

MASS-INDEPENDENT OXYGEN ISOTOPE FRACTIONATION IN EARTH WIND: FIRST PRINCIPLE CALCULATION. Akinori Yamada¹, Shinkoh Nanbu², Yasuko Kasai³, and Minoru Ozima¹. ¹University of Tokyo, Japan, E-mail: yamada@eps.s.u-tokyo.ac.jp, ²Sophia University, Japan, ³National Institute of Information and Communications Technology, Japan

Introduction: Mass-independently fractionated oxygen have been reported on metal particles extracted from Apollo lunar soils [1, 2, 3]. Since the substantial fraction of Earth-escaping O⁺ flux (Earth Wind, EW hereafter), comparable to the amount of the anomalous oxygen implanted on the metal particles, could reach the lunar surface [4], Ozima et al. [5] suggested that EW may be responsible to the anomalous oxygen. Here, we report the results of detailed quantum mechanical calculations of photo-dissociation of O₂, which shows considerable mass-independent isotopic fractionation of oxygen, thereby in conformity with the EW hypothesis.

Method: First principles reaction dynamics simulations were performed to compute the photolysis rate for the B³Σ_u⁻ ← X³Σ_g⁻ electronic transition, which corresponds to Schumann-Runge band. The Born-Oppenheimer approximation was employed in this paper; in the first step the time independent Schrödinger equation only for the electron-motion was solved, 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 [6], was used for the first calculation, and the quantum dynamics was carried out by our own program package.

Assuming the quantum yield of the corresponding photolysis is unity, the photo-absorption cross section can be correlated with the photolysis rate. 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 wavelength of excitation light was estimated by the Fourier transform of the autocorrelation function, $A(t)$. In SI unit, the absorption cross section is given by

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

, where E_i is the energy of the initial ground state, $h\nu$ is the energy of the excitation light.

Results and Discussions: Calculated absorption cross sections for C¹⁶O showed similar wavelength dependence with experiment [7], although the absolute magnitude was yet to be calibrated for a meaningful comparison. From the calculated cross sections, we estimated enrichment factors defined as $\sigma_i(\lambda)/\sigma_{16}(\lambda) - 1$ ($i = 17, 18$), which ranged from -0.4 to +0.3, suggesting large mass-independent isotopic fractionation in photo-dissociation of CO_i. Numerical values of isotopic fractionation (e.g. Δ¹⁷O) can be obtained by solving photochemical reaction equations in thermosphere conditions (>100 km) with the above estimated dissociation rates, where effective O⁺ pick-up is likely to take place. We are currently working on the latter problem with hopes that this would test the EW hypothesis.

References: [1] Hashizume & Chaussidon, 2005, Nature, 434: 619-622. [2] Ireland et al., 2006, Nature, 440: 776-778. [3] Hashizume & Chaussidon, GCA, in press. [4] Seki et al., 2001, Science, 291: 1939-1941. [5] Ozima et al., 2008, PNAS, 105: 17654-17658. [6] Werner & Knowles, <http://www.molpro.net>. [7] Ackermann et al., 1970, Planet. Space Sci., 18: 1639-1651.