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Vibrational Spectra of Nonrigid Molecule HCP in an Algebraic Model

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An algebraic Hamiltonian for the two coupled nonlinear vibrations of highly excited nonrigid molecule HCP was presented. The Hamiltonian reduces to the conventional one in a limit which was expressed in terms of harmonic oscillator operators. It showed that the algebraic model can better reproduce the data than the conventional model by fitting the observed data of HCP.

Key words: Vibrational energy levels, Algebraic methods, Fermi resonances

I. INTRODUCTION

The experimental data provided by modern spectroscopy techniques [1,2] are changed from the broad spectrum to the level structure and the time evolution of highly excited vibrational states, which motivated the development of the corresponding theoretical approaches. Those approaches such as *ab initio* calculations [3,4], an extended local-mode model [5,6], a nonlinear theory [7,8] and Lie algebraic methods [9-13] have given a good fit to the vibrational spectra of polyatomic molecules, and some important physical quantities such as band intensities and potential-energy surfaces have been satisfactorily analyzed and interpreted. Among those algebraic methods, the U(2) algebraic model has been extended and applied to polyatomic molecules, such as an algebraic force-field expansion approach for XY₂ molecules [14], a symmetry-adopted algebraic model for X₃ systems [15] and a modified vibron model for XY₂ [16,17] and XY₄ [18]. Those studies show that the convergence of the algebraic model is much faster than that of the conventional model. In present work, we shall demonstrate that a bending vibrational mode is easily taken into account in the U(2) algebraic model, and use this model to study the stretch and bend vibrational spectra of floppy HCP molecules. Fitting experimental vibrational levels gives a direct correspondence of the algebraic parameters with the conventional spectroscopic constants. It shows that the standard deviation by the U(2) algebraic model is smaller than that by the conventional model expressed in terms of harmonic oscillator operators.

The equilibrium structure of the electronic ground state of HCP is linear. Thus each vibrational level can be specified by using four quantum numbers (v_1, v_2^l, v_3), where v_1, v_2, v_3 , and l are the quantum numbers for CH stretch, degenerate bend, CP stretch,

and vibrational angular momentum, respectively. Since only the $l=0$ levels were observed and there were no experimental observations of highly excited vibrational levels with $v_1 \neq 0$ [19-21], we shall concentrate on the bend and CP stretch vibrational spectrum of the electronic ground state of HCP. The stretching oscillator is the Morse one, and the bending oscillator has Pöschl-Teller potential. However, the expression for the eigenvalues of the bound states is identical for the two potentials after the null energy is removed. Thus the Hamiltonian of the Morse or Pöschl-Teller oscillator can be realized in terms of the U(2) algebra [22]. The algebraic zero-order Hamiltonian for the bend and stretch vibrations in HCP is defined in terms of a set of the U(2) algebraic operators, in which matrix

$$\begin{aligned} \hat{H}_0 = & \omega_2 \hat{C}_2 + \omega_3 \hat{C}_3 + x_{22} \hat{C}_2 \hat{C}_2 + x_{23} \hat{C}_2 \hat{C}_3 \\ & + x_{33} \hat{C}_3 \hat{C}_3 + y_{222} \hat{C}_2 \hat{C}_2 \hat{C}_2 + y_{223} \hat{C}_2 \hat{C}_2 \hat{C}_3 \\ & + y_{233} \hat{C}_2 \hat{C}_3 \hat{C}_3 + y_{333} \hat{C}_3 \hat{C}_3 \hat{C}_3 \end{aligned} \quad (1)$$

where $\omega_2, \omega_3, x_{22}, x_{23}, x_{33}, y_{222}, y_{223}, y_{233}$ and y_{333} represent molecular parameters that will be determined by a least-squares fit, with the subscripts 2 and 3 denoting the bending and the stretching modes, and \hat{C}_i ($i=2,3$) is the algebraic operators of which matrix elements in the U(2) anharmonic oscillator states, $|N_i, v_i\rangle$, are given by [14],

$$\langle N_i, v'_i | \hat{C}_i | N_i, v_i \rangle = (v_i - v'_i / N_i) \delta_{v'_i, v_i} \quad (2)$$

where N_i , the vibron number, is related to the number of bound states for the corresponding anharmonic oscillator, and v_i represents the vibrational quantum number.

For HCP, it is well known that there are 1:2 Fermi resonances between the stretch and the bend. Those anharmonic resonances create interaction Hamiltonian as,

$$\hat{H}_f = (\lambda_{f1} + \lambda_{f2} \hat{C}_2 + \lambda_{f3} \hat{C}_3) (\hat{A}_2^\dagger \hat{A}_2^\dagger \hat{A}_3 + \hat{A}_3^\dagger \hat{A}_2 \hat{A}_2) \quad (3)$$

where λ_{fi} ($i=1,2,3$) are Fermi coupling parameters, and \hat{A}_i^\dagger and \hat{A}_i are the algebraic operators, of which matrix

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TABLE I Parameters in the algebraic Hamiltonian Eq.(5) for HCP (in cm^{-1})

	ω_2	ω_3	x_{22}	x_{23}	x_{33}	y_{222}	y_{223}	y_{233}	y_{333}	λ_{f1}	λ_{f2}	λ_{f3}
Ref.[19]	671.360	1284.629	-2.503	-2.953	-3.814	-0.026	-0.113	-0.109	-0.053	6.046	-0.484	0.276
This work	668.875	1280.536	-0.004	-3.634	-0.160	-0.059	-0.113	-0.121	-0.091	5.985	-0.071	0.126

elements in the $|N_i, v_i\rangle$ are given by,

$$\begin{aligned} \langle N_i, v'_i | \hat{A}_i^\dagger | N_i, v_i \rangle &= \sqrt{(v_i + 1) \left(1 - \frac{v_i}{N_i}\right)} \delta_{v'_i, v_i + 1} \\ \langle N_i, v'_i | \hat{A}_i | N_i, v_i \rangle &= \sqrt{v_i \left(1 - \frac{v_i - 1}{N_i}\right)} \delta_{v'_i, v_i - 1} \end{aligned} \quad (4)$$

The matrix elements of Hamiltonian \hat{H}_f are the off-diagonal matrix ones.

Now, the full algebraic quantum effective Hamiltonian for HCP is

$$\hat{H} = \hat{H}_0 + \hat{H}_f \quad (5)$$

where two properties of the Hamiltonian are worthwhile to mention. The first property is that since the anharmonic resonance creates the polyad structure, a polyad quantum number, P , defined as $P = v_2 + 2v_3$, is conserved. Thus the vibrational levels having the same P interact with each other. When the interaction among the zero-order states in a polyad becomes sufficiently strong, labeling the vibrational levels by conventional v_2 and v_3 loses its meaning. Therefore, following Field *et al.* [19], we use P and k to refer the eigenstates, where k represents the energy rank in each polyad and runs from 0 to $P/2$. The second property is that the Hamiltonian in the harmonic limit reduces to the corresponding one expressed in terms of the harmonic oscillators. Indeed, it can be easily shown that the matrix elements of \hat{C}_i , \hat{A}_i^\dagger , and \hat{A}_i become those of the harmonic oscillator Hamiltonian, respectively.

The observed vibrational data for HCP are taken from Refs.[19-21]. In the best fitting the two vibron number, N_2 and N_3 , are respectively taken to be 380 and 420. By least-squares optimization, we have determined the best values of the parameters occurring in Eq.(5). They are labeled with b and given in Table I, where the parameters obtained in Ref.[19] in the harmonic limit, $N_2 \rightarrow \infty$ and $N_3 \rightarrow \infty$, labeled a , are listed for comparison. Our results for the calculated vibrational levels of HCP are presented in Table II, where we give a compilation of the observed experimental data (E_{obs}) and the difference ($\Delta E_{\text{cal}} = E_{\text{obs}} - E_{\text{cal}}$). For comparison, the differences between the experimental data and the results of Field *et al.* [19] are included in Table II. To get an estimate of the precision of both methods, we give at the bottom of the table the standard deviation between observed and calculated data,

$$\sigma^2 = \frac{1}{o - p} \sum_{i=1}^o (E_{\text{cal}}^i - E_{\text{obs}}^i)^2 \quad (6)$$

where o is the number of observed data and p is the number of parameters used in the fitting. In our case σ is 3.4 cm^{-1} with 12 parameters, while Field *et al.* showed it is 3.9 cm^{-1} [19]. This shows that our algebraic model has a little better performance in reproducing the experimentally known vibrational band origins of HCP.

In conclusion, a U(2) algebraic model has been introduced and applied to calculate the vibrational levels of the stretching and bending modes of HCP, in which the anharmonic interactions between the stretch and the bend are taken into account. The model in a limit reduces to the model expressed in terms of harmonic oscillator operators. It shows that the U(2) model can better reproduce the data than the corresponding model by fitting the observed data. The similar conclusion can be applied to other polyatomic molecules, and results will be discussed elsewhere.

With the obtained parameters for HCP, it is possible to study the potential-energy surfaces, the corresponding classical bifurcation, the dynamical evolution of highly excited states [23], and entanglement dynamics [24] between stretching and bending models.

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TABLE II Observed and calculated vibrational energy levels for HCP (in cm^{-1})

P	k	$E_{\text{obs}}^{[19-21]}$	$\Delta E_{\text{cal}}^{[19]}$	ΔE_{cal}	P	k	$E_{\text{obs}}^{[19-21]}$	$\Delta E_{\text{cal}}^{[19]}$	ΔE_{cal}
2	0	1335.0	0.0	3.6		1	1278.3	0.0	2.2
4	0	2654.0	-0.3	3.3		1	2598.0	-3.3	2.9
	2	2545.2	-3.2	0.2	6	0	3960.0	1.5	3.8
	1	3902.0	-4.9	0.8		2	3853.0	-5.2	2.7
	3	3804.0	-5.8	-2.1	8	0	5249.0	0.5	1.3
	2	5141.0	-7.5	-0.6		3	5097.0	-8.1	1.0
10	0	6522.0	-3.5	-3.6		1	6464.0	-5.2	-4.2
	2	6411.0	-9.3	-5.6		3	6367.0	-11.0	-3.9
	4	6328.0	-12.9	-3.3	12	2	7728.0	-0.9	-1.9
14	0	9045.0	1.2	0.9		1	8977.0	-1.5	-1.9
16	0	10287.0	1.3	1.3		1	10214.7	-0.8	-1.2
	3	10095.8	-2.3	-1.7		5	10010.6	-2.3	0.1
18	0	11516.7	0.6	0.8		1	11440.7	-0.3	-0.6
	2	11373.4	-0.3	0.50		3	11314.9	0.6	1.0
	4	11264.1	1.0	2.4		5	11221.4	0.7	2.6
	6	11187.8	-0.8	-2.5		7	11161.2	-2.6	-2.2
20	0	12734.7	-0.3	0.2		1	12655.0	0.0	-0.2
	2	12583.3	0.3	0.16		3	12520.4	1.3	1.7
	4	12466.2	2.5	3.9		5	12420.2	2.5	4.1
	6	12381.9	-1.0	-3.6		7	12355.8	2.9	2.0
	8	12311.5	-0.2	2.5	22	0	13942.0	-0.1	0.5
	1	13857.5	0.2	0.1		2	13782.0	1.2	1.2
	3	13715.5	3.0	3.5		4	13657.4	4.3	5.8
	5	13607.8	4.2	5.6		6	13566.5	0.3	-3.2
	7	13534.9	3.6	1.6		9	13426.9	3.9	5.5
	10	13338.8	-7.6	-9.4	24	10	14496.6	-2.5	-2.2
26	0	16318.7	-1.6	-1.1		1	16224.1	-1.9	-2.2
	3	16063.9	0.1	0.5		4	15998.8	1.9	3.5
	5	15943.5	2.2	3.6		6	15896.4	-2.3	-7.0
	7	15858.3	4.4	0.1		8	15790.4	-5.5	-6.2
28	0	17489.3	-1.6	-1.2		1	17389.6	-2.4	-2.8
	2	17299.0	-3.0	-3.3		4	17151.6	0.8	2.5
	5	17093.3	1.0	2.5		6	17043.9	-3.1	-8.4
	13	16412.6	6.5	5.1	30	0	18648.2	-0.7	-0.4
	1	18542.7	-2.6	-3.1		2	18448.9	-2.0	-2.5
	3	18366.6	0.3	0.7		4	18292.3	0.1	1.9
	15	17172.4	-2.5	-2.67	32	0	19794.3	0.6	0.6
34	0	20928.3	2.9	2.9		1	20811.2	-1.5	-2.5
	2	20707.7	-2.1	-2.9		3	20619.3	1.9	2.2
	4	20532.6	-4.0	-1.8		5	20470.9	0.2	3.2
36	0	22048.1	4.6	4.4			σ	3.9	3.4

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