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MODEL STRETCHING ENERGY LEVELS FOR SF_6 MOLECULE*

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A four-parameter nonlinear model is introduced to the description of the X–Y stretching modes of XY_6 octahedral molecules in the electronic ground state. We here only apply it to the calculations of S–F stretches of SF_6 molecule. The model calculations appear to describe the observed data well, and predict some new vibrational bands at accurate energies not yet observed.

Keywords: SF_6, stretching vibrational energy levels, nonlinear model
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I. INTRODUCTION

There has been a lot of experimental and theoretical interest in highly vibrational states of polyatomic molecules in recent years.[1,2] The development of new experimental techniques to produce highly excited vibrations in polyatomic molecules, including the conventional infrared and Raman techniques, infrared-infrared double resonance experiments,[3,4] and microwave-detected microwave-optical double resonance experiments.[5] requires reliable theoretical models for their interpretation. One of the most interesting study areas of current research in molecular physics is the vibrational excited states of medium and large molecules, for which the 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 contain a large number of parameters which cannot be determined from the few available observed data. Hence, several theoretical models have been developed for description of the highly excited vibrations of polyatomic molecules, such as the local mode model,[6] and the vibron model.[7,8] In this paper, we will extent the nonlinear model[9−13] to the study of stretching vibrations of X–Y bonds of octahedral molecules, XY_6. As an example, we here only apply it to calculate the vibrational energy levels of S–F stretches of SF_6 molecule. We demonstrate that the four-parameter nonlinear model presented here is intrinsically suitable for description of the polyatomic molecular vibrations in highly excited states by comparing our model calculations with experiment and with other model calculations.

Ⅱ. THEORY

Of the fifteen vibrational modes of XY_6 octahedral molecules, we only consider the six stretching modes: $v_1(A_{1g}), v_4(E_g)$, and $v_3(F_{1u})$. The four-parameter nonlinear model for an octahedral molecule in the electronic ground state can be expressed as

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

where A=col$(A_1, A_2, A_3, A_4, A_5, A_6)$. $M = [m_{ij}]$ is a 6×6, real, symmetrical dispersion matrix describing the dipole-dipole interactions between X–Y vibrational modes. The diagonal matrix $D(|A|^2)$ 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 total vibrational energy. And ω_0 is the harmonic frequency of an X–Y vibrational mode. Consider the schematic representation of an octahedral molecule, XY_6. We number the bonds 1 to 6 as in Fig.1. It is obvious from the figure that all bonds are equivalent. Thus, we can take.

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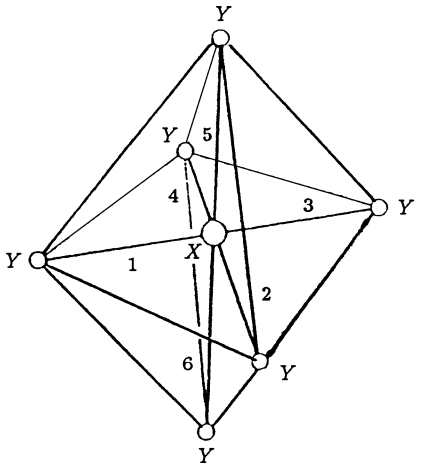


Fig.1. Schematic representation of an octahedral molecule XY_6.

$$M = \begin{bmatrix} 0 & \varepsilon_1 & \varepsilon_2 & \varepsilon_1 & \varepsilon_1 & \varepsilon_1 \\ \varepsilon_1 & 0 & \varepsilon_1 & \varepsilon_2 & \varepsilon_1 & \varepsilon_1 \\ \varepsilon_2 & \varepsilon_1 & 0 & \varepsilon_1 & \varepsilon_1 & \varepsilon_1 \\ \varepsilon_1 & \varepsilon_2 & \varepsilon_1 & 0 & \varepsilon_1 & \varepsilon_1 \\ \varepsilon_1 & \varepsilon_1 & \varepsilon_1 & \varepsilon_1 & 0 & \varepsilon_2 \\ \varepsilon_1 & \varepsilon_1 & \varepsilon_1 & \varepsilon_1 & \varepsilon_2 & 0 \end{bmatrix} \tag{2}$$

From Eq.(1), we can obtain the model Hamiltonian operator H for the stretching vibrations of XY_6 molecule

$$\hat{H} = (\omega_0 - \frac{1}{2}\lambda)\sum_{i=1}^{6}(\hat{B}_i^+\hat{B}_i + \frac{1}{2}) - \frac{1}{2}\lambda\sum_{i=1}^{6}\hat{B}_i^+\hat{B}_i\hat{B}_i^+\hat{B}_i - \sum_{i=1}^{6}m_{ij}\hat{B}_i^+\hat{B}_j, \tag{3}$$

where $\hat{B}_i^+$ and $\hat{B}_i$ are boson creation and annihilation operators, respectively, which satisfy the following relations: $\hat{B}_i^+|n_i\rangle = \sqrt{n_i+1}|n_i+1\rangle, \hat{B}_i|n_i\rangle = \sqrt{n_i}|n_i-1\rangle, \hat{B}_i|0\rangle = 0$, and $[\hat{B}_i, \hat{B}_j^+] = \delta_{ij}$, where $|n_i\rangle$ is the harmonic eigenfunction of an X–Y vibrational mode, $|0\rangle$ is the eigenfunction of 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 solve the eigenvalue equation: $\hat{H}|\Psi_n\rangle = E_n|\Psi_n\rangle$, we expand the eigenfunction, $|\Psi_n\rangle$, in terms of a suitable basis function set. In this paper, we take the basis elements in the form of, $|n,\alpha\rangle = |n_1\rangle|n_2\rangle|n_3\rangle|n_4\rangle|n_5\rangle|n_6\rangle|$, then

$$|\Psi_n\rangle = C_1|n,1\rangle + C_2|n,2\rangle + \cdots + C_{c(6,n)}|n,c(6,n)\rangle, \tag{4}$$

where $\sum_{i=1}^{c(6,n)}|C_i|^2 = 1$ (i.e. normalization condition), $n(=\sum_{i=1}^{6}n_i)$ is the total quantum number, $\alpha = 1,2,\cdot,c(6,n)$, and $c(6,n)$ is the number of ways that n particles are distributed in 6 states, i.e. $c(6,n) = (n+5)!/5!n!$. Then, the eigenvalue equation can reduce to an algebra equation on column vector $\boldsymbol{C}_n$=col$(C_1, C_2, \cdots, C_{c(6,n)})$

$$\boldsymbol{H}_n\boldsymbol{C}_n = \boldsymbol{E}_n\boldsymbol{C}_n, \tag{5}$$

where $\boldsymbol{H}_n$ is a $c(6,n) \times c(6,n)$, real, symmetrical matrix with the matrix elements: $H_{rs} = \langle n,r|\hat{H}|n,s\rangle, 1 \le r,s \le c(6,n)$. Thus, if we know the four parametric values of $\omega_0, \lambda, \epsilon_1$ and ϵ_2, the vibrational energy levels of XY_6 molecules can be obtained through solving the characteristic values of H_n. As an example, we will only calculate the S–F stretching vibrational energy levels of SF_6 molecule in this paper as follows.

Ⅲ. RESULTS AND DISCUSSION

The four parametric values of $\omega_0, \lambda, \epsilon_1$ and ϵ_2 for our model calculations are 827.19cm^{-1}, 9.60cm^{-1}, –21.866cm^{-1} and 130.510cm^{-1}, respectively, where ϵ_1 and ϵ_2 are just calculated accurately from the known fundamental frequencies using the following relations (Eqs.(6a) and (6b)), which are obtained from Eq.(5) when $n = 1$,

$$\epsilon_1 = -(v_1 - v_2)/6, \tag{6a}$$

$$\epsilon_2 = -(v_1 + 2v_2 - 3v_3)/6, \tag{6b}$$

ω_0 and λ are evaluated by the observed energy levels of SF_6 molecule.[6,7] Thus the vibrational energy levels of S–F stretches of SF_6 molecule in any highly excited states can be calculated using the above theoretical model. In Table 1, we only list our calculated results up to three quanta of vibration together with the observed results. Corresponding to energy levels obtained, we write out the appropriate symmetries. It is seen that our model calculations are in good agreement with the observed data (the corresponding r.m.s. deviation is about 1.801cm^{-1}), and with the local mode calculations of Halonen and Child[6] and the vibron model calculations of lachello and Oss.[7]

Compared with the above two models, the nonlinear model seems to be more simple. It suggests that the four-parameter nonlinear model is suitable for description of highly excited vibrations, and the model calculations should be reliable for prediction of the positions of new highly excited vibrational bands for SF_6 molecule, which have not been observed yet. (It would be very interesting to see whether or not our model calculations predict the bands at correct energies.) Moreover, the obtained results should also be useful in understanding energy transfer between different degrees of freedom in SF_6 molecule.

In conclusion, we have presented a four-parameter nonlinear model to describe the highly excited stretching vibrational energy levels of octahedral molecules, XY_6, and applied it to calculate the vibrational energy levels of S–F stretches of SF_6 molecule. The calculated results are in good agreement with the observed spectral data and with those obtained from other model calculations. It is shown that this nonlinear model could be used to predict accurately the unknown energy levels of more complicated polyatomic molecules.

Table 1. Stretching vibrational energy levels (cm^{-1}) of SF_6 molecule.

n	$\|v_1v_2v_3\rangle$	Sym.	$E_{calc.}$	$E^{6,7}_{obv.}$
1	$\|010\rangle$	E_g	643.35	643.35
	$\|100\rangle$	A_{1g}	774.54	774.54
	$\|001\rangle$	F_{1u}	948.10	948.10
2	$\|020\rangle$	A_{1g}	1283.45	
	$\|020\rangle$	E_g	1285.04	
	$\|110\rangle$	E_g	1414.70	
	$\|200\rangle$	A_{1g}	1547.49	
	$\|011\rangle$	F_{1u}	1584.90	1588.10
	$\|011\rangle$	F_{2u}	1591.45	
	$\|101\rangle$	F_{1u}	1719.60	1719.59
	$\|002\rangle$	E_g	1891.44	1891.60
	$\|002\rangle$	A_{1g}	1891.45	
	$\|002\rangle$	F_{2g}	1896.20	1896.53
3	$\|030\rangle$	E_g	1921.86	
	$\|030\rangle$	A_{1g}	1924.96	
	$\|030\rangle$	A_{2g}	1925.21	
	$\|120\rangle$	A_{1g}	2051.74	
	$\|120\rangle$	E_g	2053.17	
	$\|210\rangle$	E_g	2184.47	
	$\|021\rangle$	F_{1u}	2219.01	
	$\|021\rangle$	F_{2u}	2226.75	
	$\|021\rangle$	F_{1u}	2232.38	2227.90
	$\|300\rangle$	A_{1g}	2318.82	
	$\|111\rangle$	F_{1u}	2353.33	
	$\|111\rangle$	F_{2u}	2359.60	
	$\|201\rangle$	F_{1u}	2489.47	2489.47
	$\|012\rangle$	E_g	2521.46	
	$\|012\rangle$	A_{1g}	2521.47	
	$\|012\rangle$	F_{1g}	2529.95	
	$\|012\rangle$	A_{2g}	2534.79	
	$\|012\rangle$	E_g	2534.80	
	$\|012\rangle$	F_{2g}	2536.19	
	$\|102\rangle$	E_g	2660.21	
	$\|102\rangle$	A_{1g}	2660.22	
	$\|102\rangle$	F_{2g}	2664.50	
	$\|003\rangle$	F_{1u}	2830.04	2827.55
	$\|003\rangle$	F_{2u}	2839.55	2840.35
	$\|003\rangle$	F_{1u}	2839.55	2839.04
	$\|003\rangle$	A_{2u}	2844.30	2845.28

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