Vibrational spectra and intramolecular vibrational redistribution in methane and its isotopomers*

Hou Xi-Wen(侯喜文)[a)†], Wan Ming-Fang(万明芳)[b)], and Ma Zhong-Qi(马中骐)[c)]

[a)] *Department of Physics, Huazhong Normal University, Wuhan* 430079, *China*
[b)] *School of Natural Science, Wuhan University of Technology, Wuhan* 430079, *China*
[c)] *Institute of High Energy Physics, Chinese Academy of Sciences, Beijing* 100049, *China*

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An improved $U(2)$ algebraic model is introduced to study the stretching and bending vibrational spectra of methane and its isotopomers. The algebraic model with fewer parameters reproduces the experimental spectra with good precision. Moreover, the obtained parameters describe well the correct behavior of isotopic substitution. It is shown that the Fermi resonance leads to a very fast intramolecular vibrational redistribution among stretches and bends.

Keywords: algebraic methods, vibrational spectra, intramolecular vibrational redistribution

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1. Introduction

The dynamics of molecular vibrations are of considerable interest due to their importance for the study of unimolecular reaction dynamics and laser chemistry.[1−4] Two typical cases have been intensively studied for stretching vibrations. In the first case, the vibrational energy keeps localized in an individual stretching bond for a long time in molecules and their isotopomers.[5,6] In the second, the strong Fermi resonance between one stretching and several bending modes in some polyatomic molecules causes a fast intramolecular vibrational redistribution (IVR) between those degrees of freedom.[7−9] It is thus instructive to explore IVR among more stretching and bending vibrations in molecules.

Methane is a molecule particularly well suited to such an investigation. Experimentally, there is a number of vibrational bands that have been characterized by means of high-resolution spectroscopic techniques.[10−14] Theoretically, there are several approaches to model vibrational spectra of methane such as *ab initio* calculation,[15] the local-mode model of internal curvilinear valence coordinates,[16−18] and algebraic methods.[19−27] The former two provide potential energy surfaces, force field constants, and so forth, where many parameters are determined by fitting the spectroscopic data. Algebraic methods can be used as an effective model to describe molecular vibrations. Those studies,[15−27] however, mostly concentrated on the vibrational energy levels of the CH_4 molecule, without considering isotopic effects and quantum dynamics.

It should be remarked that algebraic methods have been applied to molecular systems for about two decades.[28] Among them, $U(4)$ and $U(2)$ algebraic models are extensively resorted to. The $U(4)$ model has two advantages: rotations and vibrations are taken into account simultaneously, and Fermi resonances are described in terms of the nondiagonal matrix elements of Majorana operators.[29,30] However, it becomes quite complicated when the number of atoms in a molecule is larger than four. The $U(2)$ model is particularly suited for the description of stretching vibrations.[31] Other algebraic schemes[19−23] are useful for the study of stretching vibrations in the XY_4 molecule. Recently, algebraic models have undergone further development.[32−35] One of the important developments is the inclusion of bending modes in polyatomic molecules.[32−35] In the present work, we will propose an improved $U(2)$ algebraic model to study the stretching and bending vibrational spectra of methane and its isotopomers as well, where the Fermi resonance is taken into account. It will be shown that the algebraic Hamiltonian with fewer

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†Corresponding author. E-mail: xwhou@phy.ccnu.edu.cn
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parameters can reproduce the observed experimental values with good precision. More importantly, isotopic effects and IVR will be examined within the algebraic model.

2. Algebraic Hamiltonian

We are going to construct an effectively algebraic model to describe the stretching and bending vibrational spectra of a molecule XY_4. A practical vibrational model is usually obtained by including the most important interactions, for example, Fermi resonances between stretches and bends, and disregarding some of the nonresonance couplings. The method for the model is quite general, and can be straightforwardly applied to larger molecules. Due to a lack of observed data, in particular bending vibration data, we have to postpone such study.

For a molecule XY_4, let atom X be located at the canter O of the tetrahedron, and four atoms Y at its vertices A, B, C, and D. The coordinate axes x, y, and z point from O to the enters of edges AC, AD, and AB, respectively. As is well known, the stretching oscillators are the Morse ones, and the bending oscillators have Pöschl–Teller potential. However, the expression for the eigenvalues of the bound states is identical for those two potentials after the null energy is removed.[28] This results in that the Hamiltonian of the Morse or Pöschl–Teller oscillator can be realized in terms of $U(2)$ algebra. For convenience we begin with enumerating ten $U(2)$ algebras for an XY_4 tetrahedral molecule as follows. The first four equivalent $U(2)$ algebras describe the stretching modes, enumerated in the order OA, OB, OC, and OD. The other six equivalent ones describe the bending states, enumerated in the order AB, AC, AD, CD, BD, and BC. Each $U_\alpha(2)$ $(1 \leq \alpha \leq 10)$ is generated by the operators $\{N_\alpha, J_{+,\alpha}J_{-,\alpha}, J_{0,\alpha}\}$, satisfying the following commutation relations

$$[J_{0,\alpha}, J_{\pm,\beta}] = \pm\delta_{\alpha\beta}J_{0,\alpha}, \qquad [J_{+,\alpha}, J_{-,\beta}] = 2\delta_{\alpha\beta}J_{0,\alpha},$$
$$[N_\alpha, J_{0,\alpha}] = 0, \qquad [N_\alpha, J_{\pm,\alpha}] = 0, \tag{1}$$

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 $|N_\alpha, v_\alpha\rangle$, where N_α is the eigenvalue of operator N_α and has the interpretation of the number of bound states in the uncoupled mode α, and v_α the number of quanta on that mode. The action of $J_{\pm,\alpha}$ on the local states is as follows:

$$J_{+,\alpha}\ |N_\alpha, v_\alpha\rangle = \sqrt{v_\alpha(N_\alpha - v_\alpha + 1)}\ |N_\alpha, v_\alpha - 1\rangle,$$
$$J_{-,\alpha}\ |N_\alpha, v_\alpha\rangle = \sqrt{(v_\alpha+1)(N_\alpha - v_\alpha)}\ |N_\alpha, v_\alpha + 1\rangle. \tag{2}$$

Those N_α of equivalent bonds are equal to each other: $N_i = N_{\rm s}$, $(i = 1,2,3,4)$ and $N_\mu = N_{\rm b}$ $(\mu = 5,6,\ldots,10)$. When emphasizing this equivalence, we use the subscripts s and b, respectively, for the two kinds of modes. By introducing the scale transformation

$$A_\alpha \equiv \frac{J_{+,\alpha}}{\sqrt{N_\alpha}}, \qquad A_\alpha^\dagger \equiv \frac{J_{-,\alpha}}{\sqrt{N_\alpha}}, \tag{3}$$

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

$$[A_\alpha, A_\beta^\dagger] = \delta_{\alpha\beta}I_{0,\alpha}, \qquad [A_\alpha, I_{0,\beta}] = -2\delta_{\alpha\beta}\frac{A_\alpha}{N_\alpha},$$
$$[A_\alpha^\dagger, I_{0,\beta}] = 2\delta_{\alpha\beta}\frac{A_\alpha^\dagger}{N_\alpha}, \tag{4}$$

where $I_{0,\alpha} = 1 - 2v_\alpha/N_\alpha$. In the limit of $N_\alpha \to \infty$, $A_\alpha(A_\alpha^\dagger)$ reduce to bosonic operators with usual boson commutation relations. Thereby the relation between algebraic Hamiltonian and the Hamiltonian written in terms of harmonic operators is easier to see.

Now we express the stretching and the bending vibrational Hamiltonian, $H_{\rm s}$ and $H_{\rm b}$, respectively, as the T_d invariant combinations of the products of one creation operator and one annihilation operator

$$H_{\rm s} = \omega_{\rm s}\sum_{i=1}^{4} A_i^\dagger A_i \ + \ \lambda_{\rm s}\sum_{i\neq j}^{4} A_i^\dagger A_j + \ \text{H.c.}, \tag{5}$$

$$H_{\rm b} = \omega_{\rm b}\sum_{\mu=5}^{10} A_\mu^\dagger A_\mu + \lambda_{\rm b}\sum_{\mu=5}^{7} A_\mu^\dagger A_{\mu+3} + \ \text{H.c.}, \tag{6}$$

where $\omega_{\rm s,b}$ and $\lambda_{\rm s,b}$ are parameters for stretches and bends, respectively, and "H.c." denotes the hermitian conjugate terms.

For Fermi interactions between the stretching and the bending vibrations, only one of the Fermi resonance terms is important for methane and its isotopomers, which is given by,

$$H_{\rm f} = \lambda_{\rm f}\left(\sum_{j=1}^{4} A_j^\dagger\right)\left(\sum_{\mu=5}^{10} A_\mu^2 - 2\sum_{\mu=5}^{7} A_\mu A_{\mu+3}\right) + \ \text{H.c.}, \tag{7}$$

where $\lambda_{\rm f}$ is Fermi coupling parameter. Also, the following fourth order interactions are needed,

$$H_{\rm bb1} = \lambda_{\rm bb1} \sum_{\mu=5}^{7} A_\mu^\dagger A_\mu A_{\mu+3}^\dagger A_{\mu+3} + \text{ H.c.}, \quad (8)$$

$$H_{\rm bb2} = \lambda_{\rm bb2} \sum_{\mu=5}^{7} A_\mu^\dagger A_\mu^\dagger A_\mu A_{\mu+3} + \text{ H.c.}, \quad (9)$$

$$H_{\rm sb1} = \lambda_{\rm sb1} \sum_{i=1}^{4} A_i^\dagger A_i \sum_{\mu=5}^{10} A_\mu^\dagger A_\mu + \text{ H.c.}, \quad (10)$$

$$H_{\rm sb2} = \lambda_{\rm sb2} \sum_{i=1}^{4} A_i^\dagger A_i \sum_{\mu=5}^{7} A_\mu^\dagger A_{\mu+3} + \text{ H.c.}, \quad (11)$$

where $\lambda_{\rm bb1}$ and $\lambda_{\rm bb2}$ are coupling parameters between bends, while $\lambda_{\rm sb1}$ and $\lambda_{\rm sb2}$ are ones between stretches and bends.

The complete vibrational Hamiltonian H is

$$H = H_{\rm s} + H_{\rm b} + H_{\rm f} + H_{\rm bb1} + H_{\rm bb2} + H_{\rm sb1} + H_{\rm sb2}, \quad (12)$$

which has a conserved quantum number, $P = V_{\rm s} + V_{\rm b}/2$, also call polyad number, where $V_{\rm s}$ and $V_{\rm b}$ stands for the total quantum number of stretching and bending vibrations, respectively. We would like to mention that other interacting terms that were omitted here can be written out as in Ref. [36]. In addition, a spurious degree of freedom was removed by the method given in Refs. [24]–[27]. Comparing the Hamiltonian with the previous models,[24−27,36] one can note that the first term with $\omega_{\rm s(b)}$ describes both harmonicity and anharmonicity of Morse oscillators. Therefore, the two interacting terms, $\sum(A_i^\dagger A_i)^2$ and $\sum(A_\mu^\dagger A_\mu)^2$, are not considered, which reduce two parameters in the improved Hamiltonian. In the next section, besides the calculation of energy levels, we will study isotopic effects and population dynamics for excited vibrational states in methane and its isotopomers.

3. Results and discussions

The calculated results by the algeberaic model are presented for methane and its isotopomers, CH_4, $^{13}CH_4$, CD_4, and $^{13}CD_4$. The parameters in the definition of the Hamiltonian are determined by using a least-squares fitting to the observed data. Consequently, we are able to discuss isotopic effects and IVR.

3.1. Vibrational energy levels

For the convenience of comparison with the results in Ref. [18], we use the same observed overtone spectra of CH_4, $^{13}CH_4$, CD_4, and $^{13}CD_4$ as in Ref. [18], which are taken from Refs. [10]–[14]. In order to get an estimate of the precision of fitting, we calculate the standard deviation (σ) between observed and calculated energy levels,

$$\sigma^2 = \frac{1}{N_{\rm o} - N_{\rm p}} \sum_{N=1}^{N_{\rm o}} \left(E_{\rm cal}^{(N)} - E_{\rm obs}^{(N)} \right)^2,$$

where $N_{\rm o}$ is the number of observed data and $N_{\rm p}$ is the number of parameters used in the fitting. In the best fitting the two vibron number, $N_{\rm s}$ and $N_{\rm b}$, are respectively taken to be 50 and 158 for CH_4. The standard deviations with 4 parameters $(\omega_{\rm s}, \lambda_{\rm s}, \omega_{\rm b}, \lambda_{\rm b})$ and with 5 parameters $(\omega_{\rm s}, \lambda_{\rm s}, \omega_{\rm b}, \lambda_{\rm b}, \lambda_{\rm f})$ are 12.770 and 11.438 $\rm cm^{-1}$, respectively, which suggests that higher order interactions are needed in the best fitting for CH_4. Moreover, in those best fits we noted that both anharmonicities of bending modes and between stretches and bends are important. Therefore, the final best fitting with 9 parameters gives the standard deviation 3.745 $\rm cm^{-1}$. The obtained parameters are listed in Table 1. The calculated vibrational energy levels of CH_4 are presented in Table 2, where we give a compilation of the observed experimental data ($E_{\rm obs}$) with normal-mode label ($\nu_1\nu_2\nu_3\nu_4$) and the difference ($\Delta E_{\rm cal} = E_{\rm obs} - E_{\rm cal}$) with our results. For comparison the differences between the experimental data and the results by Venuti *et al.* (Ref. [18]) are included in Table 2.

Table 1. Parameters (units in $\rm cm^{-1}$) in the algebraic Hamiltonian for the isotopomers of methane.

	CH_4	$^{13}CH_4$	CD_4	$^{13}CD_4$
$\omega_{\rm b}$	2987.150	2964.653	2212.989	2201.753
$\lambda_{\rm s}$	−36.092	−27.959	−46.985	−43.377
$\omega_{\rm b}$	1420.996	1416.025	1044.418	1040.110
$\lambda_{\rm b}$	115.008	115.129	47.079	51.431
$\lambda_{\rm f}$	10.535	10.623	5.738	5.809
$\lambda_{\rm bb1}$	7.696	13.564	6.507	6.293
$\lambda_{\rm bb2}$	−9.095			
$\lambda_{\rm sb1}$	−11.724			
$\lambda_{\rm sb2}$	4.103			

Table 2. Observed and calculated vibrational energy levels (units in cm^{-1}) for the isotopomers of methane.

P	Γ	$(\nu_1\nu_2\nu_3\nu_4)^a$	E^a_{abs}	ΔE^b_{cal}	ΔE_{cal}
		CH_4			
1/2	F_2	(0001)	1310.762	0.263	4.774
	E	(0100)	1533.333	−0.694	−2.671
1	A_1	(0002)	2587.044	−0.413	2.968
	F_2	(0002)	2614.261	0.158	2.285
	E	(0002)	2624.618	0.211	4.351
	F_2	(0101)	2830.315	−0.042	0.312
	F_1	(0101)	2846.076	−0.246	4.084
	A_1	(1000)	2916.480	−1.459	1.693
	F_2	(0010)	3019.494	−0.457	−3.748
	A_1	(0200)	3063.646	−0.292	−1.343
	E	(0200)	3065.143	−0.671	−3.263
3/2	F_2	(0003)	3870.487	−1.063	−2.965
	A_1	(0003)	3909.177	−0.848	−8.787
	F_1	(0003)	3920.502	−0.128	−5.747
	F_2	(0003)	3930.921	−0.112	−2.838
	E	(0102)	4105.152	2.722	−0.454
	F_1	(0102)	4128.568	0.460	−1.425
	A_1	(0102)	4132.992	1.037	1.199
	F_2	(0102)	4142.863	−0.538	0.872
	E	(0102)	4151.215	−0.113	3.480
	A_2	(0102)	4161.869	−0.128	6.023
	F_2	(1001)	4223.462	−3.054	1.458
	F_2	(0011)	4319.211	−0.489	−2.398
		CH_4			
	E	(0011)	4322.147	0.141	0.538
	F_1	(0011)	4322.582	−0.218	0.973
	A_1	(0011)	4322.720	−4.465	1.111
	F_2	(0201)	4348.773	0.323	−0.699
	F_1	(0201)	4363.309	−0.112	0.897
	F_2	(0201)	4379.102	0.168	6.230
	E	(1100)	4446.407	7.865	-3.436
	F_1	(0110)	4537.569	−0.899	−5.850
	F_2	(0110)	4543.763	−0.415	0.344
	E	(0300)	4592.033	0.588	1.458
	A_2	(0300)	4595.319	−0.043	−2.231
	A_1	(0300)	4595.555	0.194	−1.857
2	F_2	(0012)	5587.984	−0.658	2.129
	F_2	(0012)	5623.005	5.495	3.030
	F_2	(0012)	5628.395	−1.962	0.087
	A_1	(2000)	5790.252	−3.298	0.016
	F_2	(0111)	5819.722	−1.768	−0.152
	F_2	(0111)	5826.652	−17.405	−3.245
	A_1	(1200)	5968.086	0.227	−1.014
	F_2	(0020)	6004.691	−0.181	−6.724
	E	(0020)	6043.870	−0.958	−2.613
	F_2	(0210)	6054.643	−0.372	−2.134
	F_2	(0210)	6065.324	0.357	5.288
3	F_2	(0030)	8906.780	0.320	0.632
	F_1	(0030)	8947.950	2.941	−0.845
	A_1	(1400)	8975.340	−1.862	−1.037
	F_2	(0030)	9045.920	0.074	7.265
			σ	4.262	3.745

Table 2. (*Continued*)

P	Γ	$(\nu_1\nu_2\nu_3\nu_4)^a$	E^a_{abs}	ΔE^b_{cal}	ΔE_{cal}
		$^{13}CH_4$			
1/2	F_2	(0001)	1302.783	0.316	1.885
	E	(0100)	1533.493	−0.751	2.339
1	A_1	(0002)	2572.099	−0.436	0.103
	F_2	(0002)	2598.640	0.188	−3.152
	E	(0002)	2608.739	0.273	1.478
	F_2	(0101)	2822.451	−0.069	1.636
	A_1	(1000)	2915.442	−1.533	−0.139
	A_1	(0200)	3063.962	−0.402	−2.005
			σ	1.319	3.733
		CD_4			
1/2	F_2	(0001)	997.871	0.028	0.532
	E	(0100)	1091.652	−0.525	0.155
1	A_1	(0002)	1965.545	0.104	−0.040
	F_2	(0002)	1990.469	0.646	4.209
	E	(0002)	1996.833	0.304	1.457
	F_2	(0101)	2083.401	−0.092	2.299
	F_1	(0101)	2090.881	−0.154	2.045
	A_1	(1000)	2101.374	3.164	−0.084
	A_1	(0200)	2182.230	−0.196	−1.646
	E	(0200)	2182.594	−0.657	−0.769
	F_2	(0010)	2260.084	1.325	0.110
			σ	1.617	2.567
		$^{13}CD_4$			
1/2	F_2	(0001)	989.384	0.243	0.705
	E	(0100)	1091.801	−0.630	0.260
1	A_1	(0002)	1951.383	0.169	0.155
	F_2	(0002)	1973.471	0.672	−3.887
	E	(0002)	1979.643	0.379	1.420
	F_2	(0101)	2074.777	−0.185	1.854
	F_1	(0101)	2082.357	−0.213	2.137
	A_1	(1000)	2098.329	3.052	0.012
	A_1	(0200)	2182.502	−0.424	−1.418
	E	(0200)	2182.875	−0.880	−0.563
	F_2	(0010)	2245.426	0.969	0.296
			σ	1.573	2.372

[a] Normal-mode label and observed data taken from Refs. [10]–[14].

[b] calculated results in Ref. [18].

For other molecules we take the two boson numbers N_s and N_b to be 50 and 168 for $^{13}CH_4$, 70 and 180 for CD_4, and 70 and 190 for $^{13}CD_4$. In the best fitting those parameters, ω_s, λ_s, ω_b, λ_b, λ_f, and λ_{bb1}, are of primary, which are given in Table 1. The observed and calculated vibrational energy levels are also listed in Table 2. Other calculated levels are available upon request.

In the case of CH_4 the standard deviation (σ)

is 3.745 cm^{-1} with 9 parameters, while Venuti *et al.* (Ref. [18]) obtained 4.262 cm^{-1} with 24 parameters. The other standard deviations for $^{13}CH_4$, CD_4, and $^{13}CD_4$ are comparable to those by Venuti *et al.* (Ref. [18]). Those show that the algebraic model with fewer parameters performs well in reproducing the experimentally known vibrational spectra of methane and its isotopomers.

3.2. Isotopic effects

We discuss the isotopic effects from Table 1. Deuterium substitution is expected to influence the parameters in an algebraic Hamiltonian in a readily predictable fashion.[28] For the present model that fashion for the stretching modes of C–D and C–H bond is taken as

$$\omega_s^{C-D}/\omega_s^{C-H} = 1/\gamma, \quad \lambda_s^{C-D}/\lambda_s^{C-H} = 1/\gamma,$$

where $\gamma = (\mu^{C-D}/\mu^{C-H})^{1/2}$, μ^{C-D} and μ^{C-H} is the reduced mass of C–D and C–H bond, respectively. From Table 1 we have

$$\begin{aligned}
&\omega_s^{C-H}/\omega_s^{^{13}C-H} = 1.008, \quad \lambda_s^{C-H}/\lambda_s^{^{13}C-H} = 1.291,\\
&\omega_s^{C-D}/\omega_s^{^{13}C-D} = 1.005, \quad \lambda_s^{C-D}/\lambda_s^{^{13}C-D} = 1.083,\\
&\omega_s^{C-H}/\omega_s^{C-D} = 1.350, \quad \lambda_s^{C-H}/\lambda_s^{C-D} = 0.768,\\
&\omega_s^{^{13}C-H}/\omega_s^{^{13}C-D} = 1.346, \quad \lambda_s^{^{13}C-H}/\lambda_s^{^{13}C-D} = 0.645,
\end{aligned}$$

indicating that most of the expected ratio are closely followed, but the ratio obtained for $\lambda_s^{C-H}/\lambda_s^{C-D}$ and $\lambda_s^{^{13}C-H}/\lambda_s^{^{13}C-D}$ are too small. More experimental data for the isotopomers of methane are desirable to improve that ratio. To some extent, the present calculations demonstrate that the parameters derived from fitting experimental data in the algebraic model can exhibit the correct behavior on isotopic substitution.

3.3. Intramolecular vibrational redistribution

We evaluate the short-time population dynamics $p(t)$ of the excited vibrational states of methane and its isotopomers from the algebraic Hamiltonian parameters in Table 1. Previous works have studied the population dynamics of the initially excited states in the stretching mode.[7–9] Here we would like to investigate such dynamics of initially excited states in the bending modes just for theoretical interest. As an example, the results are shown in Fig. 1, where we consider the polyad $P = 3/2$ with an initial excited state, $3\nu_4$ (solid line), and two selected states, $2\nu_2 + \nu_4$ (dashed), and $\nu_1 + \nu_4$ (dotted), in CH_4 (a) and CD_4 (b). Within the first 260 fs (320 fs) the state $3\nu_4$ is depopulated almost completely, with incomplete recurrence after about 540 fs (780 fs) for CH_4 (CD_4). It is seen that the state $2\nu_2 + \nu_4$ becomes populated appreciably, its population passing through a maximum at about 45 fs (95 fs) in CH_4 (CD_4), showing that the energy flow out of the initially excited state is very fast to the state $2\nu_2 + \nu_4$ due to Fermi resonance (λ_f). Furthermore, the state $2\nu_2 + \nu_4$ serves as a pump of the energy exchange between the states $3\nu_4$ and $\nu_1 + \nu_4$, with the quad-period being about 90 fs (190 fs) in CH_4 (CD_4). It is straightforward to illustrate how the intramolecular vibrational redistribution is progressively efficient with vibrational excitation in other states and isotopomers of methane. Moreover, it is possible to study the time-dependent quantum entropy as well as the influence of rotational states on population and entropy dynamics, which will be our future work.

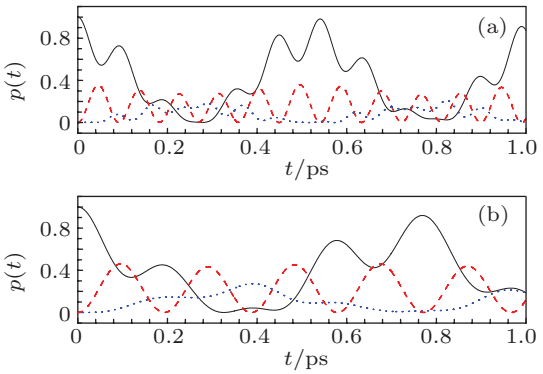


Fig. 1. (colour online) Time-dependent population $p(t)$ of three selected states $3\nu_4$ (solid line), $\nu_1 + \nu_4$ (dashed), and $2\nu_2 + \nu_4$ (dotted) for CH_4 (a) and CD_4 (b).

4. Conclusion

We have proposed an improved $U(2)$ algebraic model for the description of the stretching and bending vibrations in methane and its isotopomers. Fitting observed data indicates that the improved $U(2)$ model can well reproduce the data. Fewer parameters are needed in the algebraic approach, from which isotopic effects and intramolecular vibrational redistribution are discussed. It is shown that the model displays the correct behavior on isotopic substitution, and that the Fermi resonance leads to a very fast intramolecular vibrational redistribution between stretching and bending modes.

Finally, we remark that the algebraic model can be extended in several ways. The obtained pa-

rameters can be related to force-field constants to be used in conjunction with a kinetic energy operator in a Schrödinger equation.[16−18] The rotational degrees of freedom can be taken into account by coupling the vibrational wave functions to rotational states carrying the appropriate point symmetries.[37] With regard to the recent developments in two-mode entanglement[38−42] and nonlinear classical dynamics[43,44] in polyatomic molecules, it is thus of importance to exploit quantum entanglement dynamics and nonlinear dynamics from the algebraic model for methane and its isotopomers, where the corresponding classical model can be obtained in terms of algebraic techniques.[28,45] Such an investigation is under way.[46,47]

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