QUANTUM CHEMISTRY MOLECULAR MODELING FOR RADIO-FREQUENCY AND MICROWAVE- FREQUENCY THERMO-UPCONVERSION HEATING OF TRANSITION METAL OXIDES OF NiO AND Fe2O3

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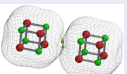
Introduction

Most solid-state inorganic materials heat up by microwave (MW) induced conductivity and dielectric loss heating, and the MW heating power to transition metal oxides, which have unpaired electron (spin), was considered to be proportional to dielectric heating relating to magnetic loss factor relating to spin in transition metal oxides. We know, however, that, nickel oxide (Ni(II)O, 25 gr)) having 2 unpaired electron, heat up to 1,300°C in 6 min under 1kW-MW irradiance, and that. ferric oxide (Fe(III)$_2$O$_3$, 25gr) having 10 unpaired electron, up to only 88°C in 30 min under the same 1kW-MW irradiance.[1] The big difference in MW heating is now attempted to rationalize on the basis of density functional theory-based molecular modeling (DFT/MM). Recently, we reported that DFT/MM verifies that water aggregates undergo absorption and emission in radio-frequency wave, MW and FIR region, resulting in thermal absorption and *dissipation, i.e., heat* of IR radication. We proposed that MW and radio frequency heating of water should instantly proceed *thermo-upconversion mechanism* under MW energy irradicance.[2]

For density functional theory-based molecular modeling (DFT/MM, B3LYP, 6-31G*)DFT/MM, we take into account that both nickel and ferrite oxides should be composed of covalent-bonding metal oxides of respective Ni(II)O or Fe(III)$_2$O$_3$, and their van der Waals (vdW) aggregates of [Ni(II)O]$_n$ (n=2~4) and [Fe(III)$_2$O$_3$]$_n$(n=2~4). We obtain their equilibrium three-dimensional molecular-aggregate structures, showing them with electron density in Table 1 and 2. Electron energy structures result in giving infrared (IR), far infrared (FIR), MW, and, radio-frequency wave- energy absorption spectra. It should be noted that stretching and bending and concerted back and forth movement between composed elements can be visualized for molecular aggregates of [Ni(II)O]$_n$ (n=2~4) and [Fe(III)$_2$O$_3$]$_n$(n=2~4) by clicking strong absorption peaks especially in 500~0 cm^{-1} region. It is very interesting to recognize that radio frequency wave, MW and FIR absorption induce back and forth movement of atoms in vdW aggregates and thermo-upconversion starts very quickly to FIR and IR absorption and emission. IR emission is heating.

DFT/MM of molecular vdW aggregates gives heat of formation ($\Box$E), the energy level of the lowest unoccupied molecular orbital (ELUMO) and energy level of the highest occupied molecular orbital (EHOMO), dipole, and electron transfer gap ($\Box$Et) that can be calculated from ELUMO (0) and ELUMO (+1). The bandgap will be a measure of conductivity. They are all summarized with IR and FIR absorption peaks with high intensity in Table 1 and 2. Clicking intense IR and FIR absorption peaks makes us understand that thermo-upconversion starts at concerted back and forth movement of atoms in molecular aggregates.

DFT/MM for quick MW heating of nickel oxides

Table 1　DFT/MM for IR and FIR absorption spectrum analysis of Ni(II) oxides

Nickel(II) oxide	Equilibrium geometry with density	Heat of formation (E/au)	Dipole (debye)	Conductivity measure: $\Delta E=\alpha LUMO\{+1\}-\alpha LUMO^{**}$	FIR region (0~500 cm⁻¹) cm⁻¹(intensity)	IR region (3500~500 cm⁻¹) cm⁻¹(intensity)
NiO Unpaired electron 2		-1583.20835	2.01	0.23	379(33.57	-
Ni_2O_2 Unpaired electron 4		-0.24919	0	1.30	198(58.1) 472(194)	639(99.3)
Ni_4O_4 Unpaired electron 8		-0.71603	0.01	1.51	172(0.2), 178(2.97) 183(3.02), 184(2.49) 430(1.89), 455(164) 456(170), 461(167)	535(58.4) 539(62.1)
Single point vdW dimer *$(Ni_4O_4)_2$ Unpaired electron 16		-1.3948*	0	0.42	133(4.35), 169(3.11) 169(3.12), 170(4.6) 264(0.06), 428(0.62)	518(477), 531(192) 536(398), 536(398) 580(4.87)

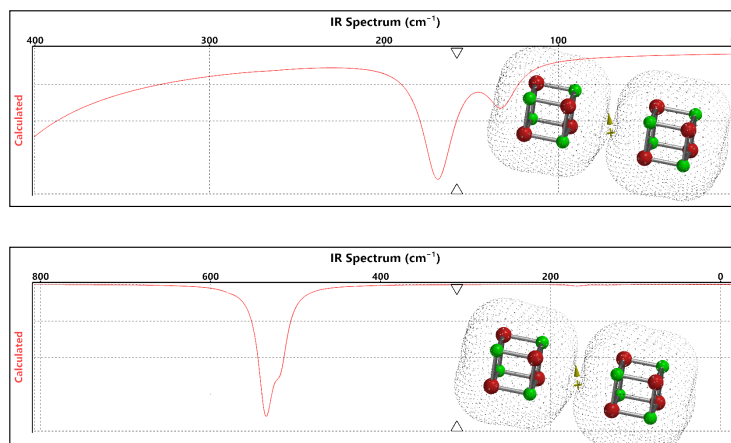* Single point calculation. ** "α" stands for alpha spin,

Fig. 1. DFT/MM-determined FIR and IR absorption spectra of single-point vdW dimer of *$[(Ni_4O_4)_2]_2$

DFT/MM of nickel oxides gives a dimer of Ni_2O_2, a tetramer (Ni_4O_4) and vdW aggregate of the tetramer (Table 1) when unpaired electron 2 for each nickel (II) atom is taken into consideration. Two of them are shown covalent bonding structures with surface electron density (dots style) and are thermally stable as proved by negative heat of formation. All of them have a small dipole. Previously we reported that conductivity of molecular aggregates should be evaluated by bandgap between electron running states (biased state) of molecules and aggregates.[3] At electron running states of nickel oxides, αLUMO (0) will become singly occupied molecular orbital (SOMO) and αLUMO(+1) will become αLUMO(0) of the electron-running-state nickel oxides ("α" stands for alpha spin). Conductivity measure of $\Delta E=\alpha LUMO\{+1\}-\alpha LUMO$ verifies that they have semi-conductivity, predicting that conductivity may contribute to MW heating at elevated temperature.
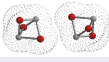
The covalent-bonding Ni(II)O dimer, Ni_2O_2, the covalent-bonding Ni(II)O tetramer, Ni_4O_4, and the vdW dimer of $(Ni_4O_4)_2$ are molecular modeled to know if thermo-upconversion mechanism is operating in the MW heating of nickel oxides. The single point energy structure of $(Ni_4O_4)_2$ is obtained and analyzed although heat of formation f is positive. Because the equilibrium geometry could not be molecular modeled contrast to the case of $Fe(III)_2O_3$ (see Table 2).

Table 1 shows that all of Ni(II)O aggregates have absorption with high intensity in 500~0 cm^{-1} region including MW and radio-frequency wave. In addition, the stronger absorption expands to the IR absorption and dissipation region. Typical FIR and IR absorption spectra shown in Fig. 1 verifies and predicts the thermo-upconversion occurs effectively during MW heating of nickel oxides.

DFT/MM for MW heating of ferric oxides

DFT/MM is extended to ferric oxides by taking into account of unpaired electron 5 for each Fe(III) atom . The equilibrium geometry of covalent-bonding of Fe_2O_3 and single pint energy structure of vdW aggregates of $[Fe(III)_2O_3]_2$ are successfully modeled and their heat of formation, dipole and conductivity measure $\Delta E=\alpha LUMO\{+1\}-\alpha LUMO$ are summarized in Table 2. They have no dipole, but have semi-conductivity comparable to the nickel oxides. Interestingly, the equilibrium geometry structure Fe_2O_3 and the single pint energy structure of vdW aggregates have no absorption in IR region of more than 500 cm^{-1}. These calculation results well verify slow MW heating of ferrite as reported.[1]

Table 2 DFT/MM for IR and FIR absorption spectrum analysis of $Fe(III)_2O_3$

$Fe(III)_2O_3$	Equilibrium geometry with density	Heat of formation (E/au)	Dipole (debye)	Conductivity measure: $\Delta E=\alpha LUMO\{+1\}-\alpha LUMO$**	FIR region (0~500 cm^{-1}) cm^{-1}(intensity)	IR region (3500~500 cm^{-1}) cm^{-1}(intensity)
$Fe(III)_2O_3$ Unpaired electron 10		-2752.8048	0	1.25	102(2.65) 117(2.78) 387(81.8)	549(0.09)
*vdW dimer $[Fe(III)_2O_3]_2$ Unpaired electron 20		0.24497	0	0.26	118(122). 155(17.1) 253(31.5), 279(24.7) 302(12.7), 356(10.84)	No absorption
vdW dimer $[Fe(III)_2O_3]_2$ Unpaired electron 20		-0.2593	0	0.79	62(9.72), 175(39.9) 208(29.1), 231(98.2) 301(0.17), 393(0.21)	535(30.8), 585(166) 644(426), 722(606)
$Fe(III)_4O_6$ Unpaired electron 20		-0.25926	0.05	0.79	58(9.5),174(40.0) 208(29.7),231(98.2), 301(0.17),393(0.21)	534(31.1), 584(166) 644(426), 666(7.5) 722(607)
vdW dimer $[Fe(III)_4O_6]_2$ Unpaired electron 20		-0.7066	0	0.35	54(0.02), 61(3.3), 72(7.4), 86(7.1) 139(0.53),142(49.2) 205(15.4), 217(24.3)	534(31.1), 584(166) 644(426), 666(426) 653(177), 658(374)

* Single point calculation, ** "α" stands for alpha spin.

Interestingly, DFT/MM for an equilibrium geometry of a vdW dimer of $[Fe(III)_2O_3]_2$ leads to covalent bonding $Fe(III)_4O_6$. The vdW dimer $[Fe(III)_2O_3]_2$ is structurally identical with the covalent bonding $Fe(III)_4O_6$ as shown in Table 2. Further DFT/MM is successful for obtaining an equilibrium geometry for the vdW dimer of $[Fe(III)_4O_6]_2$. They all have negative heat of formation and then the structure ae thermally stabilized.
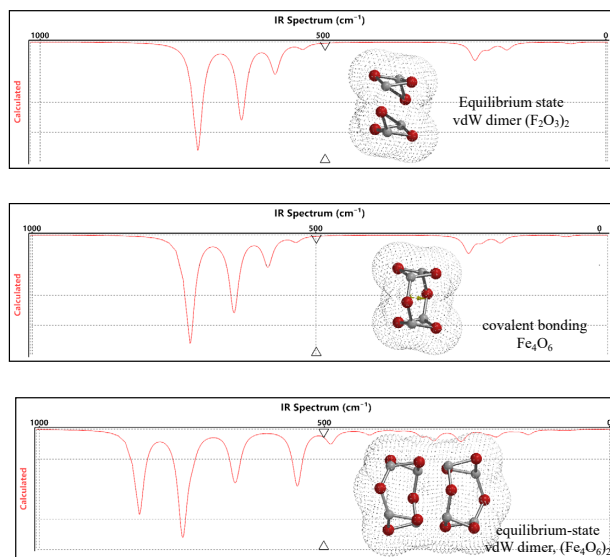

Fig. 2. DFT/MM-determined FIR and IR absorption spectra of equilibrium-state vdW dimer $(F_2O_3)_2$, Fe_4O_6 and equilibrium-state vdW dimer, $(Fe_4O_6)_2$

Fig. 2 shows IR and FIR absorption spectra of the equilibrium-state vdW dimer of $[Fe(III)_2O_3]_2$, covalent bonding $Fe(III)_4O_6$ and its equilibrium-state vdW dimer, $[Fe(III)_4O_6]_2$. Contrary to the case of $Fe(III)_2O_3$, Covalently bonding $Fe(III)_4O_6$ structures are verified to undergoes thermo-upconversion. On careful examination, Koleini and Barani reported that Fe_2O_3 heats up to 1000 °C at 6-min interval.[4] Then we conclude that ferrite heat up accompanying structural change under MW irradiance.

References

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