

UF₆ 分子的模型伸缩振动能级的计算*

程 艳^a, 白玉林^b, 陈向荣^{a, c, **}, 苟清泉^a

(a. 四川大学原子与分子物理研究所, 成都 610065 ;

b. 宜宾学院物理系, 宜宾 644000 ; c. 日本筑波大学物理学系, 筑波 305-8571)

摘 要: 利用一个四参数非线性模型, 对处于电子基态下的 XY₆ 型分子的 X - Y 键的伸缩振动进行了描述, 并将其应用于计算 UF₆ 分子中 U - F 键的伸缩振动能级. 计算中引入的模型 Hamilton 算符所包含的描述 U - F 键非谐振动的参数 λ 和描述 U - F 键之间的偶极-偶极相互作用参数 $\varepsilon_1, \varepsilon_2$ 由实验值得出, 波函数 $|\psi_n\rangle$ 按形式为 $|n\rangle, \alpha = |n_1\rangle |n_2\rangle |n_3\rangle |n_4\rangle |n_5\rangle |n_6\rangle$ 的基函数集展开, 从而把复杂的 Hamilton 方程转化为简单的矩阵代数方程. 结果显示, 该非线性模型能够较好地描述 UF₆ 分子的振动(计算误差在 1.0 cm^{-1} 之内), 同时合理地预测了一些至今还未观测到的能级值.

关键词: UF₆; 伸缩振动; 能级; 非线性模型

中图分类号: O561.3 文献标识码: A

Calculation for Stretching Energy Levels of UF₆ Molecule*

Cheng Yan^a, Bai Yulin^b, Chen Xiangrong^{a, c, **}, Gou Qingquan^a

(a. Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065 ;

b. Department of Physics, Yibin University, Yibin 644000 ;

c. Institute of Physics, University of Tsukuba, Tsukuba 305-8571, Japan)

Abstract A four-parameter nonlinear model is applied to describe the X - Y stretching modes of XY₆ octahedral molecules in the electronic ground state and used in the calculation of U - F stretches of UF₆ molecule. In this model, the Hamiltonian operator includes not only the anharmonic parameter, but also the dispersive parameters describing dipole-dipole interactions, reflecting the character of molecular stretching vibrations. The results obtained show that the model calculation describes the observed data well (with the accuracy within 1.0 cm^{-1}) and reasonably predicts some new vibrational bands at accurate energies not yet observed.

Key words UF₆, Stretching vibration, Energy levels, Nonlinear model

1 Introduction

There have been a lot of experimental and theoretical interests in highly excited vibrational states of polyatomic molecules in recent years^[1-3]. The appearance and development of new experimental techniques to produce highly excited vibrations in polyatomic mole-

cules, including the conventional infrared and Raman techniques, Fourier infrared interferometers and various laser techniques, infrared-infrared double resonance experiments^[1,3] and microwave-detected microwave-optical double resonance experiments^[4], require reliable theoretical methods for their interpretation. However, the highly excited vibrational energy levels

* 国家自然科学基金资助项目(10274055). ** 通讯联系人, E-mail: chen@cm.ph.tsukuba.ac.jp

收稿日期: 2002-07-04; 修回日期: 2002-12-16.

are difficult to calculate directly by solving the Schrodinger equation with interatomic potentials when the number of atoms in the molecules is larger than three. For these molecules, models based directly on the solution of many-body differential Schrodinger 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 by the few available observed data. Moreover, the theoretical models at present^[2,5-7] are difficult to be applied to deal with them.

Recently, a nonlinear model system^[8-10] has been proposed for the anharmonic system and used widely in the studies of dynamics of small molecules, molecular crystals and globular proteins. The studies on the highly excited vibrations of symmetrical hydride molecules, such as H_2X , XH_3 and XH_4 type molecules^[11-13], have shown the success of this nonlinear model. In this work, we will extend this model (the model systems calculated before have only three parameters) to the study of a series of octahedral molecules, XY_6 , which have six stretching vibrations of X-Y bonds (here, the model system has four parameters). In this work, we only apply the model to calculate the vibrational energy levels of U-F stretches of UF_6 molecule. It is demonstrated that the four-parameter nonlinear model presented here is intrinsically suitable for the description of the polyatomic molecular vibrations in highly excited states by comparing our model calculations with experiments and with other model calculations.

2 Theoretical model

In XY_6 octahedral molecule, there are fifteen vibrational modes. Here we are only interested in the six stretching vibrational modes: $\nu_1(A_{1g})$, $\nu_2(E_g)$ and $\nu_3(F_{1u})$. The four-parameter nonlinear model for an XY_6 octahedral molecule in the electronic ground state can be expressed as^[8-13]

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

where $A = \text{col}(A_1, A_2, A_3, A_4, A_5, A_6)$. $M = [m_{ij}]$

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 and 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; ω_0 is the harmonic frequency of an X-Y vibrational mode. Considering the schematic representation of a XY_6 octahedral molecule, 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 M in the following form

$$M = \begin{bmatrix} 0 & \varepsilon_1 & \varepsilon_2 & \varepsilon_1 & \varepsilon_1 & \varepsilon_1 \\ \varepsilon_1 & 0 & \varepsilon_1 & \varepsilon_2 & \varepsilon_1 & \varepsilon_1 \\ \varepsilon_2 & \varepsilon_1 & 0 & \varepsilon_1 & \varepsilon_1 & \varepsilon_1 \\ \varepsilon_1 & \varepsilon_2 & \varepsilon_1 & 0 & \varepsilon_1 & \varepsilon_1 \\ \varepsilon_1 & \varepsilon_1 & \varepsilon_1 & \varepsilon_1 & 0 & \varepsilon_2 \\ \varepsilon_1 & \varepsilon_1 & \varepsilon_1 & \varepsilon_1 & \varepsilon_2 & 0 \end{bmatrix} \quad (2)$$

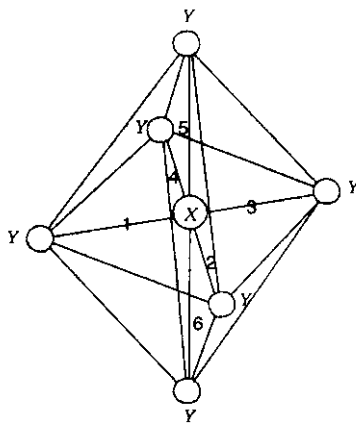


Fig. 1 The schematic representation of a XY_6 octahedral molecule

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

$$H = \left(\omega_0 - \frac{1}{2}\lambda\right) \sum_{i=1}^6 \left(B_i^+ B_i + \frac{1}{2}\right) - \frac{1}{2}\lambda \sum_{i=1}^6 B_i^+ B_i B_i^+ B_i - \sum_{i \neq j}^6 m_{ij} B_i^+ B_j \quad (3)$$

where B_i^+ and B_i are boson creation and annihilation operators, respectively, which satisfy the following relations:

$$B_i^+ | n_i \rangle = \sqrt{n_i + 1} | n_i + 1 \rangle ,$$

$$B_i | n_i \rangle = \sqrt{n_i} | n_i - 1 \rangle ,$$

$$B_i | 0 \rangle = 0 , [B_i , B_j^+] = \delta_{ij}$$

where $| n_i \rangle$ is the harmonic eigenfunction of an X - Y vibrational mode and $| 0 \rangle$ is the eigenfunction in the ground state. Here we have already taken $\hbar = 1$ and assume that both frequencies and energies are measured in the same units (cm^{-1}).

To solve the eigenvalue equation :

$$H | \psi_n \rangle = E_n | \psi_n \rangle$$

we expand the eigenfunction , $| \psi_n \rangle$, in terms of a suitable basis function set. We take the basis elements of the XY₆ molecule 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

$$| \psi_n \rangle = C_1 | n \ 1 \rangle + C_2 | n \ 2 \rangle + \dots + C_{c(6 \ n)} | n \ c(6 \ n) \rangle \quad (4)$$

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 , $\alpha = 1 \ 2 \dots \ c(6 \ n)$ and $c(6 \ n)$ is the number of ways that n particles are distributed in 6 states , i. e.

$$c(6 \ n) = \frac{(n+5)!}{5 \ n!}$$

The eigenvalue equation can reduce to an algebra equation on column vector $C_n = \text{Co}(C_1 \ C_2 \ \dots \ C_{c(6 \ n)})$

$$H_n C_n = E_n C_n \quad (5)$$

where H_n is a $c(6 \ n) \times c(6 \ n)$, real , symmetrical matrix with the matrix elements :

$$H_{rs} = \langle n \ r | \hat{H} | n \ s \rangle , \quad 1 \leq r , s \leq c(6 \ n)$$

Thus , if we can decide the four parametric values of ω_0 , λ , ε_1 and ε_2 from the observed spectral data of XY₆-type molecules , then the vibrational energy levels of them can be easily obtained through solving the characteristic values of H_n . In the next section , we use the model to calculate the U - F stretching vibrational energy levels of UF₆ molecule.

3 Results and discussion

The four parametric values of ω_0 , λ , ε_1 and ε_2 for our model calculations are 608.013 , 6.046 , -22.167 and 23.533 cm^{-1} , respectively , where ε_1 and ε_2 are

Table 1 Comparison between calculated and observed energy levels (cm^{-1}) of the UF₆ molecule

n	$ \nu_1 \nu_2 \nu_3\rangle$	Sym.	$E_{\text{cal.}}$	$E_{\text{obv.}}^{[15]}$
1	1010	E _g	534.10	534.10
	1100	A _{1g}	667.10	667.10
	1001	F _{1u}	625.50	625.50
2	1020	A _{1g}	1066.14	1066.50
	1020	E _g	1067.16	1066.30
	1110	E _g	1199.08	1197.00
	1200	A _{1g}	1333.24	
	1011	F _{1u}	1155.51	1156.90
	1011	F _{2u}	1159.60	
	1101	F _{1u}	1290.65	1290.90
3	1002	E _g	1248.12	
	1002	A _{1g}	1247.98	
	1002	F _{2g}	1251.00	
	1030	E _g	1597.13	
	1030	A _{1g}	1599.13	
	1030	A _{2g}	1599.23	
	1120	A _{1g}	1729.02	
	1120	E _g	1729.99	
	1210	E _g	1863.11	
	1021	F _{1u}	1688.63	1687.50
	1021	F _{2u}	1683.83	
	1021	F _{1u}	1692.18	
1300	A _{1g}	1998.41		
1111	F _{1u}	1822.57	1821.00	
1111	F _{2u}	1818.45		
1201	F _{1u}	1954.85	1955.00	
1012	E _g	1782.18		
1012	A _{1g}	1782.13		
1012	F _{1g}	1779.05		
1012	A _{2g}	1774.11		
1012	E _g	1773.98		
1012	F _{2g}	1783.02		
1102	E _g	1911.54		
1102	A _{1g}	1911.21		
1102	F _{2g}	1914.13		
1003	F _{1u}	1867.71		
1003	F _{2u}	1873.62	1874.60	
1003	F _{1u}	1873.52		
1003	A _{2u}	1876.50		

just calculated accurately from the known fundamental frequencies using the following relations (Eqs. (6) and (7)) , which are obtained from Eq. (5) when $n = 1$

$$\varepsilon_1 = -\frac{\nu_1 - \nu_2}{6} \quad (6)$$

$$\varepsilon_2 = -\frac{\nu_1 + 2\nu_2 - 3\nu_3}{6} \quad (7)$$

The parameters ω_0 and λ are evaluated by the observed energy levels of the UF_6 molecule^[14,15]. The calculated results are listed in Table 1. We here only present the energy levels of U - F stretches up to three quanta of vibration , but we can certainly calculate the vibrational energy levels up to all numbers of quanta. Corresponding to all 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 1.0 cm^{-1}) and also in good agreement with the local mode calculations of Halonen and Child^[14] and the vibron model calculations of Iachello and Oss^[15]. 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 the description of highly excited vibrations. In view of the high accuracy of our calculations , we think that the model calculations should be reliable for prediction of the positions of new highly excited vibrational bands for UF_6 molecule , which have not been observed yet. Moreover , the obtained results should also be useful in understanding the energy transfer between different degrees of freedom in UF_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 the calculations of the vibrational energy levels of U - F stretches of the UF_6 molecule with the high accuracy within 1.0 cm^{-1} . The calculated results agree well 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.

References

- [1] Chevalier M , De Martino A. *J. Chem. Phys.* , 1989 , **90** : 2077
- [2] Halonen M , *et al.* *J. Phys. Chem.* , 1992 , **96** : 4225
- [3] Lukka T , Kauppi E , Halonen L , *J. Chem. Phys.* , 1995 , **102** : 5200
- [4] Coy S L , Lehmann K K. *Spectrochim. Acta* , 1989 , **A45** : 47
- [5] Mills I M , Robiette A G. *Mol. Phys.* , 1986 , **56** : 743
- [6] Child M S , Hononen L. *Adv. Chem. Phys.* , 1984 , **57** : 1
- [7] Lemus R , Frank A. *J. Chem. Phys.* , 1994 , **101** : 8321
- [8] Eilbeck J C , Lomdahl P S , Scott A C. *Physica* , 1985 , **D16** : 318
- [9] Scott A C , Christiansen P L. *Phys. Scr.* , 1990 , **42** : 257
- [10] Pang X F. *The Theory of Nonlinear Quantum Mechanics* , Chongqing Press , Chongqing , 1994.
- [11] Chen X R , Gou Q Q , Pang X F. *Chin. Phys. Lett.* , 1996 , **13** : 660
- [12] Chen Xiangrong , Gou Qingquan , Pang Xiangfeng. *Chin. J. Chem. Phys.* 1998 , **11** : 240
- [13] (a) Chen Xiangrong , *et al.* *Chin. J. Chem. Phys.* 1999 , **12** : 455
(b) Chen Xiangrong , *et al.* *Acta Phys. Sin.* , 1999 , **8** : 131
- [14] Halonen L , Child M S. *J. Chem. Phys.* , 1983 , **79** : 559
- [15] Iachello F , Oss S. *Phys. Rev. Lett.* , 1991 , **66** : 2976