

## Measuring and Modeling Equilibrium and Non-Equilibrium Isotope Effects on Cold Dust Grain Surfaces

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### Introduction

The distribution of elements and chemical phases in the solar system is in disequilibrium. This basic observation also appears to apply to the distribution of oxygen isotopes in the solar system, whose distribution in triple-oxygen isotope space is characterized as being mass-independent in the sense that the ratio of  $\delta^{17}\text{O}/\delta^{18}\text{O}$  of CAIs and chondrules deviate significantly from the slope that characterizes the terrestrial fractionation line ( $\delta^{17}\text{O}/\delta^{18}\text{O}$ ) [1, 2]. This anomalous slope suggests that mass-dependent kinetic and equilibrium fractionations, as we know them, are not the main physical-chemical processes controlling the distribution of isotopes (and elements and chemical phases) in the solar system. Because of these reasons, it may be reasonable to suggest that understanding the origins of the distribution of oxygen isotopes in the solar system can be used to place robust constraints on our understanding of protosolar cloud collapse and planetary system formation.

### Models of Non-equilibrium/Anomalous Isotopic Fractionation

A theory of equilibrium and kinetic isotopic fractionations has existed since the mid 1940s [3, 4] and is a derivative of a much more general theory of kinetic rates known as Transition State Theory (TST) [5]. Kinetic rates of reaction, under TST, are functions of isotopic mass and this dependence on isotopic mass largely explains the slope 1/2 terrestrial fractionation line (TFL) for oxygen isotopes.

In 1983, it was discovered that chemical processes involving the reaction of atomic oxygen with molecular oxygen and a third body can produce isotopically anomalous oxygen during the formation of ozone ( $\text{O} + \text{O}_2 \rightarrow \text{O}_3$ ) in the gas-phase [6]. At the time of its discovery, the physical chemical mechanism responsible for this effect remained unclear, with quantum symmetry and self-shielding of molecular oxygen suggested as possibilities. A potential connection between chemically derived isotopic anomalies and the “anomalous” distribution of oxygen isotopes in the solar system was suggested, although no direct astrophysical mechanism was provided.

Most recently, photochemical non-equilibrium isotope effects such as self-shielding of CO [7, 8] have been proposed to explain the “anomalous” distribution

of isotope in the solar system. Laboratory tests of self-shielding of CO, however, do not support the assumptions that self-shielding models are based on, and their relevance for the early-solar system are the subject of intense debate [9, 10, 11].

Recently, it was proposed that the photochemically-driven surface chemical reactions that form  $\text{H}_2\text{O}$  on interstellar dust grains may involve precursor species such as  $\text{O}_3$  and  $\text{HO}_2$  that are well known to acquire “anomalous” fractionations during their formation [12]. The question of whether or not these species, when formed on cold-dust grain surfaces also acquire anomalous fractionations, is an open question and is the focus of our current work.

Before proceeding to describe our experimental apparatus and preliminary results, we provide more details as to why it is that highly oxidized species are able to form on cold dust grains that are embedded in the highly reducing conditions of a molecular cloud.

### Dust Grains as Catalysis and Concentrators of Oxygenated Species

Given the highly reducing conditions expected in a gas of cosmic composition ( $[\text{H}] \gg [\text{O}]$ ), it is at first glance surprising that molecular clouds can support the production of a species such as  $\text{O}_3$ . Indeed, simple estimates of the rate of formation of  $\text{O}_3$  in the gas-phase lead to time-scales of formation that exceed the age of the Universe. However, it is long been recognized that gas-phase production of other species such as  $\text{H}_2$  requires the presence of dust grain surfaces to augment gas-phase rates. These dust grains have other consequences and are also implicated in the formation of complex molecular species through the following processes: surface adhesion onto a dust grain, surface diffusion (hopping), evaporation from a dust grain surface, and collisions and chemical reactions to form new compounds. Other processes such as UV photolysis (gas and surface phase) and cosmic-ray ionization and secondary UV production couple the gas and surface species in these environments and may lead to non-equilibrium isotope effects that are analogous to those that occur in Earth’s atmosphere [12]. The most consequential of these processes in determining the relative concentrations of H and O on dust grain surfaces are the adhesion and evaporation of atomic and molecular species on dust grain surfaces.

As a general rule of thumb, since sticking and evap-

oration processes are electrostatic processes, atoms and molecules with higher atomic mass (which correlates with the number of electrons for neutral species), have higher activation energies of evaporation ( $E_A$ ). These rates of evaporation can be written as:

$$k_{\text{evap}} \simeq \nu_r \exp \frac{-E_A}{T} \quad (1)$$

where  $E_A$  is expressed in units of the temperature  $T$ . The pre-exponential frequency is typically assumed to be constant and on the order of  $10^{12} \text{ s}^{-1}$ , although this frequency as a function of isotopic mass can be determined from first principles or empirically.

Atomic Hydrogen is largely believed to have a lower activation energy ( $E_A \sim 600\text{K}$ ) compared with atomic oxygen ( $E_A \sim 800 \text{ K}$ ). This 200K difference in activation energy means that H evaporates  $\sim e^{20}$  times faster than atomic O when  $T = 10 \text{ K}$ . This mismatch in evaporation rates is largely responsible for the enhanced ratios of O to H on the surfaces of dust grains in molecular clouds [13].

### Experimental Tests of Molecular Cloud Isotope Photochemistry on Cold Dust Grains

The suggestion by Dominguez that heterogeneous chemistry on cold surfaces may be partly or wholly responsible for the “anomalous” distribution of oxygen isotopes in the solar system suggests that surface chemical and transport processes need to be understood at the isotopic level of resolution. Given this motivation, we have designed and constructed a vacuum system to simulate and measure isotope effects associated with surface chemical reactions and transformations in molecular cloud conditions. This experimental set-up consists of a Advanced Research Systems liquid He cooled cryostat with UV transparent windows that allow us to introduce UV ( $\lambda > 254 \text{ nm}$ ) light onto a cold ( $T=10\text{-}300 \text{ K}$ ) surface. A manifold is used to introduce gas-phase species ( $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ , etc.) into the vacuum system. At the lowest temperatures, these molecular species are expected to condense onto the cold surface with negligible vapor pressures.

### Results

We are currently in the process of measuring the relative rates of evaporation (and condensation) of  $^{16}\text{O}^{16}\text{O}$ ,  $^{16}\text{O}^{17}\text{O}$ , and  $\text{O}^{16}\text{O}^{18}\text{O}$ . In addition, we will present results on the triple-oxygen isotopic composition of  $\text{O}_3$  produced on cold ( $T = 10 - 50 \text{ K}$ ) surfaces.

### Future Work

Future work will consider adapting the current system to undertake measurements of CO and other astrophysically important species at the isotopic levels of precision.

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