Volume 9, Number 3
1009-1963/2000/09(03)/0180-04
CHINESE PHYSICS
March, 2000
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STRETCHING VIBRATIONS OF BENZENE MOLECULE IN THE NONLINEAR MODEL*

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(Received 20 September 1999)

A five-parameter nonlinear model is introduced to the description of the stretching vibrational modes of benzene molecule in the electronic ground state, and is applied for the first time to the calculations of energy levels of C–H and C–D stretches of C_6H_6 and C_6D_6 in vapor phase. The results obtained agree well with the experimental vibrational energy levels and with the results obtained from other model calculations. Moreover, our model calculations predict accurately some new overtone and combination bands that have not been studied experimentally.

PACC: 3310; 0365

I. INTRODUCTION

The development of new experimental techniques, including the conventional infrared and Raman techniques, infrared-infrared double resonance experiments[1,2], and microwave-detected microwave-optical double resonance experiments[3], has made possible the measurement of highly excited vibrations in polyatomic molecules. To interpret the experimental results requires reliable theoretical models. In the last few years, there has been considerable interest in the overtones of stretching vibrations of X–Y bonds in medium size and large molecules. Among these, the benzene molecule, C_6H_6, and its deuterated form, C_6D_6, play a very important role. For the benzene molecule, models based directly on the solution of many-body differential Schrödinger equation with interatomic potentials become rather cumbersome and difficult to apply. Similarly, straightforward Dunham-like expansions are also difficult to perform because the large number of parameters in the expansions cannot be determined from the known available experimental data. Hence, several theoretical models have been developed for the description of the highly excited vibrations for the benzene molecule, such as the local mode model[4] and the vibron model.[5]

Recently, a simple nonlinear model system, i.e. the discrete self-trapping equation[6−8], has been introduced and widely used for anharmonic polyatomic molecular systems. The nonlinear model not only reflects the effect of bond anharmonicity, but also reflects the dipole-dipole interbond interaction. Recent studies[9−11] on the highly excited stretching vibrations of symmetrical hydride systems, such as H_2X, XH_3, XH_4 type molecules, have demonstrated that the nonlinear model is suitable for the description of polyatomic molecules and predict accurately the X–H stretching overtone and combination band eigenvalues. In the nonlinear model used before, there exist only three parameters. In this paper, we will extend it to a five-parameter nonlinear model, which is then applied for the first time to the study of stretching vibrations of C–H (C–D) bonds of C_6H_6 (C_6D_6) in vapor phase. We find that the model calculations appear to be able to describe the experimental data accurately in terms of fewer parameters.

II. THEORY

It is known that the benzene molecule in ground state belongs to D_{6h} point group symmetry and has thirty vibrational modes. Of all these vibrational modes, we only deal with the six stretching modes. In the notation of Wilson, these are $v_2(A_{1g})$, $v_{13}(B_{1u})$, two $v_{20}(E_{1u})$ and two $v_7(E_{2g})$ (In the notation of Herzberg, they are $v_1(A_{1g})$, $v_5(B_{1u})$, two $v_{12}(E_{1u})$ and two $v_{15}(E_{2g})$. Here we use Wilson' notation.). Thus, the five-parameter nonlinear dynamical model for the benzene molecule with six coupled anharmonic vibrations C–H (C–D) in the electronic ground state can be expressed as

$$\left(\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t} - \omega_0\right)A + MA + \lambda D(|A|^2)A = 0, \qquad (1)$$

where A=col(A_1, A_2, A_3, A_4, A_5, A_6) is a 6-dimensional column vector of complex mode amplitudes. $M = [m_{ij}]$ is a 6×6, real, symmetrical dispersion matrix describing the dipole-dipole interaction

* Project supported by the National Natural Science Foundation of China (Grant No. 29673028), and by the Youth Science Research Foundation of Sichuan University (Grant No. 1998-37).

between C–H (C–D) vibrational modes. The diagonal matrix D ($|A|^2$),

$$D(|A|^2)=\begin{bmatrix} |A_1|^2 & 0 & 0 & 0 & 0 & 0 \\ 0 & |A_2|^2 & 0 & 0 & 0 & 0 \\ 0 & 0 & |A_3|^2 & 0 & 0 & 0 \\ 0 & 0 & 0 & |A_4|^2 & 0 & 0 \\ 0 & 0 & 0 & 0 & |A_5|^2 & 0 \\ 0 & 0 & 0 & 0 & 0 & |A_6|^2 \end{bmatrix}, \tag{2}$$

represents the tendency of A to self-trapping through a nonlinear interaction with the adjacent structure, the strength of this interaction is specified by an anharmonic parameter λ which describes the main contribution of the anharmonic terms in molecular vibrational potential energy to the total vibrational energy; ω_0 is the harmonic frequency of a C–H (C–D) vibrational mode. Considering the schematic representation of benzene molecule, we number the bonds 1 to 6

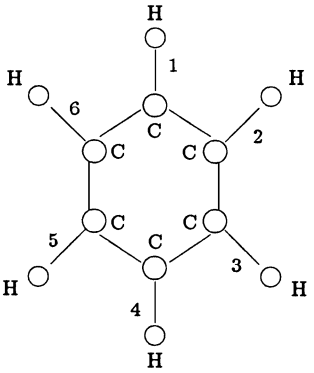


Fig.1. Schematic representation of C_6H_6 molecule.

as in Fig.1. It is obvious from the figure that all C–H (C–D) bonds are equivalent. Thus, we can take

$$M=\begin{bmatrix} 0 & \varepsilon_1 & \varepsilon_2 & \varepsilon_3 & \varepsilon_2 & \varepsilon_1 \\ \varepsilon_1 & 0 & \varepsilon_1 & \varepsilon_2 & \varepsilon_3 & \varepsilon_2 \\ \varepsilon_2 & \varepsilon_1 & 0 & \varepsilon_1 & \varepsilon_2 & \varepsilon_3 \\ \varepsilon_3 & \varepsilon_2 & \varepsilon_1 & 0 & \varepsilon_1 & \varepsilon_2 \\ \varepsilon_2 & \varepsilon_3 & \varepsilon_2 & \varepsilon_1 & 0 & \varepsilon_1 \\ \varepsilon_1 & \varepsilon_2 & \varepsilon_3 & \varepsilon_2 & \varepsilon_1 & 0 \end{bmatrix}. \tag{3}$$

Under quantization (i.e. $A_i \to \widehat{B}_i, A_i^* \to \widehat{B}_i^+$)[7,8], we can obtain the number operator $\widehat{N}$ and the model Hamiltonian operator $\widehat{H}$,

$$\widehat{N}=\sum_{i=1}^{6}\left(\widehat{B}_i^+\widehat{B}_i+\frac{1}{2}\right), \tag{4}$$

$$\widehat{H}=\left(\omega_0-\frac{1}{2}\lambda\right)\widehat{N}-\frac{1}{2}\lambda\sum_{i=1}^{6}\widehat{B}_i^+\widehat{B}_i\widehat{B}_i^+\widehat{B}_i - \sum_{i\neq j}^{6} m_{ij}\widehat{B}_i^+\widehat{B}_j, \tag{5}$$

where $\widehat{B}_i^+$ and $\widehat{B}_i$ are boson creation and annihilation operators, respectively, which satisfy the following relations:$\widehat{B}_i^+|n_i\rangle = \sqrt{n_i+1}|n_i+1\rangle, \widehat{B}_i|n_i\rangle = \sqrt{n_i}|n_i-1\rangle, \widehat{B}_i|0\rangle = 0, [\widehat{B}_i, \widehat{B}_j^+] = \delta_{ij}$, where $|n_i\rangle$ is the harmonic eigenfunction of a C–H (C–D) vibrational mode, $|0\rangle$ is the eigenfunction for the ground state. Here we take $\hbar = 1$, and assume that both frequencies and energies are measured in the same units (cm^{-1}).

In order to obtain the eigenvalues of the model Hamiltonian operator $\widehat{H}$, we may expand the common eigenfunction, $|\psi_n\rangle$, of both operators $\widehat{N}$ and $\widehat{H}$ in terms of a suitable basis function set with the basis elements, $|n,\alpha\rangle = |n_1\rangle|n_2\rangle|n_3\rangle|n_4\rangle|n_5\rangle|n_6\rangle$, as follows

$$|\psi_n\rangle = C_1|n,1\rangle + C_2|n,2\rangle + \cdots + C_{c(6,n)}|n,c(6,n)\rangle \tag{6}$$

where $\sum_{i=1}^{c(6,n)}|C_i|^2 = 1$ (i.e. normalization condition), $n\left(=\sum_{i=1}^{6}n_i\right)$ is the total quantum number, $\alpha = 1,2,\cdots,c(6,n)$, and $c(6,n)$ is the number of ways that n particles are distributed in six states, that is, $c(6,n) = (n+5)!/5!n!$. Thus, the eigenvalue equation, $\widehat{H}|\psi_n\rangle = E_n|\psi_n\rangle$, can be reduced to an algebraic equation for the column vector, $\boldsymbol{C}_n = \mathrm{col}(C_1, C_2, \cdots, C_{c(6,n)})$, consisting of the coefficients in the expansion of Eq.(6)

$$\boldsymbol{H}_n\boldsymbol{C}_n = \boldsymbol{E}_n\boldsymbol{C}_n, \tag{7}$$

where $\boldsymbol{H}_n$ is a $c(6,n)\times c(6,n)$, real, symmetrical matrix with matrix elements: $H_{rs} = \langle n,r|\widehat{H}|n,s\rangle, 1 \le r,s \le c(6,n)$. Thus, if we could determine the parametric values of $\omega_0, \lambda, \varepsilon_1, \varepsilon_2$, and ε_3, the vibrational energy levels of the benzene molecule can be obtained through solving the characteristic values of matrix H_n.

Ⅲ. RESULTS AND DISCUSSION

The parametric values of $\omega_0, \lambda, \varepsilon_1, \varepsilon_2$, and ε_3 for our model calculations are shown in Table 1, where $\varepsilon_1, \varepsilon_2, \varepsilon_3$ is just calculated accurately from the fundamental frequencies using the following relations

$$\varepsilon_1 = \frac{1}{6}(-v_2 + v_{13} - v_{20} + v_7), \tag{8a}$$

$$\varepsilon_2 = \frac{1}{6}(-v_2 - v_{13} + v_{20} + v_7), \tag{8b}$$

$$\varepsilon_3 = \frac{1}{6}(-v_2 + v_{13} + 2v_{20} - 2v_7), \tag{8c}$$

which are obtained from Eq.(7) when $n = 1$, ω_0 and λ are evaluated from the experimental vibrational energy levels.[4,5] Thus, the vibrational energy levels of

C–H (C–D) stretches of the benzene molecule in vapor phase at any highly excited states can be calculated using the above theoretical model. In Table 2, we only list our calculated results up to three quanta of vibration together with the experimental data. Corresponding to all vibrational energy levels obtained, we write out the appropriate symmetries. From the parametric values in Table 1, we find the frequency ratio: $\omega_0(C_6H_6)/\omega_0\ (C_6D_6) \doteq 1.351$. As compared with the theoretical ratio: $(13/7)^{1/2} \doteq 1.363$, the agreement is good. The corresponding ratio of the anharmonic parameter is: $\lambda\ (C_6H_6)/\lambda\ (C_6D_6) \doteq 1.703$.

Table 1. Parametric values (cm^{-1}) for our model calculations

Mole.	ω_0	λ	ε_1	ε_2	ε_3
C_6H_6	3181.067	118.992	−4.118	−1.662	−0.234
C_6D_6	2355.175	69.835	−5.837	−4.440	2.527

It is clear from Table 2 that our model calculations are in good agreement with the experimental values (with the r.m.s. deviations $1.975\,cm^{-1}$ for C_6H_6 and $0.360\,cm^{-1}$ for C_6D_6), and with the local mode model caluclations and the vibron model calculations.[4,5] (Compared with the above two models, the nonlinear model presented here seems to be more simple.) It suggests that the five-parameter nonlinear model be suitable for the description of highly excited vibrations and the model calculations should be reliable for prediction of the positions of new highly excited vibrational bands of the benzene molecule that have not been studied experimentally. (It would be interesting to see whether or not our model calculations predict the overtone and combination bands at accurate energies.) Therefore, the results obtained should also be useful in understanding the energy transfer between different degrees of freedom in the benzene molecule.

Table 2. Model stretching vibrational energy levels (cm^{-1}) of C_6H_6 and C_6D_6 in vapor phase

n	$\lvert v_7v_{13}v_{20}v_2\rangle$	Sym.	C_6H_6		C_6D_6	
			Calc.	Exp.[4,5]	Calc.	Exp.[4,5]
1	$\lvert 1000\rangle$	E_{2g}	3056.599	3056.600	2272.500	2272.50
	$\lvert 0100\rangle$	B_{1u}	3056.999	3057.000	2285.073	2285.00
	$\lvert 0010\rangle$	E_{1u}	3064.367	3064.367	2289.264	2289.30
	$\lvert 0001\rangle$	A_{1g}	3073.939	3073.940	2303.439	2303.44
2	$\lvert 2000\rangle$	A_{1g}	6004.842		4494.792	
	$\lvert 2000\rangle$	E_{2g}	6005.728		4498.280	
	$\lvert 1100\rangle$	E_{1u}	6005.203	6006.000	4497.878	4497.00
	$\lvert 1010\rangle$	B_{1u}	6005.892		4498.891	
	$\lvert 1010\rangle$	B_{2u}	6120.673		4561.800	
	$\lvert 1010\rangle$	E_{1u}	6116.841		4559.679	
	$\lvert 1001\rangle$	E_{2g}	6114.978		4552.645	
	$\lvert 0200\rangle$	A_{1g}	6113.433		4559.615	
	$\lvert 0110\rangle$	E_{2g}	6122.462		4573.623	
	$\lvert 0101\rangle$	B_{1u}	6127.502		4581.513	
	$\lvert 0020\rangle$	A_{1g}	6124.901		4575.091	
	$\lvert 0020\rangle$	E_{2g}	6129.135		4577.988	
	$\lvert 0011\rangle$	E_{1u}	6132.023		4584.646	
	$\lvert 0002\rangle$	A_{1g}	6143.975		4602.615	
3	$\lvert 3000\rangle$	A_{1g}	8831.720		6644.038	
	$\lvert 3000\rangle$	E_{2g}	8831.742		6644.126	
	$\lvert 3000\rangle$	A_{2g}	8831.750		6644.220	
	$\lvert 2100\rangle$	B_{1u}	9055.869		6759.738	
	$\lvert 2100\rangle$	E_{1u}	8831.727	8827.000	6643.991	6644.00
	$\lvert 1200\rangle$	E_{2g}	9056.848		6764.927	
	$\lvert 0300\rangle$	B_{1u}	9659.862		6768.302	

Table 2. (*Continued*)

n	$\|v_7v_{13}v_{20}v_2\rangle$	Sym.	C_6H_6		C_6D_6	
			Calc.	Exp.[4,5]	Calc.	Exp.[4,5]
	$\|2010\rangle$	E_{1u}	9058.842		6765.862	
	$\|2010\rangle$	B_{1u}	9063.334		6772.412	
	$\|2010\rangle$	B_{2u}	9063.958		6779.841	
	$\|2010\rangle$	E_{1u}	9061.786		6777.663	
	$\|1110\rangle$	A_{1g}	9061.620		6776.354	
	$\|1110\rangle$	E_{2g}	9060.600		6776.442	
	$\|0210\rangle$	E_{1u}	9066.813		6780.025	
	$\|1020\rangle$	E_{2g}	9068.700		6788.370	
	$\|1020\rangle$	A_{1g}	9072.082		6795.146	
	$\|1020\rangle$	E_{2g}	9077.981		6799.056	
	$\|1020\rangle$	E_{2g}	9074.320		6795.728	
	$\|0120\rangle$	B_{1u}	9065.094		6785.212	
	$\|0120\rangle$	E_{1u}	9070.944		6792.940	
	$\|2001\rangle$	A_{1g}	9075.821		6796.449	
	$\|2001\rangle$	E_{2g}	9079.689		6802.308	
	$\|1101\rangle$	E_{1u}	9079.491		6842.459	
	$\|0201\rangle$	A_{1g}	9077.883		6798.822	
	$\|0030\rangle$	B_{1u}	9080.563		6802.735	
	$\|0030\rangle$	B_{2u}	9173.091		6836.150	
	$\|0030\rangle$	E_{1u}	9179.571		6846.510	
	$\|1011\rangle$	B_{1u}	9174.964		6861.292	
	$\|1011\rangle$	B_{2u}	9177.427		6863.013	
	$\|1011\rangle$	E_{1u}	9186.420		6858.625	
	$\|0111\rangle$	E_{2g}	9183.818		6846.640	
	$\|0021\rangle$	A_{1g}	9190.963		6863.870	
	$\|0021\rangle$	E_{2g}	9188.309		6862.633	
	$\|1002\rangle$	E_{2g}	9193.193		6868.600	
	$\|0102\rangle$	B_{1u}	9194.475		6873.971	
	$\|0012\rangle$	E_{1u}	9096.774		6876.542	
	$\|0003\rangle$	A_{1g}	9209.812		6896.538	

We note that the five-parameter nonlinear model describes the splittings of local C–H bond (C–D bond) stretching vibrational modes of C_6H_6 (C_6D_6) molecule due to interbond interaction. The splittings of the fundamentals are about $17.34\,\mathrm{cm}^{-1}$ and $30.94\,\mathrm{cm}^{-1}$ for C–H and C–D, respectively. The patterns of splittings (E_{2g}, B_{1u}, E_{1u}, A_{1g}) determine the nature of the interaction (i.e. our parameters $\varepsilon_1, \varepsilon_2$, and ε_3). Once these parameters are fixed, we can predict the splittings of highly excited energy levels of the benzene molecule. Similar to the X-H stretching vibrations of symmetrical hydride molecules[9−11], the near local mode degeneracy is also found in the (deuterated) benzene molecule, as is due to $\lambda \gg \varepsilon_i$ (i=1,2,3). By comparison, we find that C_6H_6 molecule is more local in its vibrational behavior than C_6D_6 molecule, as is seen easily from Table 2.

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