EXCITATION OF $^{12}\text{C}^{16}\text{O}$ BY HYDROGEN LYMAN $\alpha$ RADIATION: POTENTIAL CAUSE OF SELECTIVE $^{16}\text{O}$ FRACTIONATION IN PROTOstellAR CLOUDS. G. Arrhenius, M. J. Corrigan and R. W. Fitzgerald, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA. 92093

Chemical isotope fractionation in the interstellar cloud medium has been studied by microwave emission spectra of molecular species containing hydrogen and carbon (ref. in [1]). Fractionation is also suggested for several other light elements by the heterogeneity of their isotopic distributions (ref. in [12]). Because of the relative insensitivity of this technique in its present stage, only the larger fractionation effects are seen. More subtle variations (although still large in terms of natural terrestrial isotope effects) are found in the solid materials presumably condensed from the interstellar cloud medium and now found aggregated into meteorites. In such materials notable isotopic abundance variations are found in hydrogen, carbon, nitrogen, oxygen, neon, magnesium, aluminum and other light elements; smaller anomalies are also found in some heavier elements; for ref. see e.g. [2]. While microwave emission from interstellar matter makes it possible to observe reactant and product molecules and ions in ongoing processes, the frozen isotope distributions in meteorite condensates result from reactions that took place billions of years ago. This provides potential information on the conditions in the circumsolar region at the time of formation of our solar system, but it is more difficult in this case to reconstruct the specific processes responsible for the isotope effects observed. It is unclear in some cases whether a specific isotope "anomaly" is due to nucleosynthesis or to fractionation.

Chemical mechanisms can be invoked to explain the large fractionation effects in two-isotope systems such as hydrogen, carbon and nitrogen in the interstellar cloud medium and in meteorite components. Such mechanisms depend on the high reactivity of the space medium even at low kinetic temperature (characteristically $10-100$ K). This reactivity is due to the fact that the translationally cold reactants as a result of excitation and ionization may have high internal temperatures [3,4]. Furthermore isotopic fractionation reactions which may take place in grain-gas systems in space are likely to be enhanced by the large temperature differentials that are known to develop between effectively radiating cool solids and the hot gas or plasma in which they may be immersed [5].

Several different types of chemical mechanisms lead to selective fractionation of one isotope without affecting others [2]. Such mechanisms are highly specific, hence their effects, if seen in the space medium or in preserved space condensates would be particularly useful as indicators of the reaction conditions. Since they cannot be easily distinguished from mass dependent fractionation in diisotopic systems, the mass distributions in polyisotopic systems offer the best possibilities for recognizing such effects. The oxygen isotope distribution found in some specific refractory minerals in carbonaceous meteorites suggests an admixture to normal oxygen of a component enriched solely with $^{16}\text{O}$ [6]. Such an effect could be due to selective excitation of molecular species containing $^{16}\text{O}$, e.g. $^{12}\text{C}^{16}\text{O}$; the ensuing chemical reaction e.g. formation of oxides or silicates would then lead to enhancement of $^{16}\text{O}$ in the reaction product. Alternatively the excitation into reactive state could be isotopically non-selective as in collisional excitation but the isotope fractionation would occur in a subsequent predissociation reaction [2]. Isotopically selective reactions are known to result from excitation by ultraviolet line sources. Studies of single isotope fractionation of oxygen in $\text{CO}_2$ produced by excitation of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ by
the resonance line of iodine at 2062.4 Å were pioneered by [7]. Enrichments with 16O and 13C up to factors of 6 and 3 resp. were found. More recently, selective excitation of these molecules by the 1235.8 Å line of Kr was demonstrated by [8] who also reported enhancement of 18O in the product CO2. In these experiments the exciting radiation line nearly coincides with one single rotational line of an electronic vibrational band in the absorption spectrum of the reactant molecule. The resulting excited molecule then may undergo collisional reaction. The probability for such processes to be of importance in nature would at first thought appear to be low. The resonance lines of I and Kr are obviously unimportant in interstellar space. The selectivity of excitation is furthermore in these cases decreased when neighboring rotational lines of different isotopic species are excited by the broader emission lines which are characteristic of astrophysical sources.

A comparison of the absorption spectra of common interstellar (and atmospheric) isotopic molecules with prominent stellar far UV emission lines reveals situations where isotopically selective excitation may become cosmochemically significant, e.g. in fractionating 16O as observed by [6]. An interaction found to be potentially important in this context is the excitation of carbon monoxide by the Lyman α line of hydrogen at 1215.7 Å, the single most intense line source in space. In this part of the spectrum, the bands of the various isotopic species of CO are well resolved from each other (Fig. 1), precluding the need for sharply monoenergetic sources to achieve selective isotopic excitation. Furthermore, the line widths of H Lyα, characteristically observed in space, are sufficiently large (> 2 Å) to overlap 27 of the low lying rotational states of the A-X (14-0) transition. These factors would contribute to efficient coupling between H Lyα and the molecule 12C16O in the ground state, exciting it to a reactive electronic state, less than 1 ev below the dissociation limit, while leaving 17O and 18O unaffected. In the experiments of [7] the prevalent fractionation reactions were shown to be: 13C16O* + 12C16O → 12C16O2 + 13C and 12C18O* + 12C16O → 12C16,18O2 + 12C followed by reaction of the carbon atom with carbon monoxide to form CO2. In contrast the only excited reactant expected to be of importance in the case of H Lyα excitation would be 12C18O, and the prevalent reaction would be 12C18O* + 12C16O2 → 12C16O2 + 12C with enrichment of 16O in the product CO2. Carbon dioxide and its dissociation products would under conditions discussed below transfer oxygen particularly to such metal ions and atoms in the cloud medium, whose oxides have large negative free energies of formation ("refractory" oxides).

The rate at which 12C16O2 forms by the H Lyα excited reaction is determined by the collision cross section σ for reaction to occur and the

Fig. 1 High resolution absorption spectrum of a section of the 4th positive band system of carbon monoxide at two different pressures (at room temperature). The positions and wavelengths of the A-X (14-0) and (13-0) band heads of isotopic CO species, and of the line centers of H Lyman α (from the source lamp) and Kr (not present) are indicated. Modified from [9].
collision rate CO-CO* which depends on the kinetic temperature T(kin), the number density n(CO) of neutral CO and of CO*. The H Lα photon flux density U (La) determines n(CO*), so that dC02/dt = a (8kt(kin)/nm)1/2 n(CO) U (La) where m is the reduced mass of the collision pair.

The 16O selective mechanism discussed above would assume importance in astrophysical situations where an interstellar or protostellar cloud medium is compressed while being irradiated by a high flux of H Lα radiation. Such conditions are observed around hot stars and supernovae, where pressure increases of the order of 10^5 are postulated in shock fronts [10] and H Lα is considered the dominant radiation. Transfer of 16O from selectively produced 12C16O2 to refractory condensates, now in meteorites, where excess 16O is observed, would imply the growth of solids in these protostellar cloud regions as a result of compression and of cooling by radiation from molecules and grains. At compression of the medium compounds with high bond strengths would be expected to form first, i.e. refractory metals and oxides [11].

Experimental modeling of the isotope selection reaction discussed is now being attempted. Only relatively low power is achievable with present laboratory H Lα sources (≤ 10^15 photons/cm^2 sec) compared to one to three orders of magnitude higher in VUV line sources such as I2 and Kr. This makes it necessary to extend the experiments over periods of many hours to several days in order to discern a selective 16O fractionation in product CO2 where the effect is also diluted by the isotopically normal CO molecules that form collision partners with the selectively excited 12C16O. The apparatus constructed to perform these experiments is shown schematically in Fig. 2.


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