

Quantum Chemical Calculations on Photo-dissociation of CO:

$E^1\Pi \leftarrow X^1\Sigma^+$ with Non-Adiabatic Transition Akinori Yamada¹, Shinkoh Nanbu², Minoru Ozima¹, ¹Department of Earth and Planetary Science, University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo, 113-0033 Japan, yamada@eps.s.u-tokyo.ac.jp; ²Department of Materials and Life Sciences, Sophia University, Tokyo, Japan

Introduction: Since Clayton et al. [1] found oxygen isotope anomaly in meteorites, there have been a number of studies. It is well established that oxygen isotopic ratios of typical CAIs are $\Delta^{17}\text{O} \sim -20\text{‰}$, those of chondrites are from -5‰ to 3‰ , and those of achondrites are $\Delta^{17}\text{O} \sim 0\text{‰}$ ($\Delta^{17}\text{O} \equiv \delta^{17}\text{O} - 0.52\delta^{18}\text{O}$, $\delta^i\text{O} \equiv [(^i\text{O}/^{16}\text{O})/(^i\text{O}/^{16}\text{O})_{\text{SMOW}} - 1] \times 1000$). Important questions about oxygen isotopes in the solar system materials are what is a mean value of the solar system and how the isotope anomaly is made. There are two different interpretations for the origin of oxygen isotopic anomalies. One group advocates that the oxygen isotopic compositions of CAIs being the same as that of the average Solar system and CO self-shielding produced the isotope anomaly [2, 3]. Besides its unusual implication that CAI oxygen must be the same as the solar oxygen, the self-shielding hypothesis is based on several dubious premises including no isotopic effect of photo-dissociation of CO. The other group advocates that the isotopic compositions of the Earth being the same as that of the Solar system and Oxygen isotopic anomalies of minerals such as found in CAIs and chondrules must be made by chemical/physical processes [4, 5].

We focus on photo-dissociation process. Photo-dissociation process is a rapid process. Photo-dissociation can make isotope anomalies before homogenize. Isotope anomalies is produced by isotopic selective photo-dissociation of CO molecule [6]. CO self-shielding model, however, assume photo-dissociation spectra of minor isotopologues shift from that of major isotopologue in wavelength [3]. Isotopic selective photo-dissociation spectra have not been attracted attention. Here, we report photo-dissociation spectra of CO molecules by using quantum chemical calculations.

Method: First principles reaction dynamics simulations were performed to compute the photolysis rate for the $E^1\Pi \leftarrow X^1\Sigma^+$ electronic transition with non-adiabatic transition to $^1\Pi$ state. 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 wavepacket dynamics for the nuclei-motion in the potential energy curves determined by the first step calculation. Quantum chemical program package, MOLPRO 2010.1 [7], was used for calculation of the potential surface of CO, and the quantum dynamics was carried out by our own program package.

We use two potential energy surfaces with non-adiabatic transition which are described as adiabatic potentials and coupling element.

$$V(R) = \begin{pmatrix} E_1 & -\frac{\hbar^2}{2M}\Xi_{12}\frac{\partial}{\partial R} \\ -\frac{\hbar^2}{2M}\Xi_{21}\frac{\partial}{\partial R} & E_2 \end{pmatrix}$$

Coupling element Ξ is

$$\Xi_{ij} = \left\langle \psi_j \left| \frac{d}{dR} \right| \psi_i \right\rangle = \frac{1}{E_i - E_j} \left\langle \psi_j \left| \frac{\partial \mathcal{H}_{\text{el}}(r)}{\partial R} \right| \psi_i \right\rangle,$$

ψ is electron wave function, E_i is a eigenvalue of electron hamiltonian ($\mathcal{H}_{\text{el}}\psi_i = E_i\psi_i$). We solve nuclei Schrödinger equation $i\hbar\frac{\partial}{\partial t}\phi = \mathcal{H}_{\text{nu}}\phi$. Nuclei hamiltonian is

$$\mathcal{H}_{\text{nu}} = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2} + V(R).$$

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 [8].

Results and Discussion: We show calculated potential surface of $E^1\Pi$ state and next $^1\Pi$ state in Figure 1. This transition is considered one of the important transition for a CO self-shielding model. Roughness of calculated potential surface

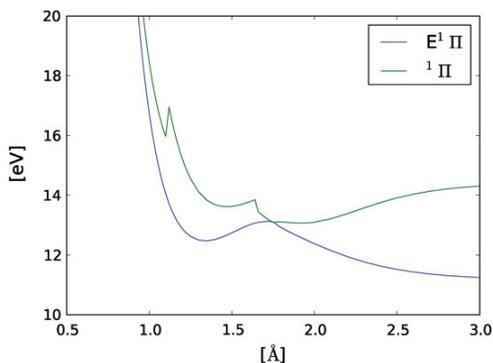


Figure 1: Excited potential surface of $E^1\Pi$ and $^1\Pi$ states.

and low accuracy of potential energy make cross sections incorrect. Nevertheless we can discuss about cross section difference between isotopologues and isotopic signature.

We calculated cross sections from $X^1\Sigma^+$ to $E^1\Pi$ with non-adiabatic transition to $^1\Pi$. Wavelength range of calculation results is 85–96 nm whereas that of laboratory experiment is 95–105 nm because calculation of potential energy are overestimated. In this calculation, we assume that CO molecules are in the vibrational ground state. The peak wavelength of cross sections of $C^{17}O$ and $C^{18}O$ shift to the long wavelength from that of $C^{16}O$. However, amplitudes of each peak are different. Cross section of $C^{16}O$ is maximum for some transitions, cross section of $C^{17}O$ or $C^{18}O$ is maximum for other transitions. For isotope selective photo-dissociation, considering only wavelength shift is insufficient. Amplitude changes of cross sections must also be considered.

Using cross section calculated above, we calculate isotopic ratios of dissociated O atoms. Production rates of oxygen atoms are get from $[^iO]/dt = J_i[C^iO]$, where brackets $[]$ means density of molecules, J_i is photo-dissociation rate. We calculate photo-dissociation rate

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

where suffix i is the insignia of isotopes ($i=16, 17, \text{ or } 18$), $I(\nu)$ is the intensity of light. We assume that $I(\nu)$ is the 6000 K black body radiation here. Figure 2 shows the fractionation factors ($\epsilon_i \equiv (J_i/J_{16} - 1) \times 1000\text{‰}$), ϵ_{17} is from -500‰ to 2200‰ and ϵ_{18} is from -800‰ to 3500‰ .

Now, we are calculating more accurate potential energy surfaces to figure out accurate cross section.

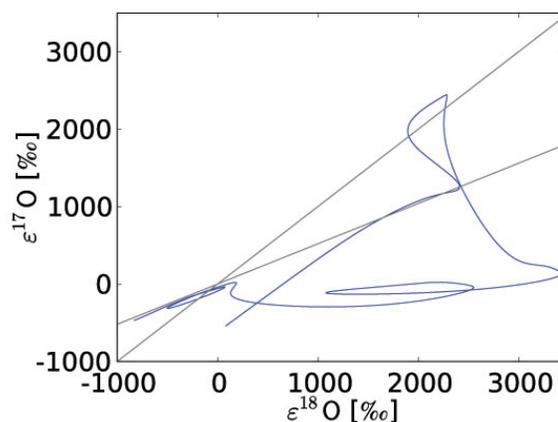


Figure 2: Isotopic fractionation constants.

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