

Quantum Chemical Calculations on Photo-dissociation; Isotope Effect of the Rotational Levels of the Ground State O₂ Molecules with Relevance to Exotic Oxygen in Lunar Metals

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Introduction: It is well established that the Earth and the Moon (Apollo samples and lunar meteorites) have almost identical oxygen isotopic ratios. However, oxygens implanted within a few hundred nanometers below the surface of metal particles separated from lunar soils show large mass-independently fractionated isotopic ratios with $\Delta^{17}\text{O} \equiv \delta^{17}\text{O} - 0.52\delta^{18}\text{O}$, $\delta^i\text{O} \equiv [(i\text{O}/^{16}\text{O})/(i\text{O}/^{16}\text{O})_{\text{SMOW}} - 1] \times 1000$ ranging from $\sim -20\text{‰}$ [1] to $\sim +26\text{‰}$ [2]. Since a substantial amount of Earth escaping O⁺ flux from the upper atmosphere (Geotail Mission [3]) is likely to reach the lunar surface [4], Ozima et al. [5] suggested that the extraordinary oxygen implanted on lunar metals could be attributed to terrestrial oxygen picked up from the upper atmosphere by the Solar Wind, which we call the Earth Wind. To test this hypothesis, we have been investigating isotopic fractionation of O⁺ ions in the upper atmosphere (above 100 km), from where O⁺ cations most likely to be picked up by the solar wind.

There are isotope exchange reactions and photolysis (photo-ionization and photo-dissociation due to UV solar radiation), which may yield mass independent isotopic fractionation (MIF) of oxygen in the Earth's upper atmosphere. We reported that photochemical reactions would produce large MIF provided that reaction rates for different isotopes differ substantially [6],[7], and that UV photo-dissociation make MIF when we assume that O₂ molecules are in the vibrational ground state or obey the Boltzmann distribution, and rotational level is zero [8]. The cross section of the Schumann-Runge band (170-200 nm) has a serrated shape, which is come from the energy difference between rotational levels. So, the Schumann-Runge band ought to make large MIF of oxygen. Here, we report calculated photo-dissociation rate with concerning rotational levels and estimation of isotopic ratio of the thermosphere.

Method: First principles reaction dynamics simulations were performed to compute the photolysis rate for the $B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ electronic

transition, which corresponds to the Schumann-Runge band. The Born-Oppenheimer approximation was employed in this paper; in the first step the time independent Schrödinger equation was solved only for the electron-motion, and then we performed the wave-packet dynamics for the nuclei-motion in the potential energy curves determined by the first step calculation. Quantum chemical program package, MOLPRO 2006.1 [9], was used for calculation of the potential surface of O₂, and the quantum dynamics was carried out by our own program package. The photo-dissociation cross section can be calculated by quantum molecular dynamics. Therefore, following the time dependent approach, the autocorrelation function was numerically computed by the second step calculation. Finally, the theoretical spectrum as a function of wavenumber of the excitation light was estimated by the Fourier transform of the autocorrelation function, $A(t)$. In SI unit, the dissociation cross section is given by

$$\sigma(\nu) = \frac{\pi\nu}{3c\epsilon_0\hbar} \int_{-\infty}^{\infty} dt \exp[i(E_i + h\nu)t/\hbar] A(t),$$

where E_I is the energy of the initial ground state, $h\nu$ is the energy of the excitation light [10].

Results and Discussion: We show calculated cross section in Figure 1 and 2. In these figures, we assume that O₂ molecules are in the vibrational ground state. It is difficult to get absolute value of cross section using our method, but it is important that the shape of our calculation is similar to reference [11]. It has the continuum absorption (peak at $\sim 140\text{ nm}$) and the fine structured band absorption spectra around 170-200 nm. In the continuum absorption, the excitation energies shift mass-dependently between isotopomers. In the band spectra, peak of cross section also shift mass-dependently, while magnitude relations are different between transitions. For example, some transitions the largest is for $^{16}\text{O}^{16}\text{O}$, another is for $^{16}\text{O}^{18}\text{O}$. One important note is that ratio of cross sections between major isotope and rare isotopes is changing with

wavenumber, because we focus in isotopic effect of photo-dissociation.

Using cross section calculated above, we calculate isotopic ratios of UV-dissociated oxygen. Production rates of oxygen atoms are get from $[^i\text{O}]/dt = J_i [C^i\text{O}]$, where brackets '[]' means density of species, J_i is photo-dissociation rate. We calculate photo-dissociation rate as a function of the altitude

$$J_i(z) = \int \sigma_i(\nu) I(z, \nu) d\nu,$$

where subscript i is the insignia of isotopes ($i = 16, 17, 18$), z is the altitude, $I(z, \nu)$ is the intensity of light at the altitude of z . For considering the shielding effect which is a popular idea for mass independent fractionation, the light intensity I has z -dependency $I(z, \nu) = I_0(\nu) \exp[-\tau(z, \nu)]$, where I_0 is a initial intensity which we use the 6000 K black body radiation here, τ is the optical depth $\tau(z, \nu) = \sum_{i=16}^{18} \sigma_i(\nu) \int_{\infty}^z [C^i\text{O}] dz$. We show blue circles which is the results of this paper in Figure 3. Each point correspond to another mixing ratio of rotational levels. $\Delta^{17}\text{O} = -2.0\text{‰}$ to -0.6‰

While red squares which correspond to different temperatures of the boltzmann distribution in Figure 3 show large variation (from negative to positive) in isotopic ratio, all blue points show negative $\Delta^{17}\text{O}$. At 200 K, the population of the vibrational ground state is major, so we compare blue circles ($\Delta^{17}\text{O} = -2.0\text{‰}$) with 200 K red point ($\Delta^{17}\text{O} = -5.5\text{‰}$). When we consider rotational levels, magnitude of anomaly are smaller, but they keep negative. Now, we are calculating cross sections with rotational levels at high temperature in the expectation that signs of isotopic ratios don't change.

References: [1] Hashizume & Chaussidon, *Nature* **434**, 619-622 (2005). [2] Ireland et al., *Nature* **440**, 776-778 (2006). [3] Yau & André, *Space Science Reviews* **80**, 1-25 (1997). [4] Seki et al., *Science* **291**, 1939-1941 (2001). [5] Ozima et al., *Icarus* **186**, 562-570 (2007). [6] Hiraki et al., *LPS XXXIX*, Abstract #1175. [7] Yamada et al., *Annual Meeting of MetSoc*, Abstract #5205. [8] Yamada et al., *LPS XXXX*, Abstract #1478. [9] MOLPRO is a package of ab initio programs written by Werner & Knowles, <http://www.molpro.net>. [10] Heller, *Journal of Chemical Physics* **68**, 2066-2075 (1978). [11] Brasseur & Solomon, *Aeronomy of the middle atmosphere* (1984)

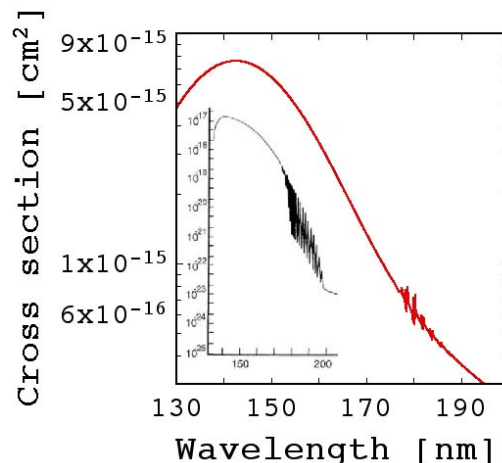


Figure 1: Photo-dissociation cross section of O_2 . A red line is a calculated cross section for $^{16}\text{O}^{16}\text{O}$, a black line of a subplot is a reference from [11]

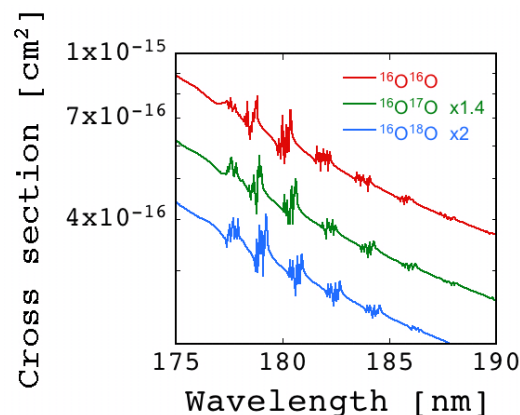


Figure 2: Closeup of Figure 1 with isotopomers. We can see wavelength shifts and differences in the serrated shape.

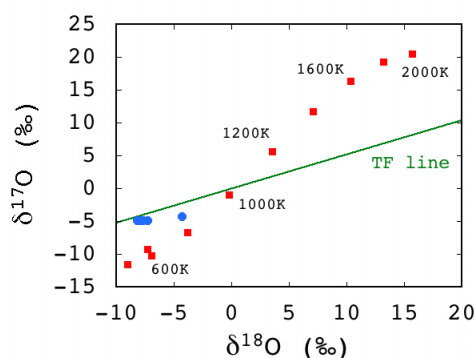


Figure 3: Oxygen three isotope plot of oxygen atom produced per unit time. Blue circles are results changing Boltzmann distribution of rotational levels in the ground state. Red squares are our results presented at metsoc2009 for comparison.