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Simulation of SIMS for monomer and dimer of lignin under the assumption of thermal decomposition using QMD method

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Abstract

The thermal decomposition of the monomer and dimer of lignin has been simulated by a quantum molecular dynamics (DMD) method. In the calculation, we controlled the total energy of the system using Nóse-Hoover thermostats in the total energy range of 0.69 ~ 0.95 eV, and the sampling position data with a time step of 0.5 fs were carried out up to 3000 (1.5 ps) or 5000 (2.5 ps) steps in *ab initio* and semiempirical MO methods, respectively. We obtained the thermally decomposed fragments with positive, neutral and negative charges from SCF MO calculation at each data of the last MD step, and simulated the fragment distribution of the monomer and dimer lignins from the last step in 30 ~ 40 runs. Simulated mass numbers of positively and negatively charged fragments for lignin monomer and dimer showed considerably good accordance with the experimental results in TOF-SIMS observed by Saito and co-workers.

Keywords: thermal decomposition; lignin; molecular dynamics simulation; SIMS

Introduction

Molecular dynamics (MD) and quantum molecular dynamics (QMD (MD with MO or DFT method)) computer simulations will become powerful tools to study a wide variety of events to obtain quantities that can be directly compared with experimental results as well as yield microscopic pictures about the mechanisms and reaction pathways unavailable from experimental data. The MD approach without MO method has also been quite successful in providing quantitative agreement with experimental energy and angular distributions of sputtered particles from a solid,[1] the high-energy particle bombardment of organic film adsorbed on a metal substrate,[2-5] and a polyethylene crystal.[6]

Normal MD methods use the empirical potential functions[7-11] to solve the motion equations. On the other hand, we are able to obtain the solution of motion equations automatically by QMD method because the potential functions can be determined from the MO or DFT calculations. Then, we propose to solve, within a reasonable computational time, the motion equations by a QMD method with *ab initio* and semiempirical MO methods.

In the present study, we will simulate the thermal decomposition of the monomer and dimer of lignin by QMD with *ab initio* and semiempirical AM1 MO methods, in order to compare with the experimental results of SIMS under the main assumption of thermal decomposition process for the cleavage of chemical bonds of organic substances.

Computational Details

In the NVT (the number of particles, volume, temperature) ensemble, we used the following Nóse-Hoover Hamiltonian in the hypothetical system,[12, 13]

$$\hat{H} = \sum_i \frac{P_i^2}{2m_i} + V_N(r^N) + \frac{p_\eta^{\ 2}}{2Q} + NkT_0\eta\,, \qquad (1)$$

In Eq. (1), the Hamiltonian corresponds to the sum of the kinetic and potential energies associated with (the molecular motion) and (the Nóse-Hoover thermostats), respectively. In the MD calculation, we assume that the total energy is constant, N particles in the thermal bath exists in the Maxwell-Boltzmann's distribution, and they move with translational motions. The potential energy

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$V_N(r^N)$ is given from the force function as the differential calculus of the potential energy in the following equation.

$$F_i(r^N) = -\frac{dV_N(r^N)}{dr_i} \qquad (2)$$

In our QMD method, the force function was evaluated automatically from the Hartree-Fock SCF MO calculations of model molecules. In order to solve the equations of motion for particles, we used a predictor-corrector algorithm[14] with the 5-values Gear method.[15]

In our MD calculations we started to use a semiempirical AM1 method and an *ab initio* MO with 6-31G** basis for the simulation of decomposition of lignin monomer model to obtain force constants automatically. Since the computational time of QMD with the AM1 method is much shorter in the time range of 10^{-2} order than that with the *ab initio* MO method, we used semiempirical AM1 method for lignin dimer model. The thermal energy was controlled with the Nóse-Hoover thermostats and sampling position data carried out up to (1.5 and 2.5 ps (3000 and 5000 steps)) for *ab initio* and AM1 methods, respectively.

We obtained thermally decomposed fragment products with positive, neutral and negative charges to the main chain carbon numbers, or the atomic mass unit from the SCF calculation of MO methods due to the output data of 3000 and 5000 steps. The fragment distribution of each electric charge was evaluated from the total of the output in 30 ~ 40 random initial states for the motion of nuclear particles. Thus, the calculated distribution of the decomposition products to the number of main chain carbon may be compared with the experimental results due to the thermal decomposition gas mass spectrometry. On the other hand, for the lignin monomer and dimer sputtering process after bombardments of primary heavy metal positive ions with a few of ten keV kinetic energy in SIMS, cleavage of the bonds in monomer and dimer molecules on the outer most surface is considered as examples due to thermally decomposed reactions. Thus we are able to compare the calculated positive- or negative-ion fragment spectra of the lignin monomer and dimer molecules with the experimental ion mass spectra in static and TOF-SIMS.

Experimental

TOF-SIMS analysis was performed using a TRIFT III (ULVAC-PHI, Japan) spectrometer. Positive spectra were obtained using a 15 keV primary beam $^{69}Ga^+$ liquid metal ion source at a current of 2 nA, with a pulse width of 18.0 ns(<1 ns after bunched). The primary ion beam was rastered over a 100 × 100 μm^2 area, and the total ion dose was kept under 1×10^{12} ions/cm^2. A low-energy pulsed electron gun (28.0 eV) was used for surface charge compensation. The mass resolution was 2000 ~ 3000 at m/z = 23 (Na^+ peak).

For the investigation, samples of lignin monomer and dimer were prepared by drop-drying of the compounds in acetone onto a silicon wafer.

Results and Discussion

Several investigators[16-18] already described the model of desorption-ionization (DI) processes for organic molecules in mass spectrometry, and the detailed example and discussion was indicated by Lenaerts and co-workers:[19] Fast thermal processes are assumed to be responsible for generating primarily neutrals in the selvedge. Electrons and protons that are also present in the selvedge give rise to, respectively, electron ionization (EI) and adduct ionization (AI) of these neutrals. The radical molecular ions are believed to produce the majority of the fragments, according to the rules of EI mass spectrometry of organic molecules (cleavages, rearrangements, and so on). In other words, the DI model takes explicitly certain ionization mechanisms into account, and allows to obtain satisfactory agreement between the tentative theory and experiment in SIMS spectra.

On the other hand, we assume that the results of the dissociation for organic molecules correspond to the thermal decomposition in mass spectrometry. By considering the thermal decomposition, we are able to simulate the decomposition of the monomer and dimer of lignin by QMD method in order to compare with experimental results of SIMS.[20, 21] As an example of data, Fig. 1 shows the snap shots of the thermal decomposition of the dimer at 0, 2000, and 4000 steps with 0.78 eV energy control using semiempirical AM1 method. It can be seen from the figures that decomposed small fragments increase with larger sampling MD data steps.

We obtained the thermally decomposed fragments with positive, neutral and negative charges from the atomic charge analysis in SCF MO calculation at each data of 3000 or 5000 MD step. The fragment distribution of each electric charge was evaluated from the total of the output in 40 random initial states with semiempirical AM1 method. Table 1 shows the calculated dimer lignin result for the intensity of neutral, positively, and negatively charged fragments with the atomic mass unit. We also simulated that there are 85.0, 6.0, and

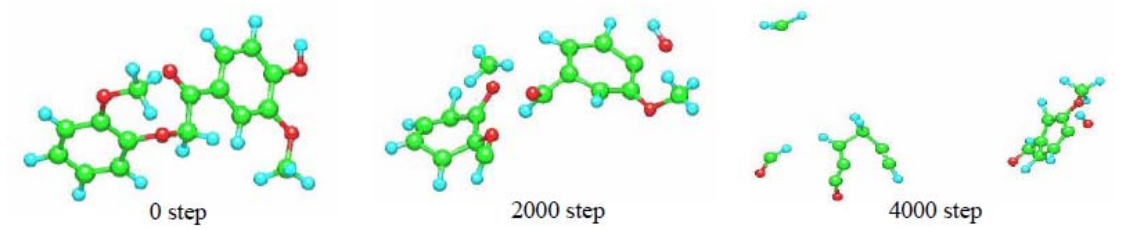

Fig. 1 Snap shots of 0.78 eV energy decomposition process of dimer lignin.

Table 1. Calculated intensity of each fragment with the atomic mass unit

Dimolecule (Dim) fragment distributions (total 5452)					
neutral charge fragments		positive charge fragments*		negative charge fragments*	
mass	formula	mass	formula	mass	formula
	(×75)				
14	CH_2	15	$80CH_3^+$,	14	$25CH_2^-$,
16	CH_4,	29	$10CHO^+$	17	$75OH^-$,
26	$7C_2H_2$,	52	$5C_4H_4^+$	28	$25CO^-$,
28	$21CO, C_2H_4$	67	$45C_4H_3O^+$,	31	$55CH_3O^-$,
29	CHO,	77	$13C_6H_5^+$	54	$5C_3H_2O^-$,
30	$9CH_2O$,	92	$15C_6H_4O^+$,	91	$40C_6H_3O^-$,
39	C_3H_3,	101	$15C_8H_5^+$,	93	$20C_6H_5O^-$,
40	C_3H_4	106	$25C_7H_6O^+$	107	$10C_6H_3O_2^-$,
42	C_2H_2O,	107	$8C_7H_7O^+$	108	$70C_6H_4O_2^-$,
52	C_3O	133	$20C_9H_9O^+$	121	$23C_7H_5O_2^-$
76	$2C_6H_4$	135	$25C_8H_7O_2^+$	123	$30C_7H_7O_2^-$,
80	$2C_5H_4O$	150	$20C_9H_{10}O_2^+$	149	$28C_8H_5O_3^-$,
92	$3C_6H_4O$	165	$20C_9H_9O_3^+$	151	$10C_8H_7O_3^-$
98	$C_5H_6O_2$	287	$C_{16}H_{15}O_5^+$	166	$50C_8H_6O_4^-$
104	$2C_7H_4O$			242	$25C_{14}H_{10}O_4^-$
136	$2C_8H_8O_2$			287	$2C_{16}H_{15}O_5^-$
152	$3C_8H_8O_3$				
180	$C_9H_8O_4$				

Neutral, positively and negatively charged fragments were estimated as 85, 5.5 and 9.0 % to the total ones.

Table 2. Characteristic chemical formulae

Neutral		
76	$2C_6H_4$	C_6H_4
80	$2C_5H_4O$	linear
92	$3C_6H_4O$	C_6H_5-OH, and linear
98	$C_5H_6O_2$	almost linear(including C3-triangle)
104	$2C_7H_4O$	linear
136	$2C_8H_8O_2$	CH_3-O-C_6H_4-O-CH
152	$3C_8H_8O_3$	CH_3-O-C_6H_3 (OH)(CHO)
180	$C_9H_8O_4$	CH_3-O-C_6H_3 (OH)(COCHO)
Positive		
77	$13C_6H_5^+$	C_6H_5
92	$15C_6H_4O^+$,	C_6H_3(OH)
101	$15C_8H_5^+$,	C_6H_4-CCH
106	$25C_7H_6O^+$	$C_6H_4(OCH_2)$
107	$8C_7H_7O^+$	$C_6H_4(OCH_3)$
133	$20C_9H_9O^+$	CH_2=CH-O- C_6H_4-CH_2
135	$25C_8H_7O_2^+$	CH_3-O-C_6H_3 (CHO)
150	$20C_9H_{10}O_2^+$	$(OCH_2)C_6H_4$-CH_2CO-
165	$20C_9H_9O_3^+$	CH_2CO-$C_6H_3(OCH_3)$(OH)
287	$C_{16}H_{15}O_5^+$	$(OCH_2)C_6H_4$-OCH_2CO-C_6H_3(O)(OCH_3)
Negative		
91	$40C_6H_3O^-$,	C_6H_5-O
93	$20C_6H_5O^-$,	C_6H_5-O, and linear
107	$10C_6H_3O_2^-$,	linear
108	$70C_6H_4O_2^-$,	O-C_6H_4-O
121	$23C_7H_5O_2^-$	O-C_6H_4-CHO
123	$30C_7H_7O_2^-$,	CH_3-O-C_6H_4-(O)
149	$23C_8H_5O_3^-$,	(OCH_2CO)-C_6H_2-O
151	$10C_8H_7O_3^-$	(OH)(CO)C_6H_3 -OCH_3
166	$50C_8H_6O_4^-$	(OH)(O)C_6H_3 ($COCH_2O$)
242	$25C_{14}H_{10}O_4^-$	C_6H_4-OCH_2CO- C_6H_3 (O) (OH)
287	$2C_{16}H_{15}O_5^-$	$(OCH_2)C_6H_4$-OCH_2CO- C_6H_3(O)(OCH_3)

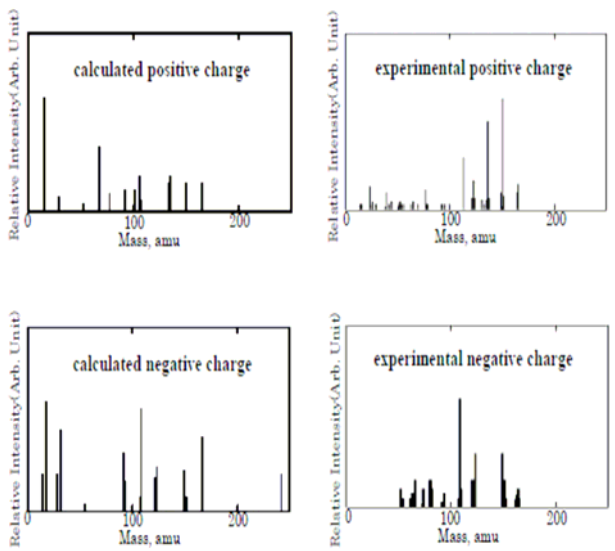

Fig. 2. Calculated SIMS of dimer lignin with the experimental ones

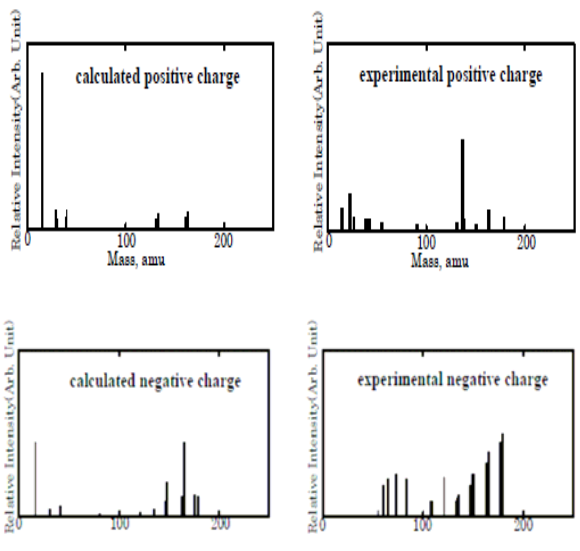

Fig. 3. Calculated SIMS of monomer lignin with the experimental ones

9.0% for neutral, positively, and negatively charged fragments, respectively at 5000 MD step. The atomic mass numbers of our calculated fragments for dimer and monomer lignin seem to correspond to experimental ones of TOF-SIMS observed by Saito and co-workers in Figs. 2 and 3. Furthermore, Table 2 indicated characteristic chemical formulae for each charged fragment in high atomic mass unit.

Conclusion

For lignin monomer and dimer sputtering process after bombardments of primary Ga^+ metal positive ions with a few of ten keV of kinetic energy in SIMS, cleavage of the bonds in lignin molecules on the outer most surface was considered as examples due to thermally decomposed reactions. Then, we have simulated the thermal decomposition of the monomer and dimer of lignin by a molecular dynamics using Nóse-Hoover thermostats with *ab initio* and semiempirical MO methods.

We can conclude the following terms from our simulations of lignin monomer and dimer, in comparison of the experimental values with Saito and co-workers: [20, 21]

(1) Simulated values of the dimer correspond pretty well to the experimental ones, as compared to the monomer. For the positive charge fragments, CH_3-O-$C_6H_3(CHO)^+$, (OCH_2)-C_6H_4-CH_2CO^+, and CH_2CO-$C_6H_3(OCH_3)(OH)^+$ were obtained at 135, 150, and 165 amu, respectively. In the case of negative charged fragments, O-C_6H_4-O^-, O-C_6H_4-CHO^-, CH_3-O-C_6H_4-$(O)^-$, (OCH_2CO)-C_6H_2-O^-, $(OH)(CO)C_6H_3$-OCH_3^- and $(OH)(O)$-$C_6H_3(COCH_2O)^-$ were simulated at 108, 121, 123, 149, 151 and 166 amu, respectively.

(2) The calculated neutral, positively, and negatively charged fragments were evaluated as (85.0, 6.0, and 9.0%) to the total ones.

Thus, QMD simulation enables us to use to analyze polymers in SIMS after a few ten of keV of primary heavy metal ion bombardment, since cleavage of organic bonds for lignin molecules on the outer most surface is considered as examples due to thermal decomposition process.

References

1. N. Winograd, B. J. Garrison, In Ion Spectroscpies for Surface Analysis; A. W. Czanderna, D.M Hercules, Eds.,;Plenum Press: New York, 1991; pp 45-141.
2. R. S. Taylor, B .J. Garrison, Langmuir, ***11***,1220 (1995).
3. K. S. S. Liu, C. W. Yong, B. J. Garrison, J. C. Vickerman, J. Phys. Chem. ***B103***,3195(1999).
4. R. Chatterjee, Z. Postawa, N. Winograd, B. J. Garrison, J. Phys. Chem. ***B 103***,151(1999).
5. A. Delcorte, X. V. Eynde, P. Bertrand, J. C. Vickerman, B. J. Garrison, J. Phys. Chem. ***B 104***,2673(2000).
6. K. Beardmore, R. Smith, Nucl. Instrum. Methods ***B 102***,223(1995).
7. M. S. Stave, D. E. Sanders, T. J. Raeker, A. E. DePristo, J. Chem. Phys. ***93***,4413(1990).
8. T. J. Raeker, A. E. DePristo, Int. Rev. Phys. Chem. ***10***,1(1991).
9. C. L. Kelchner, D. M. Halstead, L. S. Perkins, N. M. Wallace, A.E. DePristo, Surf. Sci. ***310***,425 (1994).
10. D. W. Brenner, Phys. Rev. ***B 42***,9458(1990)
11. D.W. Brenner, J. A. Harrison, C. T. White, R. J. Colton, Thin Solid Films, ***206***,220(1991).
12. S. Nóse, Mol. Phys.,52,255(1984): J. Mol. Phys., ***81***,511(1984).
13. W. G.. Hoover, Phys. Rev. ***A31***,1695(1985).
14. G. J. Martyna, M. E. Tuckerman, D. J. Tobias, M. L. Klein, Mol. Phys., ***87***,1117(1996).
15. C. W. Gear, "The numerical integration of ordinary differential equations of various orders," Report ANL 7126, Argonne National Laboratory (1985).
16. R. G. Cooks, K. L. Busch, Int. J. Mass Spectrom. Ion Proc. ***53***,111(1983).
17. S. J. Pachuta, R. G. Cooks, Chem. Rev. ***87***,647 (1987).
18. L. Van Vaeck, A. Adriaens, R. Gijbels, Mass Spectrom. Rev.***18***,1(1999).
19. J. Lenaerts, L. Van Vaeck, R. Gijbels, Mass Spectrometry ***17***,2115(2003).
20. K. Saito, T. Kato, H. Takamori, T. Kishimoto, A. Yamamoto, K. Fukushima, Appl. Surf. Sci. ***252***,6734(2006).
21. K. Saito, T. Kato, H. Takamori, T. Kishimoto, K. Fukushima, Biomacromolecules, ***6***, 2688 (2005).