Fragment distribution of thermal decomposition for lignin monomer by QMD calculations using the excited and charged model molecules

Fragment Distribution of Thermal Decomposition for Lignin Monomer by QMD Calculations using the Excited and Charged Model Molecules

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Abstract

Simulations with a quantum molecular dynamics (QMD) method (MD with MO) were demonstrated on the thermal decomposition of lignin monomer at the ground state including excited and positive charged states. Geometry and energy optimized results of the lignin monomer at the singlet and triplet states in single excitation, and at (+2) positive charged state by semiempirical AM1 MO calculations were used as the initial MD step of QMD calculations. In the QMD calculations, 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 5000 steps at 50 different initial conditions. The calculated neutral, positive and negative charged fragment distributions of the monomer model with 0.82 eV energy control were obtained as (90.6, 3.5, and 5.9%) to the total fragments, respectively. The ratios seem to correspond well with to the values observed experimentally in SIMS.

Keywords: thermal decomposition; lignin monomer; MD simulation; MS

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Introduction

Standard MD has been used extensively to investigate phase transitions, molecular transport, and other temperature-dependent properties on conformational structure. Some of the advanced MD methods with empirical force fields[1-5] have been quite successful in providing pretty good agreement with experimental energy and angular distributions of solid,[6] high-energy particle bombardment of organic film[7] adsorbed on a metal substrate,[8-10] and the bombardment of a polyethylene crystal.[11] However, we will expect the quantum molecular dynamics (QMD) (MD with MO) method to solve the motion equations automatically without using the empirical potential functions, or reactive force field. In QMD calculations, the proton and other ions recombination process of thermal decomposed reaction for organic substances can be seen, and fragment distribution due to the electric charged analysis can be obtained from SCF calculation of MO method for data at the final step of MD calculations.

The thermal decomposition of a lignin dimer in the ground state was already simulated by a QMD method (MD with a semiempirical AM1 method).[12] In the present study, we simulate the thermal decomposition of the lignin monomer including the excited and positive charged model molecules, because Saito and coworkers[13, 14] identified a specific fragment $(C_6H_3(OCH_3)(OH)CH_2^+$ at 137 amu) which may correspond to the excited, or charged molecular species.

Computational methods

(a) Lignin monomer at excited and positive charged states

For the excited and positive charged lignin monomer, we calculated the singlet and triplet states in single excitation, and at (+2) positive charged state by the semiempirical AM1 MO

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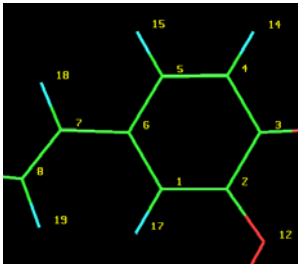Tel.: +8176-264-5924   fax: +8176-264-5742
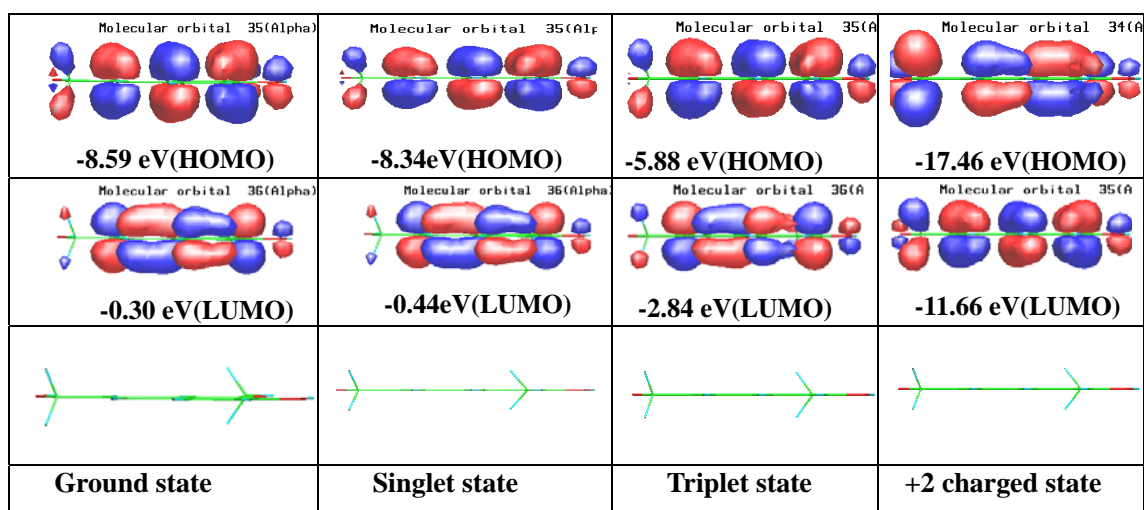*E-mail address:* endo@wriron1.s.kanazawa-u.ac.jp

method.[15]

Table 1 indicates C-C bond lengths of the monomer at ground, singlet, triplet excited state and (+2) charged states, and Fig. 1 shows the molecular structures of HOMO, and LUMO. It can be seen from the table and figure that some lengths of C-C bonds in the benzene ring at the excited and (+2) charged states becomes 1.44-1.48 Å in the single-bond length of all states in Table 1. For the MO structures of Fig. 1, there are similar MO pictures at the ground, singlet and triplet excited states. Then, since some bond lengths of the benzene ring at the excited and (+2) charged states are longer than normal values (1.40 Å) of the benzene ring in the ground state, we consider how the excited and charged monomers affect some specific fragments in the atomic mass unit.

Table 1. Bond lengths of lignin monomer at ground, excited and charged states

Structure of monomer	bond	Ground state	Singlet state	Triplet state	+2 charged state
	C1-C2	1.39	1.42	1.44	1.37
	C2-C3	1.41	1.43	1.44	1.48
	C3-C4	1.40	1.41	1.39	1.44
	C4-C5	1.39	1.37	1.38	1.35
	C5-C6	1.40	1.44	1.44	1.47
	C6-C1	1.40	1.43	1.39	1.44
	C6-C7	1.45	1.41	1.42	1.38
	C7-C8	1.34	1.36	1.38	1.41

| -8.59 eV(HOMO) | -8.34eV(HOMO) | -5.88 eV(HOMO) | -17.46 eV(HOMO) |
| -0.30 eV(LUMO) | -0.44eV(LUMO) | -2.84 eV(LUMO) | -11.66 eV(LUMO) |
| **Ground state** | **Singlet state** | **Triplet state** | **+2 charged state** |

**Fig. 1. MO Structures for lignin monomer at ground, excited and charged states**

(b) QMD calculations

The geometry and energy optimized results of ground, excited and positive charged models for lignin monomers by MO calculations were used as the initial MD step in QMD calculations. The thermal energy was controlled with the Nóse-Hoover thermostats[16, 17] and sampling position data carried out up to 2.5 ps (5000 steps). The equations of nuclear motions were integrated using the 5-values Gear method[18] as a predictor-corrector algorithm[19] with a time step of 0.5 fs.

We can obtain the distribution of thermal decomposed fragment products with positive, neutral and negative charges to the main chain carbon numbers, or the atomic mass unit from the output data of 5000 steps due to the changes of 50 random initial states for the motion of nuclear particles. Thus, the calculated distribution of the decomposition products to the number of main chain carbon atoms may be compared with the experimental results due to thermal decomposition gas mass spectrometry. On the other hand, we are able to compare the
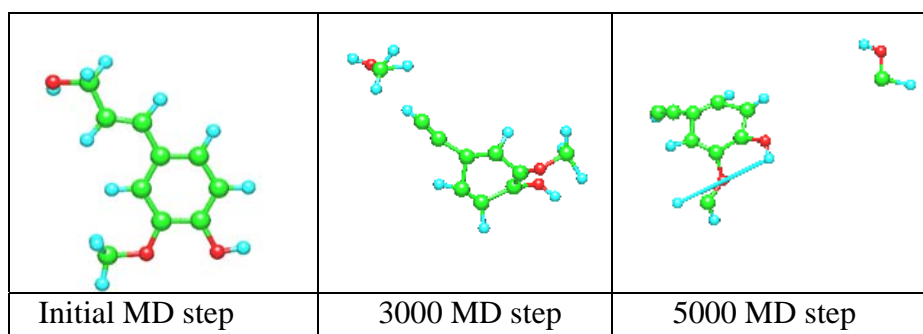
Fig.2. MD steps of lignin monomer at 0.78 eV
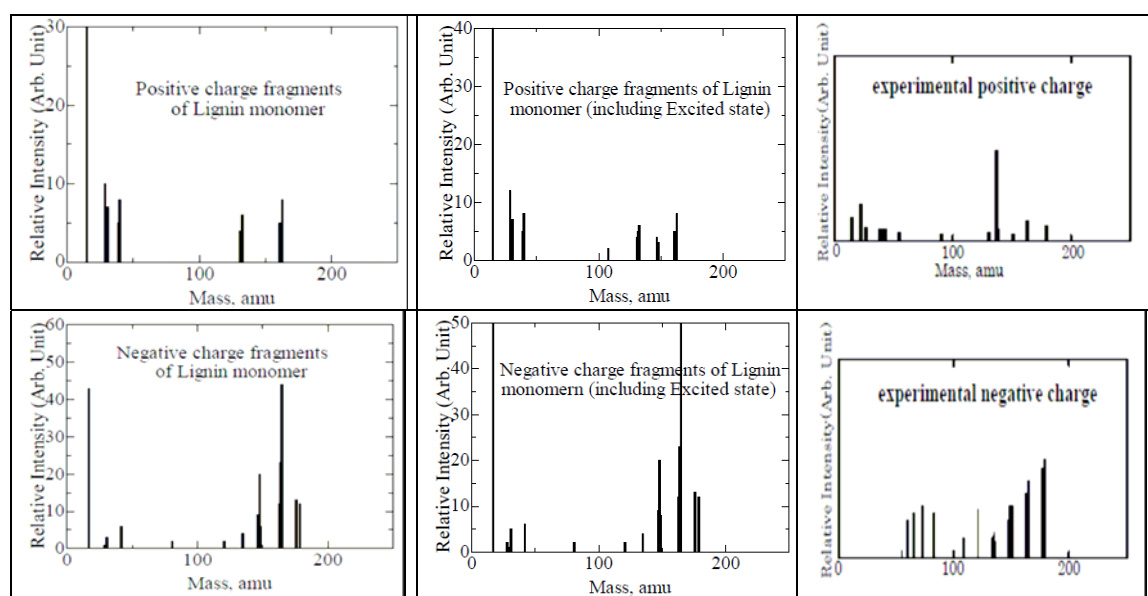
Fig. 3. Calculated distribution of the positive and negative ion charged fragments for lignin monomer with the experimental results

calculated positive- or negative-ion fragment spectra of the lignin monomer with the experimental ion mass spectra in static SIMS, or time-of-flight (TOF)-SIMS.

Results and Discussions

a) *Thermal decomposition process*

We simulated the thermal decomposed process of lignin monomer at the ground state, and including excited and charged states by QMD program. Fig. 2 shows the thermal decomposed data of the lignin monomer at initial, 3000, and 5000 steps with 0.78 eV thermal energy control. It can be seen from the figure that the smaller fragments exist with the increasing sampling data step.

For lignin monomer, we obtained the distribution of thermal decomposed fragment products with positive, neutral and negative charges to the main chain carbon number from

the output data of 5000 steps due to the changes of 50 random initial states for the motion of nuclear particles. Thus, the calculated distribution of the decomposition products to the carbon numbers enables us to make comparisons with the experimental results due to thermal decomposition gas mass spectro-metry.

b) *Secondary ionized fragment spectra*

Some investigators[20-22] already described the desorption-ionization processes for organic molecules in mass spectrometry. In the model processes, energy deposited by the primary particle ends up being absorbed by molecules in small quanta to produce thermal/vibrational motion. Ionized species can be desorbed directly, pass through the upper most surface layers affected (the selvedge region), and into vacuum without neutralization. In the selvedge

region desorbed neutral clusters may be ionized by attachment of small ions by electron impact or via ion-molecule reactions.

In a similar simplified emission process of a fragment ion from a solid lignin surface, an impact cascade and excited area are created around the point of primary particle impact through energy and momentum transfer from the bombarding particle to the solid, when a lignin sample is bombarded by a source of ions of a few ten of keV of kinetic energy. The surface fragment ions are then formed by dissociation of sputtered neutral molecular species on the outer most surface layer. The surface fragment ions are thus emitted, if a sufficient amount of energy is transferred.

Here we can consider that the results of the dissociation lignin correspond to the thermal decomposition in mass spectrometry. By considering the thermal decomposition, we are able to simulate the decomposition of the lignin monomer by the QMD method in order to compare the decomposed data at 5000 MD step in 50 runs with the experimental results in SIMS.

For the lignin monomer, we obtained the distribution of thermally decomposed fragments with neutral, positive, and negative charges to the atomic mass unit from the output data of 5000 step in the 50 runs. The calculated neutral, positive and negative charged fragment distributions of the monomer including the monomer at triplet excited state (10% contribution to total fragments) with 0.82 eV energy control were obtained as 90.6, 3.5, and 5.9% to the total fragments, respectively. Fig. 3 shows the calculated distribution of the positive and negative ion charged fragments for the lignin monomer at ground state and including the triplet state with the experimental results in TOF-SIMS.[13, 14] In the figure, the calculated positive charge fragment distribution for the lignin monomer including the triplet state is much close to the experimental result, in comparison with the calculated one at the ground state. On the other hand, the negative charge fragment including the triplet state is similar to the calculated result at the ground state. Especially for the positive charge fragments at the triplet state, we obtained $C_9H_8O^+$ (132 amu), $C_9H_7O_2^+$ (147 amu), and $C_9H_8O_2^+$ (149 amu) fragments.

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