

CALCULATION OF INFRARED SPECTRA BY MOLECULAR DYNAMICS METHOD

Souhei Matsumoto, Shigeo Maruyama and Masahiro Shoji

Department of Mechanical Engineering
The University of Tokyo, Bunkyo-ku, Tokyo, 113 Japan

Abstract

Since the radiant heat transfer properties of each substance are deeply related to the characteristics of the thermal motions of molecules, molecular simulation is considered to be an effective method to investigate those properties, especially when the objective system is not simple. In this study, the infrared spectra are calculated in terms of absorption cross section for systems which consist of carbon monoxide molecules, using molecular dynamics method for the simulation of both the rotation and vibration of molecules. The results of a set of calculations with various densities indicate that qualitative behavior of the spectra of gas and liquid phases are expressed satisfactorily by current technique.

Introduction

In the conventional approaches to the radiant heat transfer problems, total energy emitted or absorbed by any kind of solid is evaluated by applying the gray-body approximation, in which the spectroscopic properties of the substance are represented by a constant emissivity. It is usually considered to be valid because spectra of many kinds of solid do not exhibit very strong dependence on the frequency, and also only the total energy is required in most cases. Lately, however, there are several problems which do need more precise information of thermal radiation spectra of materials. So called far infrared rays heating technique is a typical example. On the other hand, gas phase spectra generally show very sharp features, so special care about the frequency range must be taken for the radiant heat transfer problems with gas.

As described above, the knowledge of spectroscopic properties specific to each substance is important when considering certain sorts of radiant heat transfer phenomena. The characteristic of that knowledge is such that very precise

structures are not required as in the case of spectroscopic analysis, but the objects tends to be complicated systems such as mixture of several substances or special structures like ceramics.

Correct description of the interaction between light and substances is possible only by applying quantum mechanics. However, to be described purely by quantum mechanics, the objects must be very simple systems. As a result, for most of practically interesting cases, the experimental measurements have been the only way to obtain thermal radiation properties. Recently, accompanied by the improvement of the capability of computers, a method has been developed and is often used in the field of chemical physics which utilize molecular simulation based on classical mechanics to calculate spectrum as an approximated solution⁽¹⁾. The spectral region covered by this technique is that of infrared rays, because they are given rise to by molecular motions. Since the main contribution to the energy transfer by thermal radiation is from this frequency region, applying this method allows to obtain thermal radiation properties by numerical calculations. The advantages of such a method are:

- Applicable to many types of systems by modifying the molecular simulation for each of those systems.
- Each phenomenon in the molecular level which affects the spectrum can be investigated individually and visually.

While it requires:

- Molecular motion of interest must be reproduced correctly.
- The molecular motion should be connected to the fluctuation of dipole moment properly.
- Correction for the errors due to the classical approximation should be considered in some cases.

In this paper, molecular dynamics simulation for systems composed of interacting diatomic molecules which have permanent electric dipole moment is performed to calculate far and near infrared spectra which are related to rotational and vibrational motion of molecules, respectively. Choosing carbon monoxide (CO) as a sample molecule, molecular dynamics simulations under several conditions with various densities are performed and obtained spectra are compared.

Fig.1 shows quantum mechanically calculated infrared spectrum for a simple isolated carbon monoxide molecule at 120K. This corresponds to the far and near infrared spectra under the condition with no interactions between molecules. It should be noted that the curve was derived by merging fine peaks coming from discrete rotation energy levels with the Gaussian functions.

Theoretical Background

Since the target system here is gas or liquid the absorption cross section per molecule $\alpha(\omega)$ should be introduced in order to represent the spectrum (ω is the angular frequency of the incident electro magnetic wave). $\alpha(\omega)$ is the property defined in the Beer's law

$$I = I_0 \exp(-\alpha N x), \quad (1)$$

where I is the intensity of light (I_0 is the initial intensity), N is the number density of the molecules, and x is the distance from the point of incidence in the medium. The technique used here is such that at first the formulation for the absorption cross section is established within the framework

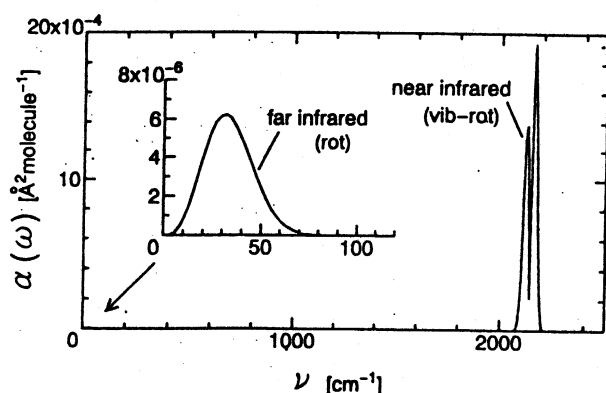


Fig.1 Far and near infrared absorption cross section of CO (120K) calculated quantum mechanically using a rotating oscillator model.

of quantum mechanics, then the result of classical molecular dynamics simulation is substituted into a part of the formulation which requires calculations of transition matrix elements.

If the energy absorbed by a dipole moment placed in an electro magnetic field oscillating with the angular frequency ω and the amplitude E_0 is denoted by $-\dot{E}$, it is then related to $\alpha(\omega)$ as

$$\alpha(\omega) = \frac{1}{nc} \frac{-\dot{E}}{\bar{E}}, \quad (2)$$

where n is the refractive index (set to 1 here), c is the velocity of light, $\bar{E} = \epsilon_0 E_0^2 / 2$ is the average energy density of the electro magnetic field, with ϵ_0 being the permittivity. Quantum expression for $-\dot{E}$ is given as

$$-\dot{E} = \sum_i \sum_f \hbar \omega_{fi} \cdot \rho_i \cdot P_{f \leftarrow i}. \quad (3)$$

The initial and final states are denoted by i and f , respectively, $\hbar \omega_{fi}$ (\hbar is the Planck's constant) means the energy absorbed in a transition $f \leftarrow i$, ρ_i is the density of state i , and $P_{f \leftarrow i}$ is the probability of transition $f \leftarrow i$ in unit time. Applying the perturbation theory to $P_{f \leftarrow i}$ leads to the following form,

$$-\dot{E} = \frac{E_0^2 \pi \omega \{1 - \exp(-\beta \hbar \omega)\}}{6 \hbar} \cdot I(\omega). \quad (4)$$

Where β stands for $(kT)^{-1}$, k is the Boltzmann's constant, T is the temperature of the system. $I(\omega)$ is called the absorption line shape, and is expressed as

$$I(\omega) = \sum_i \sum_f \rho_i |\langle f | \mu | i \rangle|^2 \delta(\omega_{fi} - \omega), \quad (5)$$

where μ is the dipole moment operator and δ is the Dirac's delta-function. From the Eqs.(2) and (4) quantum expression for $\alpha(\omega)$ becomes

$$\alpha(\omega) = \frac{\pi \omega \{1 - \exp(-\beta \hbar \omega)\}}{3 \epsilon_0 \hbar n c} \cdot I(\omega). \quad (6)$$

By utilizing the Fourier transform of the delta-function and taking account that summation over i with the weight of ρ_i is equivalent to the equilibrium average, $I(\omega)$ can be written as⁽²⁾

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-i\omega t) dt \langle \mu(0) \cdot \mu(t) \rangle_0. \quad (7)$$

It should be noted that the equilibrium average can be replaced by the auto-correlation function of $\mu(t)$ at equilibrium state. The approximation to be introduced is the

substitution of the dipole moment obtained by the molecular simulation based on the classical mechanics into $\mu(t)$ in Eq.(7). Since this operation corresponds to taking the limit of $\hbar \rightarrow 0$, one needs to use the classical limit of absorption cross section $\alpha^C(\omega)$, which is

$$\alpha^C(\omega) = \lim_{\hbar \rightarrow 0} \alpha(\omega) = \frac{\pi\beta\omega^2}{3\epsilon_0 n c} \cdot I^C(\omega). \quad (8)$$

$I^C(\omega)$, which is the classical limit of $I(\omega)$, can be obtained as the power spectrum of the dipole moment calculated by molecular dynamics simulation. If an equilibrium state between the radiation field and the molecules is considered, the behavior of the molecules is the same as where there is no effect of photons on the motion of molecules. Therefore required dipole moment can be obtained from a simulation of a system under the thermal equilibrium state. It should be noted that when the calculated system contains multiple molecules, $\alpha^C(\omega)$ must be divided by the number of molecules in the system to yield the absorption cross section per molecule.

Calculation Procedures

For this study, carbon monoxide is chosen as the model molecule for this study because it is a simple diatomic molecule with the permanent electric dipole moment. Parameters of the molecule used in the simulation is summarized in Table 1. In order to calculate vibration of the molecule, an intra-molecular potential is assumed between carbon and oxygen atoms which are connected to each other by a chemical bond. This potential function includes up to the fourth order derivative so that the effect of unharmonicity can be taken into account (see Table 2). The interaction between molecules is represented by assuming a potential function between two atoms which belong to different molecules, assuming the Lennard-Jones and Coulomb forces as following,

$$\Phi(r) = 4\epsilon \left\{ \underbrace{\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6}_{\text{Lennard-Jones}} + \underbrace{\frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r}}_{\text{Coulomb}} \right\}. \quad (9)$$

Where r is the distance between atoms i and j , q_i and q_j being the static charges on them (see Fig.2). The evaluation of the electric dipole moment of the system is very important in this method. It is currently calculated simply as the sum of dipole moment vector of each molecule contained in the calculation region. The induced dipole moment is not considered here though in certain cases it plays an important

Table 1 Molecular parameters used in the MD simulation.

Weight of atom1(C)	12.0 amu
Weight of atom2(O)	16.0 amu
Equilibrium bond length	1.13 Å
L-J potential parameter ϵ	81.0×10^{-23} J
L-J potential parameter σ	3.11 Å
Point charge on each atom	3.26×10^{-21} C

Table 2 Intra-molecular potential function derivative values at the equilibrium distance r_e .

$\phi''(r_e)$	$\phi'''(r_e)$	$\phi^{(4)}(r_e)$
$1.92 \times 10^3 \text{ Jm}^{-2}$	$-1.36 \times 10^{14} \text{ Jm}^{-3}$	$8.08 \times 10^{24} \text{ Jm}^{-4}$

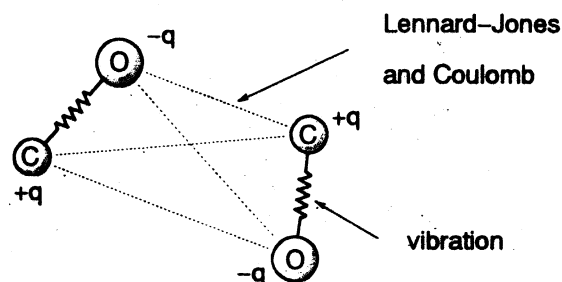


Fig.2 Interactions considered between particles.

role. The magnitude of dipole moment on each molecule is evaluated as a linear function of bond length R ,

$$\mu = \mu_0 + \mu_1(R - R_e), \quad (10)$$

where R_e is the equilibrium length, and $\mu_0 = 0.11D$ and $\mu_1 = -3.1D/\text{Å}$ are assumed.

The molecular dynamics simulation was carried out for 125 molecules contained in a cubic region with periodic boundary condition. The size of the cubic region was determined at the beginning of the calculation so that desired density of the system would be attained, and was fixed through the whole calculation steps. The effect of the potential was cut off on the boundary of the cubic region on the center of which the considered molecule was positioned. Initial velocity of each molecule was given so that the temperature of the system would be the intended value of 120K. For the purpose of creating gas and liquid states of carbon monoxide, three cases with different densities were performed: 6 kg/m^3

for thin gas phase, 60kg/m^3 for gas phase near the saturation, and 600kg/m^3 for liquid phase. Rather fine time step of 0.2 femto second was required to generate the vibration of molecules with sufficient time resolution. Since the molecular dynamics applied here is the NVE ensemble, the temperature of the system is not exactly constant. At the beginning of a calculation, about 50,000 steps of preliminary run was required to control the temperature of the system because the potential energy in the system was not necessarily optimized at the initial configuration and its relaxation could significantly change the temperature. After this procedure the molecular dynamics calculation was performed for 1,000,000 steps for each run, recording the dipole moment of the system at every 10 steps. $I^C(\omega)$ in Eq.(8) was then obtained from the resulting 100,000 data points applying the FFT technique. Spectra on the figures in the following section are the results of smoothing process with a Hanning type digital filter.

Results And Discussions

Before beginning to study the spectra results, a confirmation should be made on whether the states of the calculated systems were actually as expected. For this purpose, the pair-correlation functions, which indicate averaged number density of particles at a given distance from an atom, normalized by the bulk average, were obtained for two cases out of the three: the cases with density 60kg/m^3 and 600kg/m^3 . Fig.3 shows the pair-correlation functions for these cases (averaged over every possible combination of atoms: O-O, C-C, and O-C), with each panel accompanied by a picture illustrating the corresponding calculation region. On the top panel (60kg/m^3) there is only one peak near the distance represented by the σ parameter of the Lennard-Jones potential. This single peak is the general characteristics of gas phase. On the other hand, the bottom panel (600kg/m^3) exhibits slightly oscillating behavior that indicates the existence of a short range periodic structure, which is specific to liquid phase. The intended phases therefore have been achieved by the current simulations.

Figs.4 and 5 are the resulting far (rotational) and near (vibrational) infrared spectra, respectively, of carbon monoxide at 120K. For each of the figures, x-axis is the wave number per 1cm and y-axis is the absorption cross section per molecule. The result of quantum calculation which is the same as Fig.1 is also plotted on both figures for the sake of comparison.

From the results of far infrared spectra (Fig.4), it is observed that for each condition a peak appears at about 30 to 40cm^{-1} . The shape of the peak for the liquid is lower in the intensity and wider in the range (extended to higher frequency region), compared with those of two results for gas. It is understood by considering the difference between the nature of the dipole moment fluctuation due to molecular rotation of the system in the gas phase and that in the liquid phase. In the gas phase, since the opportunities of the collision between molecules are small, the behavior of the dipole moment function of a molecule is similar to the sine wave with the frequency of the molecule's angular motion. Because the dipole moment of the system is determined as the superposition of such functions, resulting spectrum reflects the angular velocity distribution of the molecules. In the liquid phase molecules experience interaction with others continuously and the orientation of each molecule changes almost randomly. It is considered to be

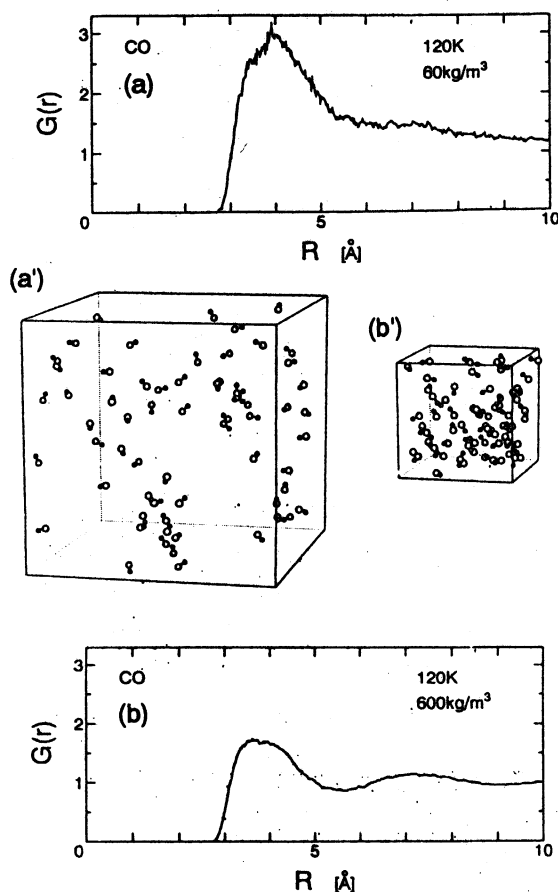


Fig.3 The top panel(a) is the pair-correlation function of the system with density 60kg/m^3 , which is illustrated on picture (a'). The bottom panel(b) is the same for 600kg/m^3 case, illustrated on picture (b').

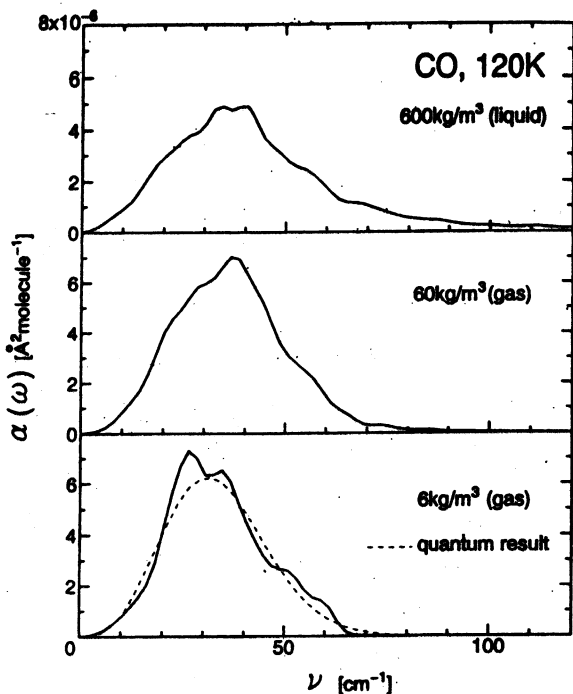


Fig.4 Far infrared spectrum of CO calculated by MD.

the random nature that gives rise to the frequency components observed in the wide frequency region. Both of the two gas phase spectra show good agreement with the quantum solution. Although the collision between molecules can occur more frequently in the case of near-saturation gas, no significant effect on the spectrum is detected. Some local peaks visible in the figure are considered merely as noises, and are expected to reduce as the amount of sampled data would increase.

In Fig.5, near infrared spectrum for each of two cases under the gas conditions shows two peaks at about 2160 and 2200 cm^{-1} , well-known as P- and R-branches, respectively. By quantum mechanics, they are explained as following. When a transition of energy levels occurs as a diatomic molecule absorbs a photon, accompanied with the change of vibrational states, the selection rule forces the state of rotation also to change by +1 or -1. The former makes the R-branch, and the latter the P-branch. In the spectrum obtained from the classical molecular simulation, these two peaks appears basically by following reason. When the intra-molecular potential is assumed as harmonic and there is no interaction between molecules, the eigen frequency of the intra-molecular vibration can be denoted as ω_v , and the angular velocity of rotation of the molecule as ω_r . When the dipole moment of this molecule is observed, one of its

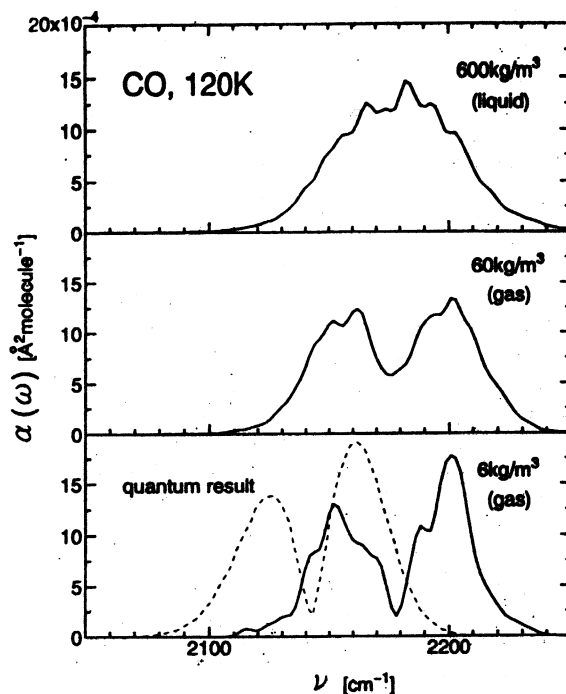


Fig.5 Near infrared spectrum of CO calculated by MD.

components is proportional to $\cos(\omega_v t) \cdot \cos(\omega_r t)$, which can be separated into two frequency component, $(\omega_v + \omega_r)$ and $(\omega_v - \omega_r)$. Since $\omega_v \gg \omega_r$ holds, and ω_v has a narrow range while ω_r distribution has the width expected from the rotational spectrum, two peaks are formed at both sides of ω_v (about 2180cm^{-1} here). The influence of changing the density of the system is more clearly recognized in near infrared spectra than in far infrared. Even in two gas states, for which little difference is observed in far infrared region, certain change of shape can be pointed out. It could be said that as increasing the density from gas to liquid, the separation of two peaks becomes less clear, and they eventually merge into single peak. This tendency is considered to be analogous to the widening of peak observed in far infrared spectrum of liquid. The result for thin gas is compared with the quantum solution. The most remarkable discrepancy between them is the shift noticed in the frequency on which the peaks appear. Two peaks in the quantum result appear at about 2125 and 2160cm^{-1} . This would be attributed to the fact that unharmonicity of the intra-molecular potential is more emphasized in a quantum situation, because of the discontinuity of the energy levels. It suggests that by using the approximation based on classical mechanics, energy states which are not realistic are created, and that a correction is necessary if a for more accurate prediction of the spectrum is required.

Concluding Remarks

Far and near infrared spectra of carbon monoxide in gas and liquid phases are calculated using molecular dynamics simulations to evaluate the dipole moment fluctuation of the system. Although the results are satisfactory at this stage, there are several problems to be solved in order to apply this technique to more practical objectives:

- The potential functions must be appropriate to describe the motion of molecules. Slight modifications of parameters can lead to a considerable change of the nature of molecular motion, so they should be well examined carefully before applied.
- Since calculated system is limited to a small region, it is possible that the periodicity obliged by the boundary condition should affect the results, or that some effects which exist when the system is larger might be failed to be observed in the calculation.
- In this paper, the dipole moment of a molecule was rep-

resented by a simple linear function. It must be determined more carefully for further applications.

- Usually a large number of repetition is required to accumulate sufficient amount of data to obtain a meaningful spectrum. It is an obstacle for the computation of more complicated cases.

In spite of the problems above, this technique provides with fairly comprehensible route to the thermal radiation processes, so it is hoped to help understanding various properties related to the radiant heat transfer problems.

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