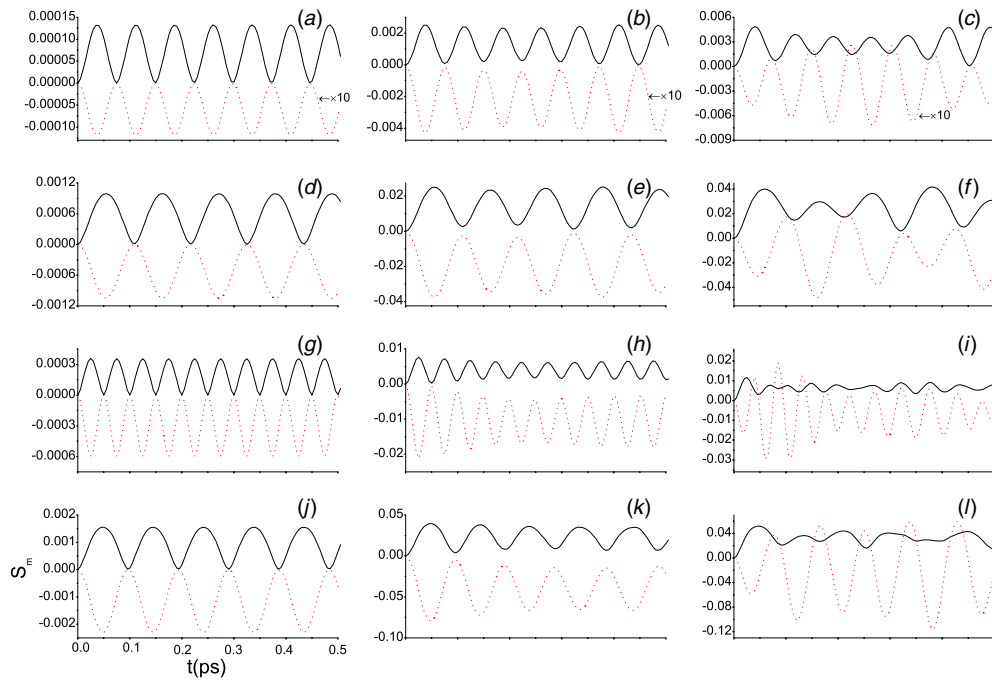
where  $S_s$  and  $S_b$  are the von Neumann entropy of the stretch and the bend, respectively, and  $S_{sb}$  is the von Neumann entropy of the full system. Entropy  $S_{sb}$  is a constant for the Hamiltonian evolution governed by equation (1). It should be mentioned that for a pure state  $S_s(t) = S_b(t)$  and  $S_m(t) = 0$  [33]. Thus, the von Neumann entropy of a subsystem becomes a good measure of entanglement only for a pure state [2–6]. It should be noted that for a mixed state both the von Neumann entropy and the mutual entropy are not an entanglement measure. To quantify the entanglement of a mixed state, one can choose negativity [15, 16]. The entanglement dynamics described by negativity for mixed states in those molecules will be discussed in section 4.

Figures 2–4 show the mutual entropies in these molecules for MBSs, MTSs and MSSs, respectively, where the sum of corresponding energies  $E_s$  and  $E_b$  is plotted for comparison. For each state with small magnitudes  $(\bar{v}_s, \bar{v}_b) = (0.003, 0.001)$  the mutual entropies are anti-correlated with the sums of both energies in a good periodicity, where the period in  $\text{CH}(\text{CH}_3)_3$  is still the longest while that in  $\text{CHCl}_3$  is the shortest, which can be explained in terms of above formulas (equations (12)–(18)) for each entropy and energy. Such a correlation remains as both magnitudes increase up to 0.1. This implies that the mutual entropy is positively correlated with the interaction energy between two modes, since the total energy is also a constant for a given state in the Hamiltonian evolution. For MBSs with magnitudes  $(\bar{v}_s, \bar{v}_b) = (0.2, 0.9)$  the anti-correlation between the mutual entropy and the sum of both energies is dominant in  $\text{CHD}_3$  and  $\text{CH}(\text{CH}_3)_3$  (figures 2(c) and (f)) while the positive-correlation or anti-correlation occurs in an irregular manner in  $\text{CHCl}_3$  and  $\text{CHF}_3$  (figures 2(i) and (l)). However, for MTSs and MSSs with  $(\bar{v}_s, \bar{v}_b) = (0.2, 0.9)$  the correlation between the mutual entropy and the sum of both energies is dominantly positive in those molecules, as shown in figures 3 and 4(c), (f), (i) and (l). This indicates that for a large magnitude such a correlation depends on an initial state and a molecule.

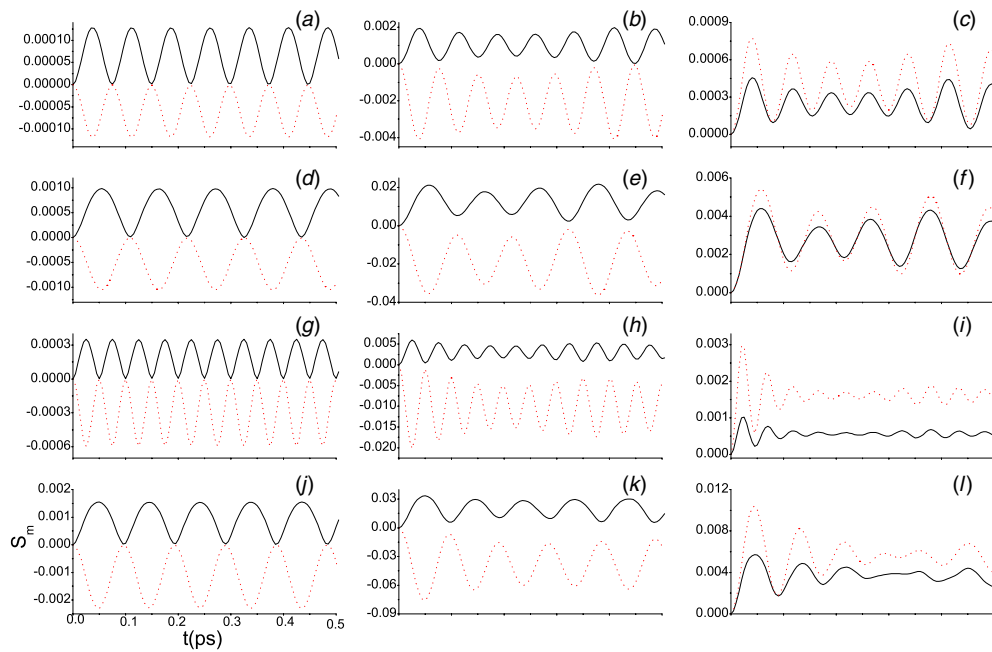
Finally, according to the above analytical forms (equations (12)–(18)), we obtain the common conditions under which the amplitude of entropies and energies reduces to zero, that is,  $K_{sbb} = 0$  or  $p(1, 0) = p(2, 0)$ . The latter leads to the following initial conditions:

$$\frac{1 - q_s}{N_s q_s} = \frac{2(1 - q_b)^2}{N_b(N_b - 1)q_b^2}, \quad (20)$$





**Figure 2.** Quantum mutual entropy  $S_m$  (solid line) and the sum (dotted line) of two energies  $E_s$  and  $E_b$  in  $\text{CHD}_3$  (a), (b) and (c),  $\text{CH}(\text{CH}_3)_3$  (d), (e) and (f),  $\text{CHCl}_3$  (g), (h) and (i), and  $\text{CHF}_3$  (j), (k) and (l) for MBSs with the same magnitudes as in the corresponding figure 1.



**Figure 3.** Same as in figure 2 but for MTSSs.

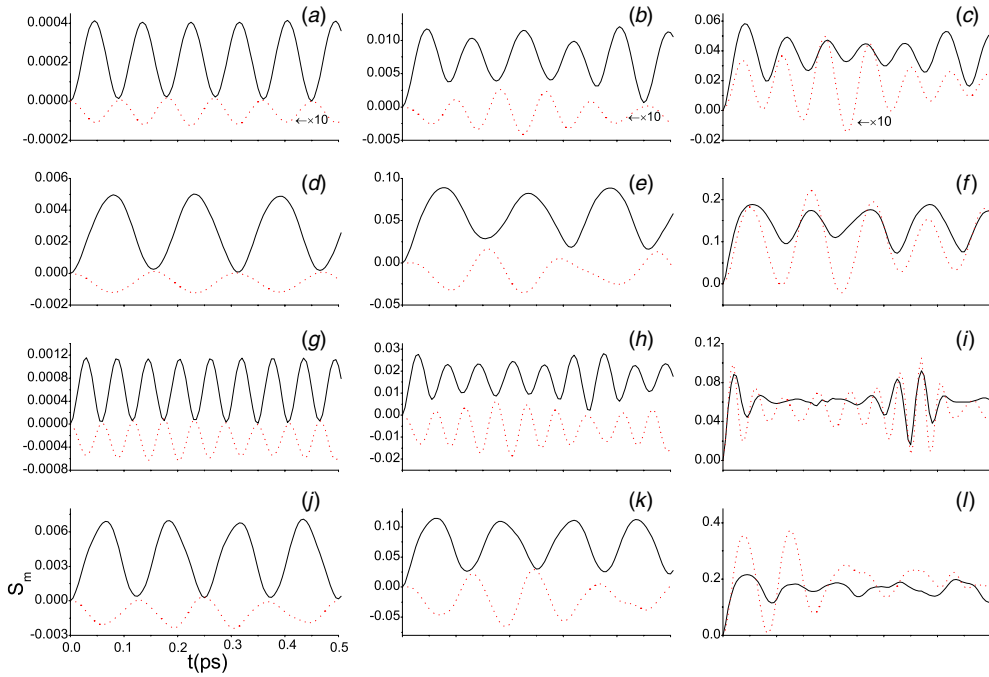


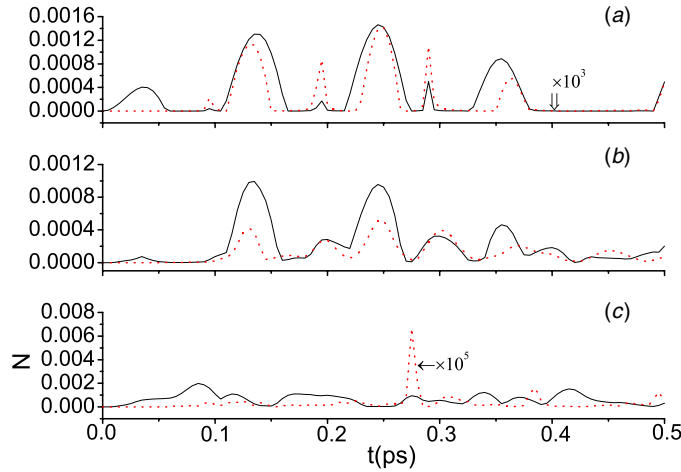
Figure 4. Same as in figure 2 but for MSSs.

$$\bar{v}_b = \bar{v}_s + \sqrt{\bar{v}_s^2 + \bar{v}_s}, \tag{21}$$

for MBSs and MTSs with small magnitudes, respectively. Thus, the partial entropy, the mutual entropy, the energy of a subsystem and the interaction energy between two modes are not at all changed with the evolution of time. We note that the partial density of matrix in the conditions of equations (20) and (21) is not yet changed with time. Those are further verified through numerical calculations with various magnitudes. We also note that the amplitude of the partial entropies in equations (12)–(14) is zero in the condition of  $z_1 = z_2$  or  $z_3 = z_4$ , which can be fulfilled with a suitable molecule and state. That condition is much harsher than equations (20) and (21). In addition, once the magnitudes in both initial states are taken to be close to those conditions, the entropy (energy) of one mode is completely anti-correlated with the one of another mode, which means that the mutual entropy and the interaction energy are very small. That is an important property for MBSs and MTSs in these molecules. Special attention should be paid to those cases when a mixed state is prepared for dynamical behaviors of entropy, energy and others. Besides the dynamical behaviors of entropy and energy, the entanglement dynamics of mixed states will be studied in terms of negativity in the next section.

#### 4. Negativity

As a quantum resource for quantum computation [34], quantum dense coding [35], quantum teleportation [36] and quantum secret protocols [37], entanglement has been extensively investigated. Although the definition of entanglement itself is not of dynamical nature, entangled states are often produced dynamically; that is, even if subsystems are not entangled initially, the interaction between them generates entanglement in the system with the evolution



**Figure 5.** Negativity in  $\text{CHF}_3$  for MBSs (solid line) and MTSs (dotted line) with magnitudes  $(\bar{v}_s, \bar{v}_b) = (0.003, 0.001)$  (a),  $(0.1, 0.1)$  (b) and  $(0.2, 0.9)$  (c), where the value of  $q$  in MBSs is set to 0.001 (a), 0.02 (b) and 0.1 (c).

of time. That results in several important ideas such as entanglement sudden death in the qubits coupling with a reservoir [38], entanglement reciprocation between qubits and continuous variables [39] and entanglement transfer from continuous variables to multiple qubits [40]. It should be remarked that those initial states we are interested in belong to continuous variables. It is thus necessary to explore the entanglement dynamics for those states in a molecule from experimental spectra.

Because the von Neumann entropy is no longer a good measure of entanglement for a mixed state, we use negativity to quantify entanglement for its wide applicability as well as its efficient simulation for any mixed state of an arbitrary bipartite system, in order to discuss its dynamical correlations with the entropy and energy calculated above. Negativity of a state  $\rho(t)$  is defined by [16]

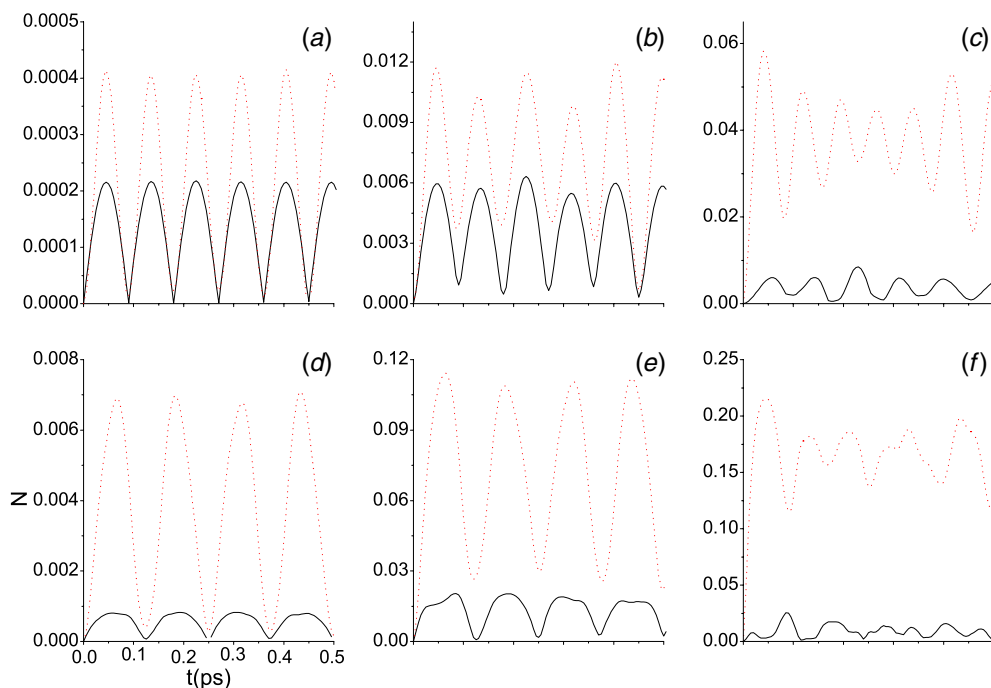
$$N(t) = \frac{\|\rho^T(t)\| - 1}{2}, \quad (22)$$

which corresponds to the absolute value of the sum of negative eigenvalues of  $\rho^T(t)$ , and  $\|\rho^T(t)\|$  is the trace norm of the partial transpose of state  $\rho(t)$ . Partial transposition that is a blockwise transposition of a matrix is given by

$$\rho_{i\alpha, j\beta}^T(t) \equiv \rho_{i\beta, j\alpha}(t), \quad (23)$$

where  $T$  is the partial transposition for the second subsystem.

We have simulated the dynamics of negativity for three kinds of initially mixed states in those molecules. As an example figure 5 shows the evolution of negativity in  $\text{CHF}_3$  for MBSs and MTSs with the same magnitudes as in figure 1. It is noted that the sudden death of negativity happens for small magnitudes  $(\bar{v}_s, \bar{v}_b) = (0.003, 0.001)$ , where the total time of death in MTSs is longer than that in MBSs. The death of negativity means that all eigenvalues of  $\rho^T(t)$  are positive, so  $N(t) = 0$  [17] in this case. Such an important behavior of entanglement is predicted in the qubits interacting with a reservoir [38]. Although the negativity we considered in this case is small, it should be pointed out that all bipartite entangled states are useful for information processing [41]. The calculation of the negative



**Figure 6.** Negativity (solid line) and quantum mutual entropy (dotted line) in  $\text{CHD}_3$  (a), (b) and (c) and  $\text{CHF}_3$  (d), (e) and (f) for MSSs with the same magnitudes as in figure 1.

eigenvalues of  $\rho^T(t)$  makes it difficult to derive the analytic negativity in this case, which is quite different from that of each entropy and energy in section 3. Nevertheless, for MSSs with small magnitudes we are able to obtain such a form that will be given below. Contrary to the entropy and energy discussed above, it is easy to differ MBSs from MTSs in the increasing rate of negativity in the early time of evolution and the maximal value of negativity, both of which are larger for MBSs. For  $(\bar{\nu}_s, \bar{\nu}_b) = (0.2, 0.9)$  the negativity in MTSs is much smaller than that in MBSs. That is because of the property of initial states and the competition between diagonal and non-diagonal elements of the density matrix. Once the magnitudes fulfil or be approximate the conditions of equations (20) and (21), the time-averaged negativity for both kinds of states is very much small. It should be remarked that for a given minimal negativity, one can find out a region for the magnitudes centered at equations (20) and (21). Similarly, one can locate the region for a given minimal exchange of entropy or energy. Vast calculations can show a strong correlation between the region characterized by the minimal entropy or energy exchange and that characterized by the minimal entanglement measured by negativity. That extends the conclusion in the study of entropy exchange and entanglement for mixed thermal states in the electromagnetic field in the resonant Jaynes–Cummings model [30]. Comparing figure 5 with figures 2 and 3, we note that obvious correlations do not appear among negativity, entropy and energy for MBSs and MTSs, nor do they for the magnitudes of interest in  $\text{CHD}_3$ ,  $\text{CH}(\text{CF}_3)_3$  and  $\text{CHCl}_3$ .

Figure 6 shows the evolution of negativity in  $\text{CHD}_3$  and  $\text{CHF}_3$  for MSSs with the same magnitudes as in figure 1, where the mutual entropy is plotted for comparison. For a given magnitude the increasing rate in the early time evolution and the oscillatory amplitude of negativity for MSSs are larger than those for MBSs and MTSs, indicating that MSSs have

the advantage over MBSs and MTSs to gain entanglement within a shorter time. It is nicely observed that the positive correlation between negativity and quantum mutual entropy indeed occurs for MSSs with small magnitudes, as shown in figures 6(a) and (d). This means that the negativity is positively correlated with the interacting energy between two modes by the discussion in section 3. Such a correlation partly remains as the magnitudes increase up to 0.1, and it breaks down with the further increasing of magnitudes and with a strong Fermi coupling, where figure 6(f) is an example. For small magnitudes the negativity is explicitly given by

$$N(t) = \frac{1}{2} \{ p(2, 2) + a_1 p(0, 2) [1 - \cos(\Omega_1 t)] - \{ \{ p(2, 2) - a_1 p(0, 2) [1 - \cos(\Omega_1 t)] \}^2 + 2a_2 p(2, 0) \{ [c_1 - c_1 \cos(\Omega_2 t)]^2 + \sin^2(\Omega_2 t) \}^{\frac{1}{2}} \}, \quad (24)$$

where  $c_1 = \frac{H_0(1,2) - H_0(2,0)}{\Omega_2}$ . It should be mentioned that for CHD<sub>3</sub> with weak Fermi coupling the analytic result by equation (24) is better in agreement with numerical simulations than that for CHF<sub>3</sub> with strong Fermi coupling. If we set the Fermi parameter  $K_{sbb} = 0$ , the negativity by equation (24) is zero as well as each entropy and energy in section 3. That is indeed in this case for other magnitudes. It is thus clear that Fermi-resonance is critical for dynamical entanglement and entropy (energy) exchange in these molecules. It should be noted that although the expressions of negativity, mutual entropy and interacting energy are quite different for MSSs with small magnitudes, they have indeed nearly the same oscillatory frequency ( $\Omega_2$ ). The positive correlation of negativity with quantum mutual entropy implies that the mutual entropy just for MSSs with small magnitudes can be regarded as a measure of entanglement. A similar conclusion is also found for vibrations in molecules H<sub>2</sub>O and SO<sub>2</sub> [22]. We conjecture that such a conclusion can be applied to other systems.

It should be mentioned that quantum entanglement has suggested a different mechanism in rationalizing proton transfer dynamics in dimers of formic acid and analogs [42]. The feasibility of using molecular vibrational states for quantum computing [43, 44] has been recently investigated. It is shown that the interplay of the anharmonicity and the coupling is of prime importance in quantum computing based on vibrational qubits [44]. Furthermore, anharmonic interactions are required for the encoded states [45]. Note that anharmonic interactions are generic among the vibrational, or rovibrational, states of molecules. The chosen model represents a typical one of spectroscopic Hamiltonians with harmonic and anharmonic coupling parameters extracted from fitting to highly excited spectral experimental results of substitute methanes. The present work can be regarded as a good alternative with potential connections to actual experiments, other than the systems more usually used in the field of entanglement. Thus, we believe that the studied dynamical behaviors of negativity, entropy and energy may be useful for dynamical entanglement and molecular quantum information processing such as quantum dense coding and quantum computing.

## 5. Conclusion and discussion

We have studied the dynamics of entropy, energy and negativity for Fermi coupling vibrations in molecules CHD<sub>3</sub>, CH(CF<sub>3</sub>)<sub>3</sub>, CHCl<sub>3</sub> and CHF<sub>3</sub> with various initial states that are taken to be MBSs, MTSs and MSSs. It is shown that positive correlations or anti-correlations among entropies and energies strongly depend on an initial state and a molecule. However, the entropy of the stretch for MBSs and MTSs with small magnitudes is anti-correlated with that of the bend in the same oscillatory frequency, so does the energy for each kind of state with small magnitudes, whereas entropies are positively correlated with the corresponding

energies. Moreover, it is demonstrated that for small magnitudes quantum mutual entropies are positively correlated with the interacting energies between two modes. The periodicity of oscillations in entropies and energies has been analytically explained, showing that the period in  $\text{CH}(\text{CH}_3)_3$  is the longest while that in  $\text{CHCl}_3$  is the shortest. It should be noted that initial conditions are presented for MBSs and MTSs with small magnitudes, in which the dynamical evolutions of entropies and energies are stationary. Those are useful for information and energy exchange [14, 30, 32].

It is still shown that the entanglement measured by negativity exhibits a sudden death for MBSs and MTSs with small magnitudes, and the time-averaged negativity has the minimum under the conditions of stationary entropies and energies. For a given magnitude MSSs can be used to generate entanglement within a shorter time than MBSs and MTSs. Furthermore, for MSSs with small magnitudes negativity is positively correlated with quantum mutual entropy and the interacting energy, indicating that the mutual entropy can be taken as a measure of entanglement just for MSSs with small magnitudes. Those are helpful to understand entanglement in molecular vibrations [6, 22, 25, 26].

It is worthwhile to discuss the influence of other degrees of freedom on the behaviors of correlation. It is possible to investigate bipartite and multipartite entanglement [46] and quantum decoherence [47], and such an analysis is in progress.

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