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CALCULATIONS OF STRETCHING VIBRATIONAL ENERGY LEVELS OF THE CH_3I MOLECULE BY A NONLINEAR MODEL*

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A nonlinear model, i.e. the quantized discrete self-trapping equation, is applied to calculate the highly excited CH stretching vibrational energy levels of the CH_3I molecule in the liquid phase at the electronic ground state up to n=8. The obtained results agree well with the experimental data and with those obtained from local mode model calculations. We note that the dominant feature of the methyl CH stretching vibrational energy levels of the CH_3I molecule is a pattern of local mode pairs. When $n \geq 7$, all the vibrational energy of the CH_3 group can nearly be localized on a single CH bond.

Keywords: CH_3I, stretching vibration, nonlinear model
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I. INTRODUCTION

There has been much experimental and theoretical interest in highly excited vibrational states of polyatomic molecules in recent years.[1−3] Many new experimental techniques have been developed and used to probe the highly excited vibrational states in polyatomic molecules, and the experimental results require reliable theoretical methods for their interpretation. The theoretical models, however, 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]

Recently, a simple nonlinear model, i.e. the quantized discrete self-trapping equation[7−15], has been proposed for anharmonic systems, and has been used widely in describing the vibrations of polyatomic molecules. In our earlier studies, we have even applied the nonlinear model to calculate the highly excited vibrational energy levels of pyramidal XH_3 molecules with considerable success.[11,12] Based on this work, we may utilize this nonlinear model in the analysis of methyl CH stretching vibrational energy levels of methyl halides molecules. In this paper, we only deal with the CH_3I molecule in the liquid phase. We show that the nonlinear model is suitable for the description of the vibrations of the CH_3I molecule in highly excited states by comparing our model calculations with experiment and with the local mode model calculations. In section II, we present a brief review of the nonlinear model. The calculated stretching vibrational energy levels of the CH_3 group of the CH_3I molecule in the liquid phase are presented and discussed in section III.

II. THEORY

The theory of the nonlinear model applied here is similar to that in the previous studies on the XH_3 molecule.[11,12] Only a brief description of this theory is presented here.

We all know that, in the CH_3I molecule, the CH_3 group belongs to C_{3v} point group symmetry and has three coupled anharmonic CH stretching vibrational modes. Thus, the corresponding discrete self-trapping equation is in the form[11,12]

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

where $A_i (i = 1, 2, 3)$ is the complex mode amplitude

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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 describing the main contribution of the anharmonic terms in molecular vibrational potential energy to total vibrational energy, and ω_0 is the harmonic frequency of CH oscillators.

Under quantization[8,9], A_i and A_i^* become the boson annihilation operator $\hat{B}_i$ and creation operator $\hat{B}_i^+$ $(i = 1,2,3)$, which satisfy the following relations: $\hat{B}_i^+|n_i\rangle = \sqrt{n_i+1}|n_i\rangle, \hat{B}_i|n_i\rangle = \sqrt{n_i}|n_i-1\rangle$, $\hat{B}_i|0\rangle = 0$, $[\hat{B}_i, \hat{B}_j^+] = \delta_{ij}$, where $|n_i\rangle$ is a harmonic eigenfunction of the ith CH stretching vibration, and $|0\rangle$ is the eigenfunction of the CH oscillator at the ground state. Corresponding to Eq.(1), two operators exist: the Hamiltonian energy

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

and the number operator

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

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

If the elements of the basis function set are chosen in the following form, $|n,m\rangle = |n_1\rangle|n_2\rangle|n_3\rangle$, where $n(= n_1 + n_2 + n_3)$ is the total vibrational quantum number, m=1,2,..., $c(n)$, and $c(n)$ is equal to the number of ways that n particles are distributed in three states, i.e., $c(n) = (n+1)(n+2)/2$, and if the common eigenfunctions $|\Psi_n\rangle$ of both operators $\hat{H}$ and $\hat{N}$ are expanded in terms of the above basis function set, then the Hamiltonian equation $\hat{H}|\Psi_n\rangle = E_n|\Psi_n\rangle$ reduces to the following matrix equation

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

where $\overline{C}_n = \mathrm{col}(C_1, C_2, ..., C_{c(n)})$ 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: $H_{rs} = \langle n,r|\hat{H}|n,s\rangle, 1 \le r,s \le c(n)$. Thus, the eigenvalues of the above 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_3I molecule can be calculated if we know the values of parameters ω_0, λ and ε. In our model calculations, ω_0, λ and ε are taken as $3139.29\,\mathrm{cm}^{-1}$, $126.62\,\mathrm{cm}^{-1}$ and $32.33\,\mathrm{cm}^{-1}$, respectively, which are obtained by the known experimental energy levels. In table 1 we list our calculated results for $1 \le n \le 8$ and the known experimental data[16]. Two different kinds of labels containing the 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 agreement between our calculated results and experimental data, and those calculated by Ahmed and Henry[13] from the local mode model are good. The reason why the agreement between the experiment and calculation is slightly less satisfactory is that strong Fermi resonance interactions exist in the CH_3I molecule which occur between levels involving CH stretching and two quanta of CH_3 deformation[17]. 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_3I molecule in the liquid phase.

We note that the dominant feature of the methyl CH stretching vibrational energy levels of the CH_3I molecule is also a pattern of local mode pairs composed of the combinations A_1 or A_2 symmetry species and E symmetry species. At 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 states, respectively. The differences of energy levels become very small as n increases. The two lowest excited energy levels of A_1 and E species with a common n are degenerate at n=7 for our calculations. This suggests that when $n \ge 7$, the CH_3I molecule could be thought of as vibrating with the three methyl CH stretching quanta trapped in a single CH bond.

Table 1. Stretching vibrational energy levels (in cm^{-1}) of CH_3I.

NM	LM	Exp.	Calc.	NM	LM	Exp.	Calc.
$v_1(A_1)$	$100A_1$	2948	2948.01	$2v_3+4v_3(A_1)$	$411A_1$		17255.56
$v_3(E)$	$100E$	3045	3045.00	$v_1+5v_3(A_2)$	$420A_2$		17210.06
$2v_1(A_1)$	$200A_1$	5845	5833.15	$v_1+5v_1(E)$	$411E$		117310.62
$v_1+v_3(E)$	$200E$	5911	5886.51	$v_1+5v_3(A_1)$	$330A_1$		17397.17
$2v_3(A_1)$	$110A_1$	6028	6026.25	$v_1+5v_3(E)$	$330E$		17422.34
$2v_3(E)$	$110E$	6082	6069.89	$6v_3(A_1)$	$321A_1$		17466.59
$3v_1(A_1)$	$300A_1$	8620	8620.00	$6v_3(E)$	$321E$		17547.72
$2v_1+v_3(E)$	$300E$	8650	8634.53	$6v_3(E)$	$321E$		17684.10
$v_1+2v_3(A_1)$	$210A_1$	8785	8803.87	$6v_3(A_2)$	$321A_2$		17738.97
$v_1+2v_3(E)$	$210E$	8840	8868.36	$6v_3(A_1)$	$222A_1$		17804.41
$3v_3(E)$	$210E$	8982	8978.04	$7v_1(A_1)$	$700A_1$		18409.56
$3v_3(A_2)$	$210A_2$		9008.38	$6v_1+v_3(E)$	$700E$		18409.56
$3v_3(A_1)$	$111A_1$	9103	9086.69	$5v_1+2v_3(A_1)$	$610A_1$		19129.65
$4v_1(A_1)$	$400A_1$	11287	11265.65	$5v_1+2v_3(E)$	$610E$		19130.03
$3v_1+v_3(E)$	$400E$	11287	11267.40	$4v_1+3v_3(E)$	$610E$		19195.06
$2v_1+2v_3(A_1)$	$310A_1$	11575	11550.61	$4v_1+3v_3(A_2)$	$610A_2$		19195.40
$2v_1+2v_3$(E)	$310E$		11603.51	$4v_1+3v_3(A_1)$	$520A_1$		19593.41
$v_1+3v_3(E)$	$310E$	11647	11669.54	$3v_1+4v_3(E)$	$520E$		19610.02
$v_1+3v_3(A)$	$310A_2$		11703.15	$3v_1+4v_3(E)$	$520E$		19652.84
$v_1+3v_3(A_1)$	$220A_1$		11813.70	$3v_1+4v_3(A_1)$	$511A_1$		19798.87
$4v_3(E)$	$220E$		11865.90	$2v_1+5v_3(A_2)$	$520A_2$		19671.58
$4v_3(A_1)$	$211A_1$		11891.67	$2v_1+5v_3(E)$	$511E$		19812.17
$4v_3(E)$	$211E$		12012.40	$2v_1+5v_3(A_1)$	$430A_1$		19876.40
$5v_1(A_1)$	$500A_1$	13817	13825.01	$2v_1+5v_3(E)$	$430E$		19886.45
$4v_3+v_3(E)$	$500E$	13817	13825.15	$v_1+6v_3(A_1)$	$421A_1$		20110.93
$3v_1+2v_3(A_1)$	$410A_1$		14266.42	$v_1+6v_3(E)$	$430E$		20096.09
$3v_1+2v_3(E)$	$410E$		14288.55	$v_1+6v_3(A_2)$	$430A_2$		20019.71
$2v_1+3v_3(E)$	$410E$		14343.81	$v_1+6v_3(E)$	$421E$		20129.53
$2v_3+3v_3(A_2)$	$410A_2$		14361.53	$v_1+6v_3(A_1)$	$331A_1$		20351.31
$2v_1+3v_3(A_1)$	$320A_1$		14503.78	$7v_3(E)$	$421E$		20226.94
$v_1+4v_3(E)$	$320E$		14540.43	$7v_3(A_2)$	$421A_2$		20285.12
$v_1+4v_1(A_1)$	$311A_1$		14728.28	$7v_3(E)$	$331E$		20451.49
$v_1+4v_3(E)$	$320E$		14698.13	$7v_3(A_1)$	$322A_1$		20474.26
$5v_3(A_2)$	$320A_2$		14648.33	$7v_3(E)$	$322E$		20607.01
$5v_3(E)$	$311E$		14764.80	$8v_1(A_1)$	$800A_1$		20536.42
$5v_3(E)$	$221E$		14965.54	$7v_1+v_3(E)$	$800E$		20536.42
$5v_3(A_1)$	$221A_1$		14899.07	$6v_1+2v_3(A_1)$	$710A_1$		21385.15
$6v_1(A_1)$	$600A_1$	16243	16155.84	$6v_1+2v_3(E)$	$710E$		21385.17
$5v_1+v_3(E)$	$600E$	16243	16155.85	$5v_1+3v_3(E)$	$710E$		21450.28
$4v_1+2v_3(A_1)$	$510A_1$		16743.68	$5v_1+3v_3(A_2)$	$710A_2$		21450.30
$4v_1+2v_3(E)$	$510E$		16747.47	$5v_1+3v_3(A_1)$	$620A_1$		22002.98
$3v_1+3v_3(E)$	$510E$		16810.62	$4v_1+4v_3(E)$	$620E$		22009.95
$3v_1+3v_3(A_2)$	$510A_2$		16813.99	$4v_1+4v_3(E)$	$620E$		22033.03
$3v_1+3v_3(A_1)$	$420A_1$		17057.28	$4v_1+4v_3(A_1)$	$611A_1$		22193.83
$2v_1+4v_3(E)$	$420E$		17081.74	$3v_1+5v_3(A_2)$	$620A_2$		22040.94
$2v_1+4v_3(E)$	$420E$		17186.95	$3v_1+5v_3(E)$	$611E$		22196.09
$3v_1+5v_3(A_1)$	$530A_1$		22318.01	$v_1+7v_3(A_2)$	$521A_2$		22732.15
$3v_3+5v_3(E)$	$530E$		22322.69	$v_1+7v_3(A_1)$	$431A_1$		22827.12
$2v_1+6v_3(E)$	$530E$		22480.79	$v_1+7v_3(E)$	$431E$		22911.24
$2v_1+6v_3(A_1)$	$521A_1$		22554.67	$8v_3(A_1)$	$422A_1$		23139.43
$2v_1+6v_3(A_2)$	$530A_2$		22487.11	$8v_3(E)$	$431E$		23075.02
$2v_1+6v_3(E)$	$521E$		22613.23	$8v_3(A_2)$	$431A_2$		23014.62
$2v_1+6v_3(A_1)$	$440A_1$		22751.92	$8v_3(E)$	$422E$		23177.60
$v_1+7v_3(E)$	$521E$		22713.18	$8v_3(A_1)$	$332A_1$		23301.57
$v_1+7v_3(E)$	$440E$		22736.17	$8v_3(E)$	$332E$		23386.38

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