Bull. Chem. Soc. Jpn., 58, 1105—1108 (1985)

Molecular Dynamics Using Internal Coordinates. I. Infrared Spectra of Sulfur Dioxide

Soichi Hayashi,* Motohisa Oobatake, Tatsuo Ooi, and Katsunosuke Machida†
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611
†*Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606*
(Received November 17, 1984)

A simulation method of molecular dynamics using internal coordinates for polyatomic molecule is described. The method permits intramolecular interaction to be expressed in terms of the internal coordinate, and produces translation, rotation, and vibration of molecule. As the first application, infrared spectra of sulfur dioxide both at gas and liquid phases are simulated by the method with an aid of the techniques proposed by Berens and Wilson. The spectrum at gas phase exhibits the pure rotational band and the vibrational-rotational bands for fundamental modes. The ν_1 and ν_2 vibrations show B-type band shape, and the ν_3 mode shows A-type band shape, in accord with the experimental result and the selection rule for a prolate symmetrical top which may practically represent the molecule. At liquid phase, multiple peaks due to rotational structure disappeared, and single-peaked bands are simulated as expected. The method can be extended so as to describe more realistic intermolecular interactions than pairwise atom-atom potentials.

Molecular dynamics simulation has become a powerful tool for the study of average structures and dynamic properties of molecular systems. Except for the simplest molecules,[1,2] however, molecules have been usually dealt with as rigid or partially flexible ones.[3] In order to perform a more physically realistic simulation, it may be necessary to make molecules flexible, that is, all degrees of freedom of atomic motion should be included. Because it is hard to describe the intramolecular potential by Cartesian coordinates for polyatomic molecules, it is desirable to express explicitly the potential in terms of the internal coordinates such as bond stretching, valence angle bending, out-of-plane bending, and torsion. We describe, in this paper, a simulation method satisfying the above requirements for polyatomic molecules. The method permits the calculation of molecular dynamics including all degrees of freedom, and produces translation, rotation and vibration of molecule.

As the first application of the method, infrared spectra are simulated of sulfur dioxide, which has two stretching and one bending coordinates, both at gas and liquid phases. The spectra are obtained with the aid of the techniques proposed by Berens and Wilson[1,2] who have reproduced surprisingly accurate infrared and Raman spectra of diatomic molecules from classical molecular dynamics, classical linear response theory and classical statistical mechanical ensemble averaging, with the use of simple quantum corrections. The spectrum obtained by the molecular dynamics simulation is compared with the experimental one.[4–6]

Method and Model

Molecular Dynamics. We consider a system of N atoms interacting through intra- and intermolecular potentials at a given energy and density. The force $\boldsymbol{F}_i$ on the ith atom is assumed to be the sum of the intra- and intermolecular forces, $\boldsymbol{F}_i^{\text{intra}}$ and $\boldsymbol{F}_i^{\text{inter}}$.

$$\begin{aligned}\boldsymbol{F}_i &= \boldsymbol{F}_i^{\text{intra}} + \boldsymbol{F}_i^{\text{inter}} \\ &= -\frac{\partial V^{\text{intra}}}{\partial \boldsymbol{r}_i} - \frac{\partial V^{\text{inter}}}{\partial \boldsymbol{r}_i}, \quad i = 1, \cdots, N, \end{aligned} \tag{1}$$

where V^{intra} and V^{inter} are the intra- and intermolecular potential energies, respectively, and $\boldsymbol{r}_i$ is the position expressed for each atom i by a vector whose components are along the three Cartesian coordinates.

The intramolecular potential energy V^{intra} is expressed in terms of the internal coordinates as

$$V^{\text{intra}} = \frac{1}{2}\sum_{tt'} f_{tt'}\cdot S_t\cdot S_{t'} + \frac{1}{6}\sum_{tt't''} g_{tt't''}\cdot S_t\cdot S_{t'}\cdot S_{t''} + \cdots \tag{2}$$

in which $f_{tt'}$ and $g_{tt't''}$ are the quadratic and cubic force constants, respectively, and S_t, $S_{t'}$, and $S_{t''}$ are tth, t'th, and t''th internal coodinates, respectively. The internal coordinate is related to the Cartesian displacement vector $\Delta\boldsymbol{r}_i$ by

$$S_t = \sum_{i=1}^{L} \boldsymbol{s}_{ti}\cdot\Delta\boldsymbol{r}_i \tag{3}$$

where the coefficient $\boldsymbol{s}_{ti}$ is the well known $\boldsymbol{s}$-vector determined by the geometry of the internal coordinate,[7] L is the number of the constituent atoms for the coordinate, and the dot represents the scalar product of the two vectors. Consequently one can write the intramolecular force as follows,

$$\boldsymbol{F}_i^{\text{intra}} = -\sum_{tt'} f_{tt'}\cdot\boldsymbol{s}_{ti}\cdot S_{t'} - \frac{1}{2}\sum_{tt't''} g_{tt't''}\cdot\boldsymbol{s}_{ti}\cdot S_{t'}\cdot S_{t''} + \cdots \tag{4}$$

Internal coordinates written in our program of molecular dynamics are increases in bond lengths Δr, in valence bond angles $\Delta\varphi$, in angles between a bond and a plane defined by two bonds $\Delta\theta$, and in torsion $\Delta\tau$. The $\boldsymbol{s}_{ti}$ vectors for these coordinates are calculated for every instantaneous structure of each molecule so as to take account of the higher-order terms omitted in Eq. 3 implicitly.

For the intermolecular part, we use the sum of the pairwise atom–atom potential terms of the two types,

$$V_1^{\text{inter}} = \sum_{ij} [-Ar_{ij}^{-6} + B\exp(-Cr_{ij})] \tag{5}$$

and

$$V_2^{\text{inter}} = \sum_{ij} e_i e_j / r_{ij} \tag{6}$$

where r_{ij} is the distance between the atoms i and j the index i runs over a single molecule and j over the others, and A, B, and C are parameters for the potential. The potential V_1^{inter} represents the exchange repulsion and dispersion interaction for atom pairs, and V_2^{inter} arises from the Coulomb interaction between the atomic charges e_i and e_i.

The classical trajectories $\boldsymbol{r}_1(t), \cdots, \boldsymbol{r}_N(t)$ are obtained by integrating Newton's second law

$$\boldsymbol{F}_i = m_i \frac{d^2\boldsymbol{r}_i}{dt^2}, \quad i = 1, \cdots, N \tag{7}$$

where m_i is the mass of the ith atom. A modified Verlet integration algorithm[8] was used with a periodic boundary condition.

Infrared Spectra. We use the same approach presented by Berens and Wilson[1] who calculated the pure rotational and vibrational-rotational absorption bands of carbon monoxide from the time history of dipole moment computed using the trajectories, classical linear response theory and classical statistical mechanical ensemble averaging, with the use of simple quantum corrections. We modified the approach so as to be applicable to oriented system. The dipole moment time history of the system $\mu_d(t)$ for the d direction is calculated by using the trajectories of the atoms and $(\partial\mu/\partial Q_i)$, where d is x, y, or z Cartesian coordinate, μ the molecular dipole moment, and Q_i is the ith normal coordinate.

The absorption spectrum for a system at equilibrium is obtained from the linear response equations:

$$\alpha_d(\omega) = \frac{4\pi^2\omega^2\beta}{3cn} I_d(\omega), \quad d = x, y, z, \tag{8}$$

and

$$I_d(\omega) = \frac{3}{2\pi}\Big[\lim_{\tau\to\infty} \frac{1}{2\tau} \Big| \int_{-\tau}^{\tau} dt \exp(-i\omega t)\mu_d(t) \Big|^2\Big], \quad d = x, y, z \tag{9}$$

in which $\alpha_d(\omega)$ is the absorption cross section as a function of angular frequency ω, $\beta=(k_BT)^{-1}$ 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 techniques. 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 $\alpha_d(\omega)$.

For the comparison with an experimental spectrum, it is necessary to obtain an ensemble average of spectra computed from very small system consisting of an order of several hundreds atoms, from very short time period, and especially from weakly interacting system such as low pressure gas phase. Therefore, for gas phase, many sets of the initial values are chosen randomly from the Maxwell-Boltzmann distribution. In order to satisfy a thermal equilibrium condition under a given temperature with the Maxwell-Boltzmann distribution, initial values of translational velocity and angular momentum of molecule and amplitude of each fundamental vibrations are chosen from normal random numbers. On the other hand, initial translational and rotational coordinates of molecule and phase of each fundamental vibrations are chosen from uniform random numbers. For liquid phase where intermolecular interaction must be dominant, the final values in one period of the time history are used as the initial values of the next.

Quantum correction for the pure rotational band contour is usually small and is

$$I^Q(\omega)/I^C(\omega) = \frac{\sinh(\beta\hbar\omega/2)}{\beta\hbar\omega/2} \tag{10}$$

in which the superscripts Q and C indicate quantum and classical, respectively, and $\hbar=h/2\pi$ where h is Planck's constant. The correction for the vibrational band is the frequency shift of $-4\pi r_e x_e$ due to anharmonicity in the potential. The rotational lineshape correction for a rotational-vibrational band is achieved by multiplying the classical band by $\exp[\beta\hbar(\Delta\omega)/2]$, in which $\Delta\omega$ is the frequency measured from the center of the vibrational band. For the liquid phase spectrum, no quantum corrections were applied.

Resolution and Frequency Range. As the resolution, we employed the most popular criterion of the full-width at half-height (FWHH). The minimum value of the FWHH ($\tilde{\nu}_{1/2}$), *i.e.* resolution, in a calculated spectrum depends on the time of one period of the time history (Δ) as follows:

$$\tilde{\nu}_{1/2} = \frac{1}{c\Delta}. \tag{11}$$

In practice, however, the resolution is lowered by an apodization (window) function,[9] which must be used to avoid distortion of the spectra caused by the use of finite time history.

Frequency range (0—$\tilde{\nu}_{\max}$) depends on the sampling time interval (Δt) and is given by

$$\tilde{\nu}_{\max} = \frac{1}{2c\Delta t}. \tag{12}$$

For example, when Δt is 1/1024 psec, $\tilde{\nu}_{\max}$ is 17067 cm^{-1}.

Model. As the first application of the molecular dynamics method using internal coordinates, a simple model of gaseous and liquid systems was adopted. The systems consist of 125 sulfur dioxide molecules, periodic in three dimensions (x, y, z). The box sizes are 3.322^3 nm^3 for gas phase, and 0.419^3 nm^3 for liquid phase. The SO bond length and OSO bond angles were assumed to be 1.43 Å and 119.05°, respectively.[10] The atomic charges on the S and O atoms were estimated from the observed values of the dipole moment;[10] $e_s=-2e_o=0.46$ in the electronic charge unit.

For the SO stretching and OSO bending harmonic force constants (k_{st} and k_{bend}/l^2) of 9.97 and 0.81 mdyne/Å respectively, were taken from the literature values.[11]

Table 1. Parameters of the nonbonded atom–atom interaction

Atomic pair	A (kcal·Å^6·mol^{-1})	$B\times10^{-3}$ (kcal·mol^{-1})	C (Å^{-1})
S···S	1430	220.8	3.62
O···O	800	745.9	4.55
S···O	1070	405.9	4.09

The parameters A, B, and C used in the Eq. 5 for the S···S, O···O, and S···O intermolecular atom-atom interactions were listed in Table 1.[11] The summation limit is placed at the distance of 8.15, 7.35, and 6.85 Å for the V_1^{inter} of the S···S, S···O, and O···O, respectively, and 16 Å for the V_2^{inter}. To reduce the error in the use of truncated potentials, the shifted force potentials were adopted.[12]

Although V_2^{inter} was calculated by the fixed charge model, the dipole moment time history of the system is evaluated by using the $(\partial\mu/\partial Q_i)$ of 0.780, -0.820, and 2.138 for ν_1, ν_2, and ν_3, respectively, in the unit of D amu$^{1/2}$Å^{-1}.[13] Normal coodinates are obtained from the following relation,

$$Q = \tilde{L}_x M X_p \tag{13}$$

where $\tilde{L}_x$ denotes the inverse matrix of the transformation matrix, M is a diagonal matrix consisting of the mass of constituting atoms, and X_p is a matrix of Cartesian displacement coordinates with respect to the coordinate system of principal axes of moment of inertia. The calculation was carried out using a FACOM M-180 II AD computer of the Institute for Chemical Research, Kyoto University. The calculations for one psec time history of the gaseous and liquid systems required 85 and 107 min of the computer, respectively.

Results and Discussion

Figure 1 demonstrates the simulated infrared spectra for the gas phase sulfur dioxide at 320 K from classical molecular dynamics using internal coordinates, and the technique proposed by Berens and Wilson.[1] The spectra were obtained by averaging over 7500 single-molecule 8 psec time histories. Ensemble average were taken over 15 runs of 42 psec duration in which initial coordinates and velocities were different and first 10 psec are discarded for thermal equilibrium. The value of the resolution is 4.17 cm^{-1} from Eq. 11, and becomes to be 6.15 cm^{-1} by using the Gaussian apodization function.[9] As one of the moment of inertia (I_A) is quite smaller than the other two (I_B and I_C), as listed in Table 2, the molecule may be regarded as a prolate symmetrical top molecule. The ν_1 and ν_2 vibrations, whose directions of transition moments are parallel to the B axis, show B-type band shape, and the ν_3 mode, whose direction of the transition moment is parallel to the A axis, shows A-type band shape, in accord with the experimental result.[5] This is consistent with the selection rule for symmetrical top molecule. The band shape and the frequency of about 50 cm^{-1} for the pure rotational band are quite similar to those of the observed spectrum.[14] The integrated intensities and standard deviations for the simulated spectrum are 24.8±5.0, 30.5±9.6, and 180.8±47.5 km mol^{-1} for ν_1, ν_2, and ν_3, fundamental bands of gaseous sulfur dioxide, respectively, and agree with the corresponding values observed of 20.6—26, 25.2—28, and 188—197 km mol^{-1}.[15—17]

Figure 2 shows the simulated infrared spectra of liquid phase sulfur dioxide at 230 K on average. The spectra were obtained by averaging over 7500 single molecule 4 psec time histories. The value of the resolution is 8.34 cm^{-1} from Eq. 11, and 12.3 cm^{-1} from the Gaussian appodization function.[9] The spectrum shows that the multiple peaks observed at gas phase disappear at liquid phase, and single-peaked bands are found at 1172, 521, and 1359 cm^{-1} for ν_1, ν_2, and ν_3 respectively. Statistical noises appeared typically at peaks of the lowest bands seen in Figs. 1 and 2, are due

Table 2. Moment of inertia of sulfur dioxide[a)]

I_A	I_B	I_C
1.38	8.13	9.53

a) in 10^{-43}·g·m^2

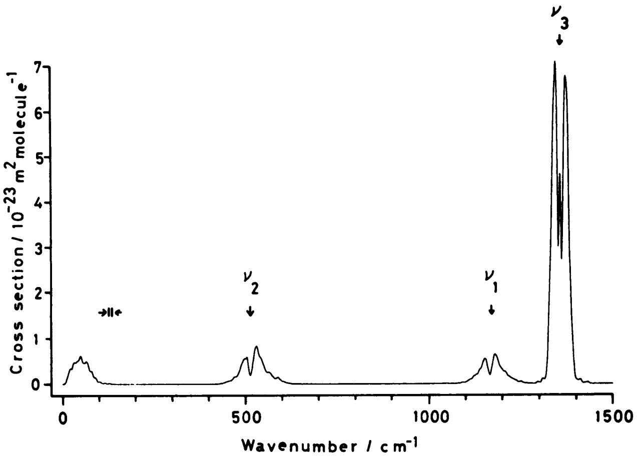

Fig. 1. Infrared spectrum for gas phase sulfur dioxide at 320 K on average.

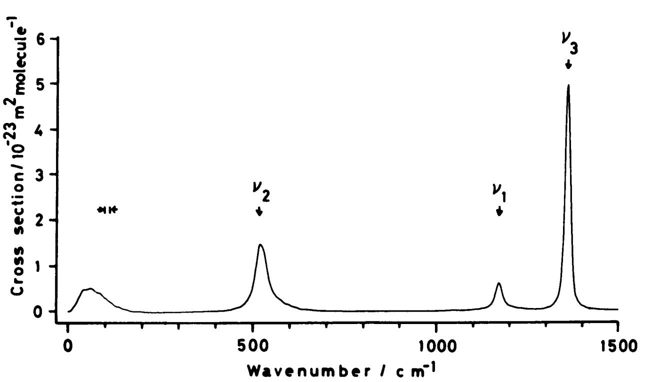

Fig. 2. Infrared spectrum for liquid phase sulfur dioxide at 230 K on average.

to ensemble sampling with only 60 runs for gas and liquid phases. Much more prolonged computation will improve the shapes of peakes, thus enabling the more detailed analysis.

Conclusion

A simulation method of molecular dynamics using internal coordinates for polyatomic molecule is proposed, and was applied to a simulation of the infrared spectra of sulfur dioxide both at gas and liquid phases. The frequencies of the fundamental vibrations of the spectra agree with those calculated by normal coordinate analysis. The bands of the ν_1 and ν_2 vibrations show B-type band shape, while that of the ν_3 mode shows A-type band shape in accordance with the selection rule. At liquid phase, the multiple peaks due to rotational structure disappeared, and single peaked bands are simulated.

The method using internal coordinates can be extended so as to describe more realistic intermolecular interactions containing multibody effects, as well as intramolecular potential, than pairwise atom–atom potentials. Although potential surfaces of multibody systems, especially in chemical reaction systems, are usually complicated, these are able to be expressed by using the four kinds of coordinates, Δr, $\Delta\varphi$, $\Delta\theta$, and $\Delta\tau$.

The authors wish to thank Dr. Y. Kataoka and Dr. K. Ishizuka of this university for their valuable discussions.

References

1) P. H. Berens and K. R. Wilson, *J. Chem. Phys.*, **74**, 4872 (1981).

2) P. H. Berens, S. R. White, and K. R. Wilson, *J. Chem. Phys.*, **75**, 515 (1981).

3) For example, P. von der Ploeg, and H. J. C. Berendsen, *J. Chem. Phys.*, **76**, 3271 (1982).

4) T. Nakanaga, S. Kondo, and S. Saëki, *J. Mol. Spectrosc.*, **81**, 413 (1980).

5) R. D. Shelton, A. H. Nielsen, and W. H. Fletcher, *J. Chem. Phys.*, **21**, 2178 (1953).

6) R. H. Maybury, S. Gordon, and J. J. Katz, *J. Chem. Phys.*, **23**, 1277 (1955).

7) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York (1955).

8) D. Beeman, *J. Comp. Phys.*, **20**, 130 (1976).

9) F. J. Harris, *Proc. IEEE*, **66**, 51 (1978).

10) B. Post, R. S. Schwartz, and I. Fankuchen, *Acta Cryst.*, **5**, 372 (1952).

11) Y. Kuroda, and K. Machida, *Bull. Chem. Soc. Jpn.*, **49**, 1475 (1976).

12) W. B. Street, D. J. Tildesley, and G. Saville, "Computer Modeling of Matter," by P. Lykas, ACS Symposium series (1978), p. 144.

13) G. C. Tejwani, K. Fox, and R. J. Corice, Jr., *Chem. Phys. Letters*, **18**, 365 (1973).

14) R. J. Larkin, R. W. Lovejoy, P. M. Silvaggio, and R. W. Boese, *J. Quant. Spectrosc. Radiat. Transfer*, **25**, 25 (1981).

15) K. Kim and W. T. King, *J. Chem. Phys.*, **80**, 969 (1984).

16) A. J. Von Straten and W. M. A. Smit, *J. Mol. Spectrosc.*, **62**, 297 (1976).

17) C. Secroun, A. Barbe, and P. Jouve, *J. Mol. Spectrosc.*, **45**, 1 (1973).