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Vibrational spectra and tripartite entanglement in hydrogen sulfide

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Abstract

In this Brief Report, an improved $U(2)$ algebraic model is proposed to study both stretching and bending vibrational spectra of a bent triatomic molecule. The model with fewer parameters is used to reproduce the observed spectra of hydrogen sulfide (H_2S) with better precision than the $U(4)$ algebraic model. Furthermore, the tripartite entanglement dynamics is investigated for vibrationally localized states in H_2S . It is shown that the entanglement of a highly excited state in the bending mode displays better quasi-periodicity than that in the stretch. Those are useful for molecular vibrations and multipartite quantum entanglement.

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In recent years, considerable research has been carried out to construct effective Hamiltonians for vibrationally highly-excited spectra in small polyatomic molecules [1–5] fostered more experimental data by new spectroscopic techniques [1,2]. In particular, various models based on the $U(4)$ and $U(2)$ algebras have been used for describing molecular vibrations and rotations [3–7]. The rotation-vibration spectra of diatomic molecules are well described in terms of an $U(4)$ algebra [6]. It has been shown that this model can be successfully applied to linear three- and four-atom molecules [7]. The $U(4)$ algebraic model becomes, however, quite complex when applied to molecules containing more than four atoms. The main advantage of the $U(2)$ algebra is its extreme simplicity from a mathematical point of view. Despite such simplicity, the $U(2)$ algebraic model is particularly well suited to analyze the stretching vibrational spectra [4], and is currently under further developments to incorporate the bending modes [5]. Those works [3–5] are mostly concentrated on vibrational energy levels with little attention to quantum dynamics. In the present Brief Report, an improved $U(2)$ model is proposed to study both stretching and bending vibrational spectra of a bent triatomic molecule, where the Fermi resonance between stretching and bending modes is considered. An application to the observed vibrational spectra of hydrogen sulfide (H_2S) [2] shows that the model with fewer parameters reproduces the experimental results with a smaller standard deviation than the $U(4)$ algebraic model [3].

More importantly, an effective Hamiltonian not only describes the observed vibrational spectra [1–5] but also provides a possibility to investigate quantum entanglement dynamics for molecular vibrations [8]. It has been demonstrated that the entanglement of initial states with local-mode character is more regular than that of ones with normal-mode character [8]. Those studies [8] are significant for molecular quantum computing since the interplay of anharmonicity and the coupling is of importance in quantum computing based on vibrational qubits [9]. More recently, the dynamical entanglement in polar symmetric top molecules has been investigated [10]. Previous works [8,10] are, however, limited to the bipartite entanglement dynamics. Here the dynamical behaviors of tripartite entanglement quantified by concurrence [11] are examined for the stretching and bending modes in the algebraic model

with parameters extracted from fitting to the experimental spectra of H₂S. Such an examination can be regarded as an alternative with potential connections to actual experiments, other than the systems more usually used in the field of tripartite entanglement in three qubits [12].

We are concerned with both stretching and bending vibrational spectra of a bent triatomic molecule, H₂X. We introduce three U_α(2) (1 ≤ α ≤ 3) algebras for two stretches (α=1, 2) and one bend (α = 3), which is generated by the operators {N_α, J_{+,α}J_{-,α}, J_{0,α}} satisfying the following commutation relations,

$$\begin{aligned} [J_{0,\alpha}, J_{\pm,\beta}] &= \pm\delta_{\alpha\beta}J_{0,\alpha}, & [J_{+,\alpha}, J_{-,\beta}] &= 2\delta_{\alpha\beta}J_{0,\alpha}, \\ [N_\alpha, J_{0,\alpha}] &= 0, & [N_\alpha, J_{\pm,\alpha}] &= 0, \end{aligned} \quad (1)$$

where N_α is related with the Casimir operator of U(2),

$$2J_{0,\alpha}^2 + J_{+,\alpha}J_{-,\alpha} + J_{-,\alpha}J_{+,\alpha} = N_\alpha(N_\alpha/2 + 1).$$

The local basis states for each bond are denoted by |N_α, v_α⟩. The action of J_{±,α} on the local states is given by J_{+,α} |N_α, v_α⟩ = √v_α(N_α - v_α + 1) |N_α, v_α - 1⟩ and J_{-,α} |N_α, v_α⟩ = √(v_α + 1)(N_α - v_α) |N_α, v_α + 1⟩. By means of the scale transformation,

$$A_\alpha \equiv \frac{J_{+,\alpha}}{\sqrt{N_\alpha}}, \quad A_\alpha^\dagger \equiv \frac{J_{-,\alpha}}{\sqrt{N_\alpha}}, \quad (2)$$

the commutation relations Eq.(1) can be rewritten as

$$\begin{aligned} [A_\alpha, A_\beta^\dagger] &= \delta_{\alpha\beta}I_{0,\alpha}, & [A_\alpha, I_{0,\beta}] &= -2\delta_{\alpha\beta}\frac{A_\alpha}{N_\alpha}, \\ [A_\alpha^\dagger, I_{0,\beta}] &= 2\delta_{\alpha\beta}\frac{A_\alpha^\dagger}{N_\alpha}, \end{aligned} \quad (3)$$

where I_{0,α} = 1 - 2v_α/N_α.

We are able to express the stretching and the bending vibrational Hamiltonian as

$$\begin{aligned} H &= \omega_s (A_1^\dagger A_1 + A_2^\dagger A_2) + \omega_b A_3^\dagger A_3 \\ &+ \lambda_s (A_1^\dagger A_2 + A_2^\dagger A_1) + \lambda_{ss} A_1^\dagger A_1 A_2^\dagger A_2 \\ &+ \lambda_{sb1} (A_1^\dagger A_2 + A_2^\dagger A_1) A_3^\dagger A_3 \\ &+ \lambda_{sb2} (A_1^\dagger A_1 + A_2^\dagger A_2) A_3^\dagger A_3 \\ &+ \lambda_{sb3} [(A_1^\dagger + A_2^\dagger) A_3 A_3 + A_3^\dagger A_3^\dagger (A_1 + A_2)], \end{aligned} \quad (4)$$

where ω_s , λ_s , and λ_{ss} are the stretch coupling parameters, ω_b is the bend one, and λ_{sb1} , λ_{sb2} , λ_{sb3} are the ones between stretches and bend with the last one for the Fermi resonance. The model has a conserved quantum number (polyad), $P = v_1 + v_2 + \frac{1}{2}v_3$, where v_α is the quantum number of vibrational mode α .

Now we apply the model to the vibrational spectra of H₂S since its complete spectra were studied in terms of U(4) model [3]. For the convenience of comparison with the results in [3], we choose the same observed overtone spectra of H₂S that are taken from Ref. [2]. In the best fitting the two vibron number, $N_1(N_2=N_1)$ and N_3 , are respectively taken to be 54 and 198. The obtained parameters are listed in Table 1.

The calculated vibrational energy levels of H₂S are presented in Table 2, where we give a compilation of the observed experimental data (E_{obs}) with normal-mode label ($\nu_1\nu_2\nu_3$) and the difference ($\Delta E_{cal} = E_{obs} - E_{cal}$) with our results. For comparison the differences between the experimental data and the calculated results [3] are included in Table 2, where the standard deviation (σ) between observed and calculated energy levels is defined by,

$$\sigma^2 = \frac{1}{N_o - N_p} \sum_{i=1}^{N_o} \left(E_{cal}^{(i)} - E_{obs}^{(i)} \right)^2, \quad (5)$$

where N_o is the number of observed data and N_p is the number of parameters used in the fitting. The standard deviation (σ) in the improved model is 1.78 cm⁻¹ with 7 parameters, while that [3] is 3.18 cm⁻¹ with 9 parameters, indicating that the model with fewer parameters has a well performance in reproducing the experimentally known vibration spectra of H₂S. Similar conclusions can be applied to other bent triatomic molecules and polyatomic molecules, and results will be discussed elsewhere [13].

Using the algebraic Hamiltonian parameters in Table 1, we explore the tripartite entanglement dynamics for pure vibrational states in H₂S. The tripartite entanglement is measured in terms of the concurrence $C(t)$ defined by [11]

$$C(t) = \sqrt{3 - \text{Tr}(\rho_1^2 + \rho_2^2 + \rho_3^2)}, \quad (6)$$

where the reduced density matrix ρ_α of subsystem α is obtained by tracing over the other two vibrational subsystems from the full density matrix. As an example, we consider two kinds of

initial states, which are localized states in one stretching and the bending mode, respectively. Figure 1 shows the time evolution of the concurrence for initial states $|8, 0, 0\rangle$, $|15, 0, 0\rangle$, $|16, 0, 0\rangle$, and $|0, 0, 30\rangle$, where $|v_1, v_2, v_3\rangle = |v_1\rangle \otimes |v_2\rangle \otimes |v_3\rangle$ with v_α being the quantum number on vibrational mode α . It is seen that within a given polyad $P = n$, the entanglement of the bending-vibrationally localized state ($|0, 0, 2n\rangle$) exhibits better periodicity than that of the stretching one ($|n, 0, 0\rangle$) with the larger maximal magnitude. For the two kinds of localization states, the oscillating magnitude of the entanglement for a stretching-localized state decreases as n increases, which is contrary to that for a bending-localized state. The concurrence for bending-vibrationally localized state ($|0, 0, 2n\rangle$) can be explained by

$$C(t) = 8\sqrt{2}B\sqrt{1 - 24B^2}, \quad (7)$$

where $B = \left| \frac{c(a-b-d+\Omega)}{8c^2+(a-b-d+\Omega)^2} \sin\left(\frac{\Omega t}{2}\right) \right|$ with $c = \frac{\lambda_{sb3}}{N_3} \sqrt{2n(2n+1)(N_3-2n+1)((N_3-2n+2))}$, $a = \frac{2\omega_b}{N_3} n(2n+1)(N_3-2n+1)$, $b = \omega_s + \frac{\omega_b + \lambda_{sb2}}{N_3} (2n-2)(N_3-2n+3)$, $d = \lambda_s + \frac{\lambda_{sb1}}{N_3} (2n-2)(N_3-2n+3)$, and $\Omega = \sqrt{8c^2 + (a-b-d)^2}$. Thus, the quasi-period is approximately given by $T = \frac{2\pi}{\Omega}$. The analytic calculation of T is respectively 0.072 and 0.093 ps for $n=8$ and 15, which is quite agreement with the corresponding result 0.070 and 0.095 ps in Fig.1 (b). The oscillating magnitude of the entanglement for a bending-localized state indeed increases as n increases. In the case of $n = 1$, the analytical and numerical calculations are identical. In addition, the influence of Fermi resonance parameter (λ_{sb3}) on the magnitude and period can be understood from the expression Eq.(7), that is, both magnitude and period become larger with a smaller λ_{sb3} . However, once λ_{sb3} is set to be zero, there is no tripartite entanglement among three vibrational modes ($C(t) = 0$). It is straightforward to investigate tripartite entanglement dynamics with vibrational excitation in other states and molecules.

In summary, we have introduced an improved U(2) model for the description of both stretching and bending vibrations in a bent triatomic molecule. Fitting observed data of H₂S indicates that the improved model with fewer parameters reproduces the data with better precision than the U(4) model [3]. Furthermore, we have studied the tripartite entanglement dynamics measured by the concurrence for three vibrational modes in H₂S. It is shown that

the entanglement of bending-vibrationally localized state ($|0, 0, 2n\rangle$) is better periodic than that of the stretching one ($|n, 0, 0\rangle$), which has been analyzed in an approximate expression of the concurrence. We believe that those properties are useful for the understanding of highly excited vibrations [1–5] as well as molecular quantum entanglement dynamics [8,10].

It is possible to take the rotational degrees of freedom into account in the model, and exploit its influence on the four-partite entanglement when the rotation is taken as the fourth subsystem. In this case, the explicit expression of multipartite concurrence has been given in [11]. It should be remarked that for a multipartite pure state the generalized concurrence is not unique. For instance, Mintert and coworkers [14] have proposed several inequivalent alternatives. Moreover, it is worthwhile to investigate nonlinear dynamics [15] from the algebraic model for H_2S .

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Table 1 Parameters (cm^{-1}) in the model for H_2S

ω_s	ω_b	λ_s	λ_{ss}	λ_{sb1}	λ_{sb2}	λ_{sb3}
2622.81	1183.57	-6.83	-2.64	1.71	-21.59	1.23

Table 2 Observed and calculated energy levels (cm^{-1}) of H_2S

$(\nu_1\nu_2\nu_3)^a$	E_{obs}^a	ΔE_{cal}^b	ΔE_{cal}
(010)	1182.57	0.27	0.99
(020)	2353.96	-0.44	1.19
(100)	2614.30	0.11	1.60
(001)	2628.46	0.26	1.17
(030)	3513.79	-0.61	0.98
(110)	3779.17	0.37	0.56
(011)	3789.27	-0.13	0.62
(040)	4661.68	1.08	0.73
(120)	4932.70	1.80	-1.03
(021)	4939.23	0.63	-0.70
(200)	5145.12	-1.38	1.62
(101)	5147.36	0.86	1.28
(002)	5243.10	1.10	1.78
(050)	5797.24	5.74	0.84
(130)	6074.58	5.78	-2.75
(031)	6077.60	3.50	-2.42
(210)	6288.14	-2.36	0.51
(111)	6289.17	-1.43	0.55
(012)	6388.73	2.83	-4.25
(121)	7420.09	-0.31	-0.71
(300)	7576.30	1.10	-0.09
(201)	7576.30	1.00	-0.15
(102)	7751.90	-0.90	1.25
(003)	7779.20	-0.50	0.84
(310)	8697.30	-3.70	0.80
(211)	8697.16	-4.04	0.77
(400)	9911.05	3.75	-3.15
(202)	10194.48	0.08	-1.06
(311)	11008.78	-7.12	1.66
	σ	3.18	1.78

^a Normal-mode label and observed data taken from [2].

^b Calculated in [3].

FIGURES

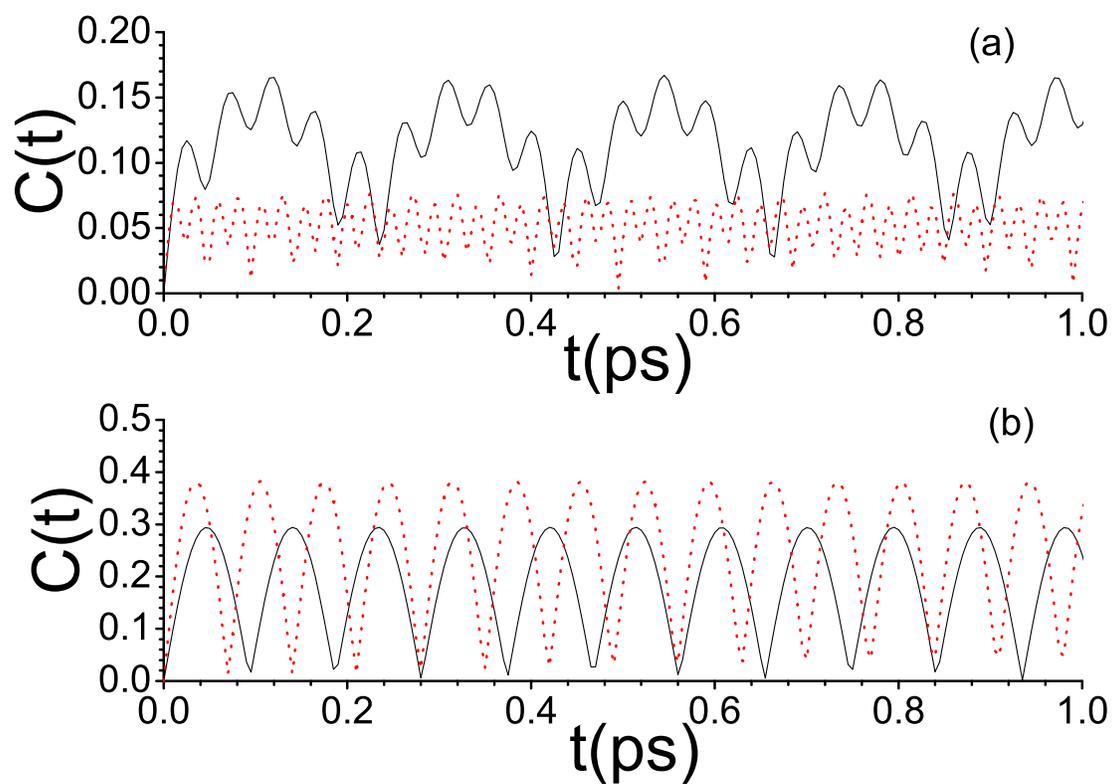


Figure 1. Concurrence $C(t)$ for initial states: (a) $|8,0,0\rangle$ (solid line) and $|15,0,0\rangle$ (dotted line), (b) $|0,0,16\rangle$ (solid line) and $|0,0,30\rangle$ (dotted line), where v_α in state $|v_1, v_2, v_3\rangle$ is the quantum number on vibrational mode α in H_2S .