

Molecular Dynamics Simulation of Infrared and Raman Spectra of Liquid Methane

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Molecular dynamics simulation has been used to investigate the infrared and Raman spectra of liquid methane. The simulation reproduced well the observed spectra in frequency and intensity. These spectra have been compared for harmonic and anharmonic models. Over tones and combination bands are produced for infrared and Raman spectra. Splitting due to Fermi resonance has occurred in the region of ν_1 coupling with $2\nu_2$ vibration.

KEY WORDS: Molecular dynamics / Liquid methane / Infrared and Raman spectra

INTRODUCTION

Infrared and Raman spectra have usually been studied on the basis of normal coordinate analysis and intensity calculation. Recently, molecular dynamics simulation has been applied to produce the spectra, besides studying structure and physical property, of a variety of molecular systems, infrared spectra of CO gas,¹⁾ Raman spectra of N₂ gas,²⁾ infrared spectra of gaseous and liquid SO₂,³⁾ infrared spectra of crystalline benzoic acid,^{4,5)} and molten LiNO₃.^{6,7)} These spectra reproduced well the observed ones in frequency, intensity, band shape and splitting due to intermolecular interactions.

In a previous paper,⁸⁾ physical properties of liquid methane were studied by using molecular dynamics simulation. The simulation reproduced well the radial distribution and the self-diffusion coefficient and suggested cooperative rotational motion as a gear wheel. In this work, infrared and Raman spectra of liquid methane simulated by the method are reported.

METHOD AND MODEL

The method of the simulation and the model of the system are described in a previous paper.⁸⁾ Two kinds of models are adopted; one is a harmonic model, the other is an anharmonic model. In the harmonic model, quadratic force constants, listed in Table I of the previous paper,⁸⁾ are used. In addition, cubic and quartic force constants for the CH stretching coordinate are introduced for the anharmonic model.

Infrared spectra are obtained from the linear response equations¹⁾

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$$\alpha_d(\omega) = \frac{4\pi^2\omega^2\beta}{3cn} I_d(\omega), \quad d=x, y, z \quad (1)$$

and

$$I_d(\omega) = \frac{3}{2\pi} \left[\lim_{\tau \rightarrow \infty} \frac{1}{2\tau} \left| \int_{-\tau}^{\tau} dt \exp(-i\omega t) \mu_d(t) \right|^2 \right], \quad d=x, y, z \quad (2)$$

where $\alpha_d(\omega)$ is the absorption cross section as a function of angular frequency ω , $\beta = (k_B T)^{-1}$ in which k_B is Boltzmann's constant and T is the temperature, c is the velocity of light, and n is the refractive index of the medium. $I_d(\omega)$ is defined as the absorption band shape, and may be computed in the form of the power spectrum by fast Fourier-transform technique. The equations are written in the form applicable to oriented systems and can be used for isotropic systems by taking an average of the three $\alpha_d(\omega)$.

Dipole moment of the system μ_d is obtained by summing over bond dipoles μ_k of all molecules in the system.

$$\mu_d = \sum_{mol} \sum_{bond} \mu_k \Phi_d \quad (3)$$

where Φ_d is direction cosine between k th dipole and d th axes. Bond dipole is assumed as follows:

$$\mu_k = \mu_k^0 + \sum_j \frac{\partial \mu_k}{\partial S_j} S_j \quad (4)$$

in which S_j is j th internal coordinate, μ_k^0 is k th bond moment at equilibrium, and $\partial \mu_k / \partial S_j$ means charge flux in k th bond induced by j th internal coordinate. Values of parameters are listed in Table 1 in the units of electronic charge and Angstrom.

The differential cross section of Raman scattering is calculated by the following equation.

$$\left(\lambda_s^4 \frac{d^2 \sigma}{d\omega d\Omega} \right)_{FF'} = \frac{1}{2\pi} \left[\lim_{\tau \rightarrow \infty} \frac{1}{2\tau} \left| \int_{-\tau}^{\tau} dt \exp(-i\omega t) P_{FF'}(t) \right|^2 \right] \quad (5)$$

where $d\omega$ is angular frequency range, $d\Omega$ is solid angle range. F and F' are space fixed coordinates. When $F=F'$, parallel spectra are obtained, and if $F \neq F'$, perpendicular spectra are evaluated. Polarizability of the system $P_{FF'}$ is obtained by summing over the bond polarizability P_i of all molecules in the system.

$$P_{FF'} = \sum_{mol} \sum_{bond} \sum_i P_i \Phi_{Fi} \Phi_{F'i} \quad (6)$$

in which P_i is principal polarizability fixed to the k th bond. Φ is direction cosine. Cylindrical polarizability is assumed, that is, P_1 is polarizability parallel to a bond, $P_2=P_3$ is polarizability perpendicular to the bond. Bond polarizability is assumed to be

$$P_i = P_i^0 + \sum_j \frac{\partial P_i}{\partial S_j} S_j \quad (7)$$

where P_i^0 is bond polarizability at equilibrium with respect to i th principal axes of polarizability, and $\partial P_i / \partial S_j$ is derivatives of the bond polarizability with respect to the j th internal coordinates of a molecule. Values of the parameters estimated from the observed polarizability of 2.61 and literature values,⁹⁾ are also listed in Table 1.

Table 1. Electro optical parameters

μ_k^0	0.241	a_1^0	0.8412
$\partial \mu_k / \partial r_k$	-0.922	$\alpha_2^0 (= a_3^0)$	0.5582
$\partial \mu_k / \partial r_j$	-0.234	$\partial \alpha_1 / \partial r_k$	2.5196
$\partial \mu_k / \partial \theta_{kj}$	-0.028	$\partial \alpha_2 / \partial r_k$	0.4186
		$\partial \alpha_1 / \partial r_j$	-0.0906
		$\partial \alpha_2 / \partial r_j$	0.0453

RESULTS AND DISCUSSION

Infrared spectra

Methane molecule has T_d symmetry, and four fundamental vibrations as follows:

$$A_1(\nu_1) + E(\nu_2) + 2F_2(\nu_3, \nu_4)$$

F_2 species is infrared active, and A_1 , E and F_2 species are Raman active. Figure 1 demonstrates a simulated infrared spectrum of an anharmonic model of liquid methane. The ν_3 and ν_4 bands are seen in the figure as expected from selection rule. The effect of anharmonicity are detected in frequency, half band width, and intensity as listed in Table 2. Anharmonicity acts to lower frequency and widen the band width for the stretching vibration ν_3 whose potential function include anharmonicity. The frequency may depend on amplitudes which are populated by Boltzmann factor. However, the bending vibration ν_4 was not affected by anharmonicity both on frequency and half band width, because the bending coordinate is treated as harmonic. Intensity for two models are the same order to the observed.

Figure 2 displays the simulated infrared spectra of an anharmonic model in the region of overtone and combination bands. Considering the F_2 species is infrared active, assignments of bands are given as indicated in the figure. The $\nu_1 + \nu_3$ combination band of stretching modes appears in the case of anharmonic model, but disappears for harmonic model. The overtone of a bending vibration ν_4 appears without anharmonic term in force field. The bending mode depicts an arc and results in transition dipole of the frequency of $2\nu_4$ in the direction of the bond.

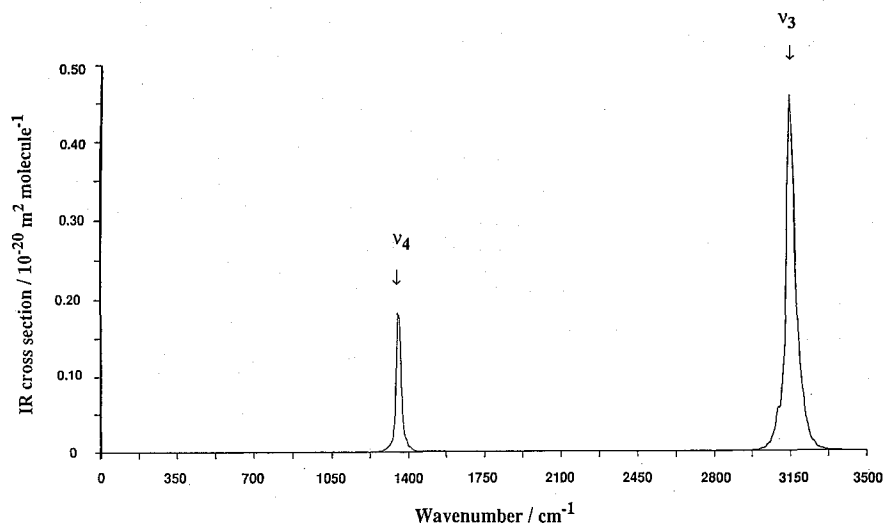


Fig. 1. Simulated infrared spectrum of an anharmonic model of liquid methane in the region of fundamentals.

Table 2. Calculated and experimental frequencies and band widths of ν_3 and ν_4 infrared bands

	Wavenumber / cm^{-1}			Half band width / cm^{-1}			Intensity / km mol^{-1}		
	harm.	anharm.	exp. ¹⁰⁾	harm.	anharm.	exp. ¹¹⁾	harm.	anharm.	exp. ¹⁰⁾
ν_3	3169	3154	3152	24	44	40	11700	14300	6729
ν_4	1357	1357	1361	24	24		4300	2900	3365

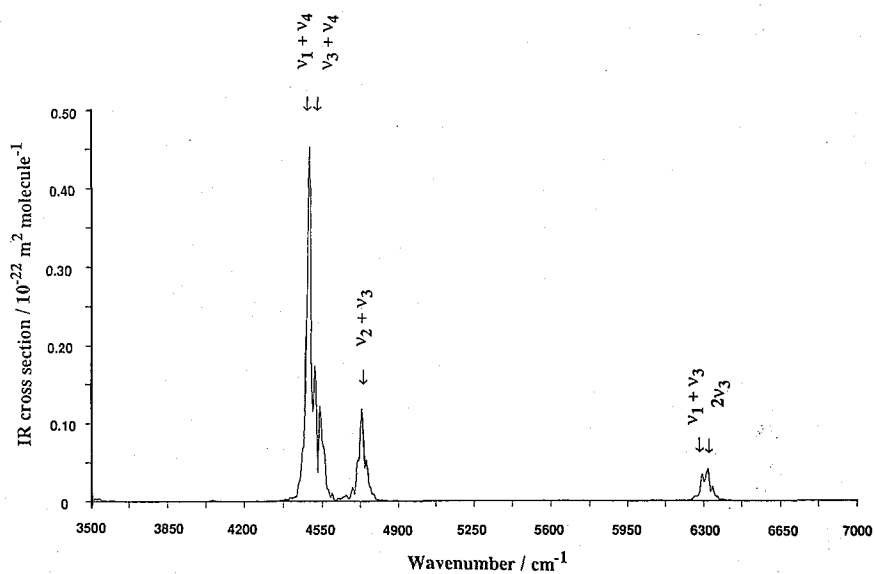


Fig. 2. Simulated infrared spectrum of an anharmonic model of liquid methane in the region of overtones and combinations.

Raman spectra

All fundamental vibrations of methane are Raman active, although totally symmetric vibration ν_1 is strong in intensity. Figures 3 and 4 display the simulated Raman spectra of harmonic model of liquid methane. The ν_1 band splits into two components. It may be due to Fermi resonance of ν_1 and $2\nu_2$ modes. Parallel component of the band is strong as expected for A_1 species.

The ν_2 band is weak, and an enlarged spectrum is shown in Fig. 4. Although statistical noises are considerably large, depolarization ratio is close to the theoretical value of $3/4$.

The ν_3 (E symmetry species) band is close to the ν_1 band, and parallel component may be hid by the ν_1 band. As the ν_4 (F_2 symmetry species) is very weak and near to the ν_2 band, the position of the mode is indicated in the figure. The $2\nu_4$ appears clearly, showing parallel polarization. Symmetry species of the overtone $2\nu_4$ consists of

$$(F_2)^2 = A_1 + E + F_2$$

The depolarization ratio may close to zero, as A_1 symmetry species is included.

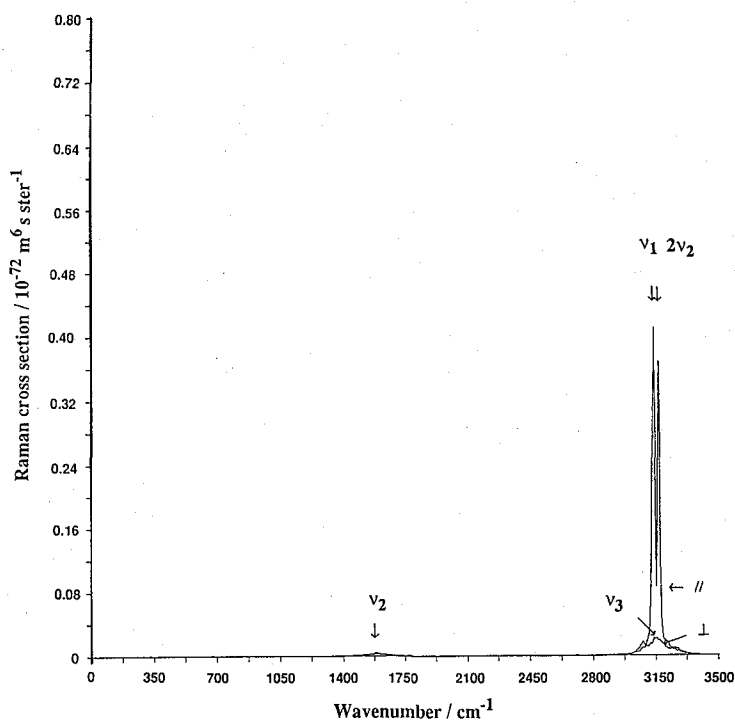


Fig. 3. Simulated Raman spectra of a harmonic model of liquid methane.

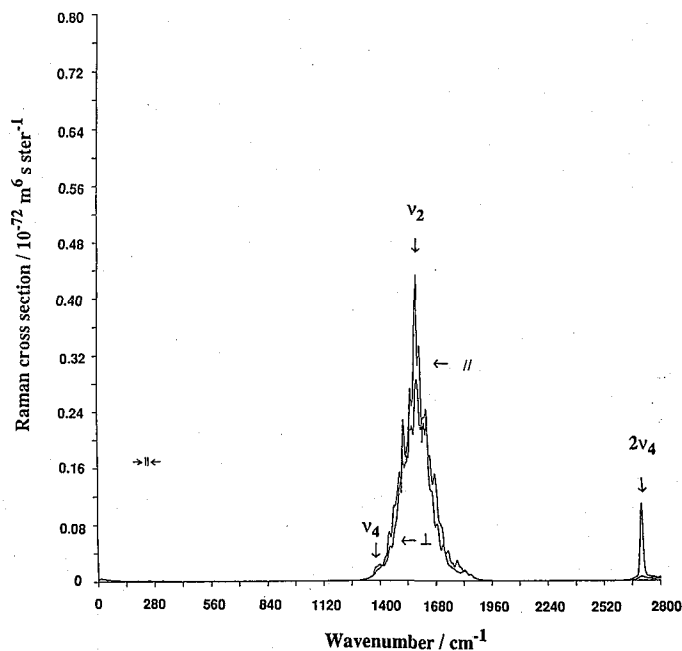


Fig. 4. Enlarged spectra of Fig. 3.

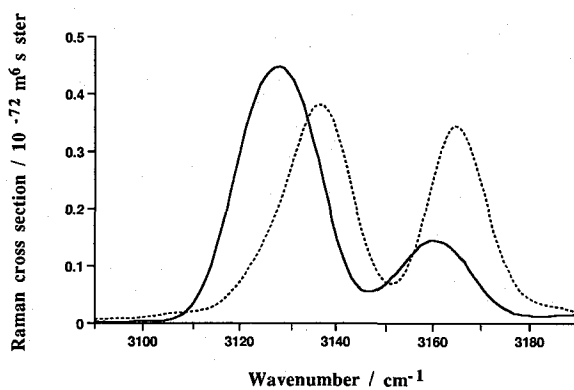


Fig. 5. Simulated Raman spectra of a harmonic (—) and an anharmonic (.....) models of liquid methane in the region of stretching vibration.

Table 3. Effects of anharmonicity on the ν_1 and $2\nu_2$ Raman bands

Wavenumber / cm ⁻¹			Half band width / cm ⁻¹	
harm.	anharm.	exp. ⁹⁾	harm.	anharm.
3137	3129	3136	16.4	20.4
3166	3162	3166	14.1	18.8

Figure 5 shows the Raman spectra of the harmonic and anharmonic models of liquid methane, respectively, in the ν_1 and $2\nu_2$ region. Anharmonicity acts to lower frequency and widen half band width for stretching vibration as shown in Table 3, however, dose not affect for bending mode as described above. The lower frequency band is contributed predominantly by the ν_1 mode and become stronger than the higher band. This is reasonable because integration of intensity of the two bands is similar for the harmonic and anharmonic models. Observed spectra shows strong ν_1 band and weak $2\nu_2$ band. Difference between the observed and simulated spectra may be caused by deference of ν_2 frequency. A slight increase of the bending force constant may improve the simulated spectra.

CONCLUSION

Molecular dynamics simulation has been used to investigate the infrared and Raman spectra of a harmonic and an anharmonic models of liquid methane. The simulation reproduced well the observed spectra in frequency and intensity. Overtone and combination bands of stretching modes are produced for infrared and Raman spectra for anharmonic model. On the other hand, these of bending models are produced for both harmonic and anharmonic models. Fermi resonance has occurred for coupling between the ν_1 and $2\nu_2$ modes.

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Erratum

**Molecular Dynamics Simulation of Infrared
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Page 171, Figure caption of Fig. 5 should be the following:

Simulated Raman spectra of a harmonic (-----) and an anharmonic (——) models of
liquid methane in the region of stretching vibration.