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CALCULATION OF HIGHLY EXCITED VIBRATIONAL ENERGY LEVELS OF CH_3CN MOLECULE BY NON-LINEAR QUANTUM THEORY

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A three-parameter nonlinear dynamical model, i.e., the quantized discrete self-trapping equation, was used to calculate the highly excited CH stretching vibrational energy levels of liquid phase CH_3CN molecule in the electronic ground state up to n=7. The calculated results show that the experimental energy levels can be well described by the model.

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I. INTRODUCTION

The developments of some new experimental techniques, such as infrared-infrared double resonance method,[1,2] microwave-detected microwave optical double resonance method,[3] and so on, have made it possible to produce highly excited states of polyatomic molecules. However, the experimental spectroscopic data require reliable theoretical analysis for their interpretation. Presently, the general models often concentrate on the use of the local mode model,[4] the normal mode model[5] with anharmonic expansions on the diagonal and Darling-Dennison resonance operators off-diagonal, and the vibron model.[6] But these models are inconvenient when applied to study the highly excited vibrations if the number of atoms in the molecule is larger than three.

Recently, a simple three-parameter nonlinear dynamical model, i.e., the discrete self-trappling equation,[7−10] has been proposed for anharmonic systems, and used widely in the studies of the dynamics of small molecules, molecular crystals, and globular proteins.[9] In our previous work, we have applied the nonlinear model to calculate the highly excited vibrational energy levels of pyramidal AsH_3 molecules with considerable success.[11] Based on this work, we may utilize the nonlinear model for analysis of methyl CH streching vibrational energy levels of methyl halide and methyl cyanide molecules containing CH_3 group. In this paper, we only deal with the methyl cyanide (CH_3CN) molecule. The calculated results show that the known experimental spectral data of CH_3CN molecule can be well described by the nonlinear model.

II. THEORY

The theoretical model employed is similar to the ones in the previous studies on AsH_3 molecule.[11] Only a brief description of it is presented here.

In the CH_3CN molecule, CH_3 group belongs to C_{3v} point group symmetry and has three coupled anharmonic CH stretching vibrational modes, and the discrete self-trapping equation is then in the form

$$\left(\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}-\omega_0\right)\begin{bmatrix}A_1\\A_2\\A_3\end{bmatrix}+\begin{bmatrix}0&\varepsilon&\varepsilon\\\varepsilon&0&\varepsilon\\\varepsilon&\varepsilon&0\end{bmatrix}\begin{bmatrix}A_1\\A_2\\A_3\end{bmatrix}+\lambda\begin{bmatrix}|A_1|^2&0&0\\0&|A|^2&0\\0&0&|A_3|^2\end{bmatrix}\begin{bmatrix}A_1\\A_2\\A_3\end{bmatrix}=0\ , \quad (1)$$

where A_i (i=1, 2, 3) is the complex mode amplitudes of a particular methyl CH bond, ε is a dispersive parameter describing the dipole-dipole interaction between CH stretching modes, λ is an anharmonic parameter, ω_0 is the harmonic frequency of CH oscillators called Einstein oscillators.

Under quantization,[8−11] A_i and A_i^* become Boson annihilation operator $\hat{B}_i$ and creation operator $\hat{B}_i^+$ (i=1, 2, 3) respectively, which satisfy the following relations: $\hat{B}_i^+|n_i\rangle = \sqrt{n_i+1}|n_i\rangle$, $\hat{B}_i|n_i\rangle = \sqrt{n_i}|n_i-1\rangle$, $\hat{B}_i|0\rangle = 0$, and $[\hat{B}_i, \hat{B}_j^+] = \delta_{ij}$, where $|n_i\rangle$ is a harmonic eigenfunction of the ith CH stretching vibration, $|0\rangle$ is the eigenfunction of any CH oscillator in ground state. Then, corresponding to Eq.(1), there exist two operators: the Hamiltonian energy

$$\hat{H} = \left(\omega_0 - \frac{1}{2}\lambda\right)\hat{N} - \frac{1}{2}\lambda\sum_{i=1}^{3}\hat{B}_i^+\hat{B}_i\hat{B}_i^+\hat{B}_i - \varepsilon\sum_{i\neq j}^{3}\hat{B}_i^+\hat{B}_j \quad (2)$$

and the number operator

$$\hat{N} = \sum_{i=1}^{3}\left(\hat{B}_i\hat{B}_i + \frac{1}{2}\right)\ , \quad (3)$$

where we take $\hbar = 1$, and assume that both frequencies and energies are measured in the same units (cm^{-1}).

By choosing the elements of the basis function set in the form: $|n, a\rangle = |n_1\rangle\,|n_2\rangle\,|n_3\rangle$, where $n(= n_1 + n_2 + n_3)$ is the total vibrational quantum number, $a = 1, 2, \cdots, c(n)$, and $c(n)$ is equal to the number of ways by which n particles are distributed in the three states, i.e., $c(n) = (n+1)(n+2)/2$, and by expanding the common eigenfunctions, $|\psi_n\rangle$, of both operators, we can obtain the following matrix equation

$$H_n\overline{C}_n = E_n\overline{C}_n\ , \quad (4)$$

where $\overline{C}_n$ = col $(C_1,\ C_2, \cdots, C_{c(n)})$ is a column vector consisting of the coefficients in the expansion, H_n is a $c(n)\times c(n)$ real symmetrical matrix, the elements of which are: $H_{rs} = \langle n, r|\hat{H}|n, s\rangle$, $1 \le r,\ s \le c(n)$, and $r \neq s$. Thus, the eigenvalues of the model Hamiltonian $\hat{H}$ can be obtained from Eq.(4) by solving the secular equation of H_n.

Ⅲ. RESULTS AND DISCUSSION

The methyl CH stretching vibrational energy levels of the CH_3CN molecule can be calculated if we know the parametric values of ω_0, λ and ε. In our model ω_0, λ and ε for calculations are taken to be: $3098.85\,\mathrm{cm}^{-1}$, $117.52\,\mathrm{cm}^{-1}$ and $18.67\,\mathrm{cm}^{-1}$ respectively, which

are obtained by the known experimental energy levels.[12] Our calculated results and the known experimental data are given in Table 1. Two different kinds of labels containing the

Table 1. The CH stretching vibrational energy levels (in units of cm^{-1}) of CH_3CN molecule.

n	NM	LM	Exp.	Calc.	n	NM	LM	Exp.	Calc.
1	$\nu_1(A_1)$	$100A_1$	2944	2944	6	$4\nu_1+2\nu_3(E)$	$510E$		16683.5
	$\nu_3(E)$	$100E$	3000	3000.0		$3\nu_1+3\nu_3(E)$	$510E$		16720.8
2	$2\nu_1(A_1)$	$200A_1$	5800	5818.9		$3\nu_1+3\nu_3(A_2)$	$510A_2$		16721.3
	$\nu_1+\nu_3(E)$	$200E$	5837	5840.2		$3\nu_1+3\nu_3(A_1)$	$420A_1$		17005.8
	$2\nu_3(A_1)$	$110A_1$	5958	5951.5		$2\nu_1+4\nu_3(E)$	$420E$		17013.9
	$2\nu_3(E)$	$110E$	6003	5986.3		$2\nu_1+4\nu_3(E)$	$420E$		17063.9
3	$3\nu_1(A_1)$	$300A_1$	8608	8579.8		$2\nu_1+4\nu_3(A_1)$	$411A_1$		17165.84
	$2\nu_1+\nu_3(E)$	$300E$	8608	8582.7		$\nu_1+5\nu_3(A_2)$	$420A_2$		17072.48
	$\nu_1+2\nu_3(A_1)$	$210A_1$	8753	8760.1		$\nu_1+5\nu_3(E)$	$411E$		17179.6
	$\nu_1+2\nu_3(E)$	$210E$	8793	8798.8		$\nu_1+5\nu_3(A_1)$	$330A_1$		17228.1
	$3\nu_3(E)$	$210E$	8858	8862.9		$\nu_1+5\nu_3(E)$	$330E$		17231.6
	$3\nu_3(A_2)$	$210A_2$		8882.5		$6\nu_3(A_1)$	$321A_1$		17322.7
	$3\nu_3(A_1)$	$111A_1$	8996	8966.0		$6\nu_3(E)$	$321E$		17392.9
4	$4\nu_1(A_1)$	$400A_1$	11217	11211.7		$6\nu_3(E)$	$321E$		17479.0
	$3\nu_1+\nu_3(E)$	$400E$	11217	11211.9		$6\nu_3(A_2)$	$321A_2$		17514.4
	$2\nu_1+2\nu_3(A_1)$	$310A_1$	11491	11517.7		$6\nu_3(A_1)$	$222A_1$		17587.1
	$2\nu_1+2\nu_3(E)$	$310E$	11491	11540.6	7	$7\nu_1(A_1)$	$700A_1$		18394.3
	$\nu_1+3\nu_3(E)$	$310E$	11600	11574.2		$6\nu_1+\nu_3(E)$	$700E$		18394.3
	$\nu_1+3\nu_3(A_2)$	$310A_2$		11591.4		$5\nu_1+2\nu_3(A_1)$	$610A_1$		19078.3
	$\nu_1+2\nu_3(A_1)$	$220A_1$		11699.6		$5\nu_1+2\nu_3(E)$	$610E$		19078.4
	$4\nu_3(E)$	$220E$		11719.3		$4\nu_1+3\nu_3(E)$	$610E$		19115.9
	$4\nu_3(A_1)$	$211A_1$		11768.7		$4\nu_1+3\nu_3(A_2)$	$610A_2$		19115.9
	$4\nu_3(E)$	$211E$		11855.3		$4\nu_1+3\nu_3(A_1)$	$520A_1$		19540.7
5	$5\nu_1(A_1)$	$500A_1$	13743	13723.7		$3\nu_1+4\nu_3(E)$	$520E$		19546.5
	$4\nu_1+\nu_3(E)$	$500E$	13743	13723.7		$3\nu_1+4\nu_3(E)$	$520E$		19558.8
	$3\nu_1+2\nu_3(A_1)$	$410A_1$		14165.9		$3\nu_1+4\nu_3(A_1)$	$511A_1$		19689.6
	$3\nu_1+2\nu_3(E)$	$410E$		14171.0		$2\nu_1+5\nu_3(A_2)$	$520A_2$		19565.2
	$2\nu_1+3\nu_3(E)$	$410E$		14205.8		$2\nu_1+5\nu_3(E)$	$511E$		19691.6
	$2\nu_1+3\nu_3(A_2)$	$410A_2$		14210.3		$2\nu_1+5\nu_3(A_1)$	$430A_1$		19756.1
	$2\nu_1+3\nu_3(A_1)$	$320A_1$		14375.1		$2\nu_1+5\nu_3(E)$	$430E$		19757.4
	$\nu_1+4\nu_3(E)$	$320E$		14388.0		$\nu_1+6\nu_3(A_1)$	$421A_1$		19948.7
	$\nu_1+4\nu_3(A_1)$	$311A_1$		14508.5		$\nu_1+6\nu_3(E)$	$430E$		19898.6
	$\nu_1+4\nu_3(E)$	$320E$		14493.0		$\nu_1+6\nu_3(A_2)$	$430A_2$		19900.0
	$5\nu_3(A_2)$	$320A_2$		14502.5		$\nu_1+6\nu_3(E)$	$421E$		19998.3
	$5\nu_3(E)$	$311E$		14562.5		$\nu_1+6\nu_3(A_1)$	$331A_1$		20170.8
	$5\nu_3(A_1)$	$221A_1$		14672.6		$7\nu_3(E)$	$421E$		20059.2
	$5\nu_3(E)$	$221E$		14726.7		$7\nu_3(A_2)$	$421A_2$		20091.0
6	$6\nu_1(A_1)$	$600A_1$	16082	16117.8		$7\nu_3(E)$	$331E$		20219.3
	$5\nu_1+\nu_3(E)$	$600E$	16082	16117.8		$7\nu_3(A_1)$	$322A_1$		20261.7
	$4\nu_1+2\nu_3(A_1)$	$510A_1$		16683.0		$7\nu_3(E)$	$322E$		20362.0

appropriate symmetries are used to identify these levels: one is the normal mode model (NM), and the other is the local mode model (LM).

It is seen that the agreements between our calculated results and experimental data, and those calculated by Ahmed and Henry from the local mode model[12] are good. The RMS deviation of our calculations from the experiment is about $22\,\mathrm{cm}^{-1}$ (almost the same as that of Ahmed and Henry). The reason why the agreement between the experiment and calculations is slightly less satisfactory is that there exist strong Fermi resonance interactions in the CH_3CN molecule, which occur between levels involving CH stretching and two quanta of CH_3 deformation.[13] Nevertheless, the calculated energy levels for prediction of the positions of methyl CH stretching vibrational band origins should be helpful in the assignment of new vibrational spectral lines of the CH_3CN molecule.

We note that the dominant feature of the methyl CH stretching vibrational energy levels of the CH_3CN molecule is a pattern of local mode pairs composed of the combinations A_1 or A_2 symmetry species and E symmetry species. In a certain local mode state, $|a\,b\,c\rangle$, where a, b, and c denote the three CH bonds in the ath, bth and cth vibrational state respectively, the difference between energy levels becomes very small when n increases. The two lowest excited energy levels of A_1 and E species with a common n are degenerate at $n = 5$ in our calculations. This suggests that when $n \geq 5$, the CH_3CN molecule could be considered as vibrating with the three methyl CH stretching quanta trapped into a single CH bond.

REFERENCES

[1] M. Chevalier and A. De Martino, *J. Chem. Phys.*, **90**(1989), 2077.
[2] T. Luka, E. Kauppi and L. Halonen, *J. Chem. Phys.*, **102**(1995), 5200.
[3] S. L. Coy and K. K. Lehmann, *Spectrochim. Acta*, **A45**(1989), 47.
[4] L. Halonen, *J. Phys. Chem.*, **93**(1989), 3386.
[5] I. M. Mills and A. G. Robiette, *Mol. Phys.*, **56**(1989), 743.
[6] R. Lemus and A. Frank, *J. Chem. Phys.*, **101**(1994), 8321.
[7] J. C. Eilbeck, P. S. Lomadahl and A. C. Scott, *Physica*, **D16**(1985), 318.
[8] A. C. Scott and P. L. Christiansen, *Phys. Scr.*, **42**(1990), 257.
[9] X. F. Pang, The Theory of Nonlinear Quantum Mechanics (Chongqing Press, Chongqing, 1994)(in Chinese).
[10] Chen Xiang-rong, Gou Qing-quan, Pan Xiao-feng, *Chinese Phys. Lett.*, **13**(1996), 660.
[11] Chen Xiang-rong, Gou Qing-quan, Pan Xiao-feng, *Acta Physica Sinica*(*Overseas Edition*), **7**(1998), 327.
[12] M. K. Ahmed and B. R. Henry, *J. Chem. Phys.*, **87**(1987), 3724.
[13] A. Badaoui and J. P. Champion, *J. Mol. Spectrosc.*, **109**(1985), 402.