KINETIC ISOTOPE FRACTIONATION IN INTERSTELLAR MEDIUM, UPPER ATMOSPHERE AND METEORITES, INFERRED FROM MODEL EXPERIMENTS. J.L. McCrumb, N. Friedman, R. Fitzgerald and G. Arrhenius, Scripps Institution of Oceanography, La Jolla, California 92093

This research aims at understanding the factors that control condensation of solids from the space medium, and specifically at clarifying the large kinetic isotope fractionation effects observed in interstellar clouds [1] and in aerosols formed in the boundary zone between the Earth's upper atmosphere and ionosphere [2]. These effects are monitored in real time by radioastronomic and aeronomic measurements. Experiments reported here attempt to model related effects in the laboratory, and to determine how they scale to natural conditions. When the mechanisms are well understood which lead to the observed kinetic isotope fractionation, including the strong nonlinear effects, it should be possible to use the presumably analogous effects seen in primordial condensates in meteorites as a tool for reconstructing the conditions of excitation in their source medium, and to place boundaries on the reaction paths leading to the formation of solids in the early history of the circumsolar region.

An alternative explanation has been proposed for oxygen isotope effects in meteorites, implying condensation of material extracted from a particular region of a supernova, hypothesized to be the seat of preferential synthesis of ^{16}O [3]. Considering that also ^{17}O and ^{18}O are believed to be synthesized in other regions of the supernovae, the ultimate isotope mixing ratios in any ejected material would, however, seem highly uncertain, even theoretically [4]. Such hypotheses can hardly be verified, but deserve consideration due to possible dynamic effects of supernova explosions suggested by astronomical observations. The recourse to nucleosynthetic effects to explain the oxygen isotope anomalies in meteorites was taken at the time of their discovery [5] when testable explanations seemed to be lacking. Since then large-scale kinetic chemical isotope fractionation has been observed to operate in two-isotope systems in the space medium and quantum phenomena that lead to nonlinearities in polyisotopic reaction systems have been observed in the laboratory. The relative plausibilities of the two types of explanations should thus be compared.

Kinetic isotope fractionation in reactions of excited species in the N*-O* system was found to result in $\delta^{15}N_{air}$ as high as 420‰ [6]. Initial studies [7] of fractionation effects in oxygen used reactions in the system C*-O* with either CO or both CO and O_2 as reactants, measuring the isotopic composition of product CO_2. The concurrent effects in $\delta^{18}O_{PDB}$ (≥ -50‰) and $\delta^{13}C_{PDB}$ (≥ -52‰) indicate that one fractionating step is the dissociation of the CO molecule or molecular ion. Among the reaction parameters determining the extent of fractionation, kinetic temperature, excitation, mixing ratio, pressure and flow rate have been studied. For investigation of nonlinear fractionation effects the assumption was made that these are most pronounced under conditions leading to the largest fractionation of ^{18}O. Accordingly, CO_2 products with high negative $\delta^{18}O$ were selected for determination of $\delta^{17}O$. A consistent positive $\delta^{17}O$ anomaly was found under these conditions, deviating as much as +48‰ from equilibrium. For technical reasons the measurements were made on CO_2; in order to secure control over the effect of ^{13}C at mass 45 due to $^{12}C^{16}O^{17}O$ and $^{13}C^{16}O_2$ the product CO_2 was completely fluorinated with BrF_5 and the O_2 formed was burned to CO_2 on carbon of accurately known isotopic composition.

Several different quantum effects can plausibly be invoked [8] to

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explain the observed differential fractionation of the lightest isotope. These include kinetic isotope effects in: 1) predissociation of excited reactant molecules [9]; 2) Franck-Condon factors for reactant excitation; and 3) rates of relaxation from excited vibrational and rotational states. Thus far, our effort has concentrated on predissociation as the relevant mechanism. We are attempting calculation of a general expression for the predissociation probability, P, to determine the nature of its isotopic selectivity, and to apply it to the known predissociation of the state $B^3\Sigma_u^-$ of O_2. Crossing of the potential curves of a bound and a repulsive state as a result of the coupling between electronic and nuclear motion allows the spontaneous, radiationless transition between these states, provided the appropriate selection rules are satisfied. The disintegration of a molecule in a bound vibrational state under these circumstances is known as predissociation; the phenomenon separates naturally into two distinct cases (Fig. 1a,b).

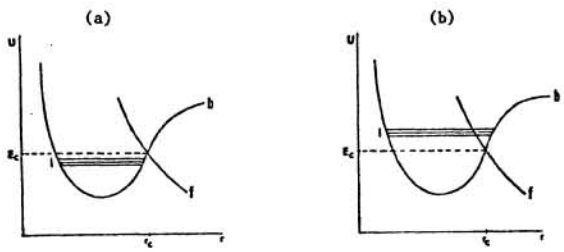

Fig. 1 (a) Classically forbidden and (b) allowed predissociation

The first case considered is predissociation in the forbidden region (a), where transition from the bound to the dissociated state takes place via quantum mechanical tunneling through the potential barrier defined by the intersecting curves. The probability of tunneling through the barrier is inversely proportional to the lifetime of the molecule in the bound vibrational state, or can be thought of as inversely related to the area bounded by the barrier and the energy of the state itself:

$$P \propto \mu^{-1/2} \exp\left\{-\frac{2}{\hbar}\int [2\mu(U(r)-E)]^{1/2}\,dr\right\} \qquad (1)$$

where E is the energy of the vibrational state, U(r) is the potential barrier, and μ is the reduced mass of the molecule. The δ value for two isotopes, say ^{16}O-^{16}O and ^{18}O-^{16}O is related to the Ps by $\delta^{18}O = 10^3\,[(1 - P(18)/P(16)]$.

Using a linear approximation for U(r) a numerical calculation was made of P for several possible predissociations of the $B^3\Sigma_u^-$ state of molecular oxygen. In general, two factors can lead to $\delta^{17}O/\delta^{18}O$ ratios in the predissociation products which are significantly different from 1/2: 1) large isotopic vibrational energy spacings and 2) shallow potential barriers. In general, however, these two effects counteract each other; as one climbs out of the potential well U(r) becomes shallower, but the vibrational spacings become closer. Present calculations thus indicate that tunneling is not important in producing nonlinear effects.

In the classically allowed region (Fig. 1b) the predissociation probability is

$$P = \frac{2\pi}{\hbar}\left|\int \psi_f^* \, v(r)\, \psi_b \, dr\right|^2 \qquad (2)$$

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where v(r) is the perturbation which gives rise to the predissociation, ψ_f and ψ_b the wavefunctions for the repulsive and the bound states. As both wavefunctions are oscillatory their overlap, and hence P, is an oscillating function of E, the energy above the crossing point. The question is thus whether the isotopic levels for a given vibrational quantum number are separated enough to give rise to significantly different predissociation probabilities. Using as a first approximation the approach of Landau and Lifshitz [10] the quasi-classical expressions for the wavefunctions ψ_f and ψ_b were evaluated at r_c, again for the three isotope systems of O_2. For energy levels just above E_c numerical calculations predict nonlinear fractionation. There is some question, however, of the validity of the quasi-classical approximations near the classical turning points. To avoid this, therefore, we are currently considering a direct calculation of the Franck-Condon factors in order to arrive at P.

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