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Cosmochemical Evolution

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Abstract: The use of chemical tracers as timing devices to discern historical trends in the evolution of the Universe, galaxies, interstellar phenomena, and other astrophysical systems, is likely to become a dominant aim of future infrared and submillimeter astronomical missions. The high sensitivities, and spatial and spectral resolving powers that will become available in the next few years will make such studies possible. Chemistry, rather than physics, will then most likely become our main tracer of the prehistory of a particular region and the influences that have shaped it.

1. INTRODUCTION

Since its inception a few decades ago, infrared astronomical spectroscopy has been used primarily to derive the current physical and chemical properties of an observed region. A star's or nebulosity's current temperature, density, pressure, chemical composition, state of ionization and line-of-sight velocity structure has often been revealed with startling clarity. Now, however, we stand on the threshold of an era in which such data will be increasingly interpreted with a view to determining not simply the current state of an observed domain but also its past history. Here, I hope to show a number of different types of historical studies that are beginning to emerge. Several have already been explored through the help of the Infrared Space Observatory, ISO. Others have been investigated by optical ground-based techniques, where a head start has always existed in spectroscopic techniques and sensitivity. However, with the vast display of chemical properties that infrared techniques can reveal, near-, mid-, and far-infrared astronomy is likely to forge ahead and ultimately take the lead.

2. ORTHO-PARA CONVERSION AS A TIMING DEVICE

Nuclear spins determine whether a hydrogen molecule is in an ortho- or para- state. When the nuclear spins are antiparallel, H_2 is in a para state, the nuclear spin factor $I = 0$, and the rotational quantum number J is restricted to even values. When the nuclear spins are parallel the molecule is in an ortho state, $I = 1$, and J can only assume odd values. The statistical weight for either configuration is $g = (2I + 1)(2J + 1)$, and radiative transitions between states

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can only proceed through changes in the quadrupole moment, for which $\Delta J = 2$. This means that under a radiative transition, an ortho molecule always retains its ortho configuration, and a para molecule remains in the para state.

If hydrogen molecules formed randomly the probability for forming molecules in the ortho state would be three times higher than forming them in the para state, since the ratio of the value $(2I + 1)$ for these respective states is 3:1. Purely radiative excitation and de-excitation would then retain this ratio for all time. In 1994, Lacy et al. however, sought to observed the $v = 0 \rightarrow 1$ rovibrational transitions of H_2 in absorption against the star IRS 2 in NGC 2024. The S(0) line at 2.223 μm was detected, while the S(1) line at 2.122 μm was not. On this basis Lacy et al. (1994) derived a 2 σ upper limit on the ratio of hydrogen molecules in the ground vibrational state: $n(\mathrm{J} = 1)/n(\mathrm{J} = 0) < 0.8$. This ortho-para ratio, while well below the value of 3:1, was consistent with a gas temperature in the range of $T_{\mathrm{g}} = 35$ - 54 K derived from observations of CO absorption spectra along the same line of sight. The $J = 1$ level lies $T_{(J=1)} = 170$ K above the ground state, corresponding to an expected ortho-para ratio of $(2I + 1)(2J + 1)e^{-T_{(J=1)}/T_{\mathrm{g}}} \sim 9e^{-4} \sim 0.2$, consistent with their observations.

The conclusions of Lacy et al. were based on the inferences of a non-detection of the $v = 0 \rightarrow 1$, S(1) transition. A set of more positive detections with the ISO Short Wavelength Spectrometer, SWS, obtained by Neufeld, Melnick, & Harwit (1998) toward the young stellar outflow region HH 54 E + K showed an alternation of intensities in the S(1), S(2), S(3), S(4) and S(5) lines of the hydrogen vibrational ground state, giving an ortho-para ratio of 1.2 ± 0.4. This ratio corresponds to an equilibrium temperature below 100 K.

The relative line strengths in this source provide an estimate of the kinetic gas temperature. For HH 54 E + K this temperature was $\sim$ 650 K. The equilibrium ortho-para ratio at this temperature would be close to 3. The explanation for these apparently discrepant observations is that the gas in the outflow has not been warm sufficiently long for appreciable ortho-to-para conversion, and that the original gas injected into the outflow was very cold.

Timmermann (1998) has estimated the ortho-para conversion rates for molecular hydrogen which, in interstellar space, are primarily due to collisions with H^+, H_3^+, atomic hydrogen, H, or dust grains. In the outflow from young low-mass stars the densities of H^+ and H_3^+ are generally low, and collisions between H_2 and H may be expected to provide the dominant means for ortho-para conversion through 'reactive' collisions – collisions in which a hydrogen atom displaces one of the H_2 atoms of opposite nuclear spin. The rate coefficient for this reaction at 650 K is $\kappa \sim 1.0 \times 10^{-13}\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$. At the estimated gas density for the observed region, $n(H_2) \geq 10^5\,\mathrm{cm}^{-3}$, the abundance of H atoms can be estimated from the knowledge that all of the oxygen not trapped in CO should be converted into H_2O at these high temperatures. In this process, two hydrogen atoms are released for each oxygen molecule through abstraction reactions from H_2. Assuming an initial oxygen abundance $n(\mathrm{O})/n(H_2) \sim 3.5 \times 10^{-4}$ (Cardelli et al. 1996), this gives a conversion time

$$\tau_{conv} = [2\kappa n(O)]^{-1} \sim 5{,}000/n(\mathrm{H_2}) \text{ years} \tag{1}$$

The history of the observed region appears to be this: The young star initially is surrounded by gas that appears to have been at a temperature well below 100 K for many tens of thousands of years, to permit most of the ortho hydrogen to be converted into the para state. A few thousand years ago, this gas was precipitously funneled into a high-velocity outflow and shock-heated to its current observed temperature $\sim$ 650 K. As the gas heated, oxygen became converted into water with the release of two hydrogen atoms for every water molecule formed.

These atoms then reactively collided with hydrogen molecules to begin a gradual para-to-ortho conversion that will eventually produce an ortho-para ratio of 3 some thousands of years from now.

Quite recently, Puxley, Howat, & Mountain (2000) have reported another extremely low ortho-para ratio for H_2 associated with the giant extragalactic HII complex NGC 5461. By observing the rovibrational spectrum of the galaxy in the 1.9 to 2.5 μm region, with the CGS4 spectrometer at the UK Infrared Telescope, they were able to measure the fluorescent H_2 lines in gas excited by ultraviolet radiation from young hot stars. The gas exhibits an ortho-to-para ratio of 1.15 ± 0.11 indicating the irradiation of material that had long been kept under ultracold conditions deep inside star-forming clouds. In deriving this low value, the authors properly corrected for an effect first noted by Sternberg & Neufeld (1999), namely that the absorbing gas has greater optical depth for ultraviolet photons exciting ortho levels than para levels. This is due to the higher statistical weight $(2I + 1)$ of the excited ortho states.

The main point of observations such as these is that they permit deduction of:

i) the temperature of a previous state of the gas, whose memory has not yet been erased, and

ii) an estimate of the time that has elapsed since that previous state was disrupted.

3. ORTHO AND PARA WATER

During 1996 and before its perihelion passage, comet Hale-Bopp was observed at several epochs, during the closest of which the comet was 2.8 AU from the Sun. The comet was observed again in late 1997 and early 1998 after passage, when it was between 3.7 and 4.9 AU from the Sun (Crovisier et al. 1997, 1999). Observations with the ISO SWS in the ν_3 water vapor bands at 2.7 μm and the ν_2 bands at 6 μm region, and with the ISO Long Wavelength Spectrometer, LWS, in the pure rotational lines $2_{12} - 1_{01}$ and $3_{03} - 2_{12}$ near 180 μm, exhibited an ortho-para ratio of 2.45 ± 0.10 corresponding to an equilibrium spin temperature of 25 K. At a distance of 2.8 AU from the Sun, a gas temperature derived from the rotational emission line strengths was estimated at $T_{\rm rot} = 28$ K. This temperature is in agreement with cooling of the comet's atmosphere during expansion. The kinetic temperature at sublimation must have been appreciably higher to produce the observed 10 tons of water per second, most likely in the range of 150 K at the comet's surface for that distance from the Sun. During the later epoch, when the comet was at a distance of 3.9 AU from the Sun, the water vapor rotational temperature was observed to be substantially lower, $T_{\rm rot} \leq 10$ K.

From a historical point of view, the most interesting aspect of these observations is the spin temperature of 25 K, which corresponds to the equilibrium temperature of a body at a mean distance from the Sun of order 100 AU. The estimated eccentricity of Hale-Bopp 0.996 and its perihelion distance 0.91 AU indicate a semi-major axis of 228 AU, an aphelion distance of ~ 450 AU and a period ~ 3450 yrs much of which would be spent near aphelion, where the equilibrium temperature would be more nearly 17 K in the interior of a rotating body. The comet spent only some 250 yrs between 150 and 50 AU as it fell toward the Sun and only about 50 yrs since then. Apparently surface layers to a depth of many meters were able to heat up to a temperature of 25 K during this short period. And para-ortho conversion apparently was also able to take place on a time scale as short as 100 yrs at these temperatures. This rate can sensitively depend on the presence of paramagnetic substances, which are known to catalytically accelerate the process (Herzberg 1950). A detailed investigation might yield a measure of the thermal conductivity of the comet's surface layers as well as the para-to-ortho conversion rate of the material.

4. MOLECULAR OXYGEN IN GIANT MOLECULAR CLOUDS

Oxygen is one of the more abundant chemical elements in the Universe. Anders & Grevesse (1989) estimate its Solar System abundance relative to hydrogen at $N(\mathrm{O})/N(\mathrm{H}) = 1.04 \times 10^{-3}$. In giant molecular cloud cores, typical number densities for molecular hydrogen are $\mathrm{n(H_2)} \geq 10^{4.5}\,\mathrm{cm^{-3}}$ and temperatures lie in the range of $25\,\mathrm{K} \leq T \leq 40\,\mathrm{K}$. In this temperature range some of the lowest rotational energy states of molecular oxygen can be excited. For molecular oxygen the nuclear spin is always $I = 0$. The total electronic spin $S = 1$ of the molecule interacts with the total angular momentum quantum number J to split the rotational level into a triplet of states, $J = N,\ N \pm 1$. A transition between states $N_J = 3_3 \rightarrow 1_2$ at 487.2492 GHz, whose upper level is 26.4 K above the ground state, and whose spontaneous decay rate is $8.5 \times 10^{-9}\,\mathrm{s^{-1}}$, has long been expected. However, because radiation in this transition would be strongly absorbed in Earth's atmosphere, a search for this line had to await the launch of sensitive spectroscopic equipment into space.

In the expectation of detecting this spectral line, the Submillimeter Wave Astronomy Satellite, SWAS, has been carrying out deep observations of giant molecular clouds, in some cases concentrating on a single source for up to 200 hours. The SWAS Full-Width-Half-Maximum beam is 3.6 arcmin $\times$5.0 arcmin at 487 GHz. The low transition probability of the O_2 line makes it optically thin even in dense clouds, and the integrated intensity observed is readily related to the total column density of a uniform source filling the field of view. Since molecular clouds cannot be expected to be uniform, a strategy of comparing the O_2 flux to the observed $C^{18}O$ emission over the same beam was adopted. The $J = 1 \rightarrow 0$, $C^{18}O$ transition, which is also expected to be optically thin, has been mapped for many clouds and its $J = 1$ level is expected to be thermalized at densities $\mathrm{n(H_2)} \geq 10^4\,\mathrm{cm^{-3}}$. For a number of local clouds, (Frerking, Langer, & Wilson 1982) adopted a ratio $N(\mathrm{C^{18}O_2})/N(\mathrm{H_2}) = 1.7 \times 10^{-7}$. With respect to four of these, NGC2264, ρ Oph A, S140, and Ceph A, the SWAS data now imply a column density ratio integrated over the SWAS beam, of $N(\mathrm{O_2})/N(\mathrm{C^{18}O}) \sim 1.5$ to 4.6 and a ratio $N(\mathrm{O_2})/N(\mathrm{H_2}) = 3$ to 8×10^{-7}. For those sources within a few kiloparsec from the Sun for which SWAS obtained the deepest integrations, Goldsmith et al. (2000) report a 3σ upper limit of $N(\mathrm{O_2})/N(\mathrm{H_2}) = 1.5 \pm 2.1 \times 10^{-7}$. This implies that at most one part in $\sim 10^4$ of the oxygen is in gaseous molecular form.

The formation rate of molecular oxygen deep in the cores of giant molecular clouds, where matter is well shielded from dissociating ultraviolet radiation, is expected to lead to buildup times of the order of 10^6 yrs. The steady-state fractional abundance $N(\mathrm{O_2})/N(\mathrm{H_2})$ has been expected to be in the range of 5 to 10×10^6, for molecular hydrogen densities between 10^3 and $10^4\,\mathrm{cm^{-3}}$ (Bergin, Langer, & Goldsmith 1995). The theories, therefore, have generally predicted abundances a factor of 100 greater than those observed.

The conclusion reached from the SWAS observations is that material in the cores of dark molecular clouds must be either frozen out on dust grains in the form of water ice, or else circulated into unshielded regions on time scales $\leq 10^6$ yrs. Circulation can take place through turbulent mixing and cycling, or through chemical diffusion driven by concentration gradients. Both the deposition on grains and chemical diffusion have the advantage of producing significant abundances of atomic carbon, while depleting gas phase H_2O, both of which agree with other observations, including data obtained by SWAS. For present purposes, however, the significant aspect of these observations is that they provide a history of the dynamical or chemical evolution of these interstellar clouds on time scales of order 10^6 yrs.

5. LOCAL NUCLEOSYNTHETIC HISTORIES

Quite apart from systematic variations in abundance ratios across galactic dimensions, the study of local deviations are also important. In their study of the shocked region in the cold neutral domain of the Orion Nebula, (Harwit et al. 1998) derived a gas phase oxygen abundance $n(\mathrm{O})/n(\mathrm{H}) \sim 4 \times 10^{-4}$, which is low by a factor of ~ 2.5 compared to the Solar System abundances of Anders & Grevesse (1989), $n(\mathrm{O})/n(\mathrm{H}) \sim 1.04 \times 10^{-3}$. This is particularly significant since the amount of oxygen tied up in solid grains is by now reasonably well-established for the nebula and does not suffice to make up the difference. The data for the Orion Nebula are also consistent with abundances Cardelli et al. (1996) had previously established for the gas phase in diffuse interstellar clouds within 600 pc from the Sun. Here the abundance of oxygen relative to hydrogen appears to be $n(\mathrm{O})/n(\mathrm{H}) \sim 3.2 \times 10^{-4}$, roughly a factor of 3 below Solar System abundances. Cardelli et al. also find an interstellar abundance for carbon $n(\mathrm{C})/n(\mathrm{H}) \sim 1.4 \times 10^{-4}$ compared to the Solar System value for given by Anders and Grevesse, $n(\mathrm{C})/n(\mathrm{H}) = 4.4 \times 10^{-4}$, again low by a factor of ~ 3. Thus, while the ratio of carbon to oxygen remains fairly constant, one finds substantial differences in the overall abundances of heavy elements in regions separated by no more than a few hundred parsec in our part of the Galaxy. These apparently reflect a complex local nucleosynthetic history that awaits more detailed analysis: What processes determine the chemical makeup of an individual region? What are the time scales on which such deviations are produced? How quickly will they be diffusively erased? All this needs to be better understood.

6. WATER VAPOR IN SHOCKED AND QUIESCENT REGIONS OF ORION

Water vapor in the shocked domains of Orion was studied by Harwit et al. (1998), who found an H_2O/H_2 ratio of $\sim 5 \times 10^{-4}$, vindicating theoretical predictions that H_2O should be copiously produced when temperatures exceed 300 K (Bergin et al. 1998). SWAS observations in the more quiescent regions of Orion, however, have shown abundances of H_2O to be orders of magnitude lower, with H_2O/H_2 ratios ranging from 1 to 8×10^{-8}, with typical values of $\sim 3 \times 10^{-8}$ (Snell et al. 2000).The standard production rates of H_2O and O_2 in well-shielded gas at ~ 30 K, at densities $n(H_2) \sim 10^5\,\mathrm{cm}^{-3}$ and with carbon-to-oxygen ratios $n(\mathrm{C})/n(\mathrm{O}) \sim 0.4$ are shown in Figure 1. They indicate water vapor production rising to a maximum reached on a time scale of 10^4 yrs (Bergin et al. 2000), with a leveling off, thereafter. Destruction of neutral carbon with the formation of CO takes place almost simultaneously, so that the ratio of C/H_2O may provide another useful clock for timing processes in dark clouds on time scales between 10^3 and 10^5 yrs. Destruction of C^+ in such clouds takes place over a period of 30 to 10^3 yrs, during which time the abundance of atomic oxygen remains almost constant. The C^+/O ratio can then provide a timer for events of this duration. For shorter periods still, from 1 to 10 yrs, the C/C^+ ratio could yield timing information. The point is that – once they are placed on a firm theoretical footing – chemical abundance ratios in dark clouds could well be used to judge their age and give an indication of their past histories.

7. DISCUSSION

The studies noted above are only an indication of directions that infrared astronomical spectroscopy may be expected to take with the introduction of increasingly powerful telescopes operating in this spectral range. The study of primeval galaxies and their chemical evolution will be one immensely important subject undoubtedly to be addressed as larger telescopes provide access to increasingly distant regions. We need to find out how the earliest galaxies managed to cool themselves in the apparent absence of heavy elements. We also need to better understand how quickly the first generation of massive stars ejected heavy elements into their surroundings to form dust and facilitate cooling that led to the formation of a further generation of stars. For these early times, red shifts will provide historical time markers. Investigations will most probably proceed statistically by relating different stages of evolution to the red shifts at which they are observed.

For the investigation of more recent, more local histories, the rates of ortho-para conversion in H_2 or H_2O, the formation and destruction of molecular oxygen, or the production or destruction of different chemical species, will provide particularly useful time markers. The use of such markers, however, will critically depend on our ability to obtain reliable chemical reaction rates, and on a deeper understanding of the interplay of chemical processes with astrophysical dynamics. If successful, such an approach will lead to new insights on cosmochemical evolution.

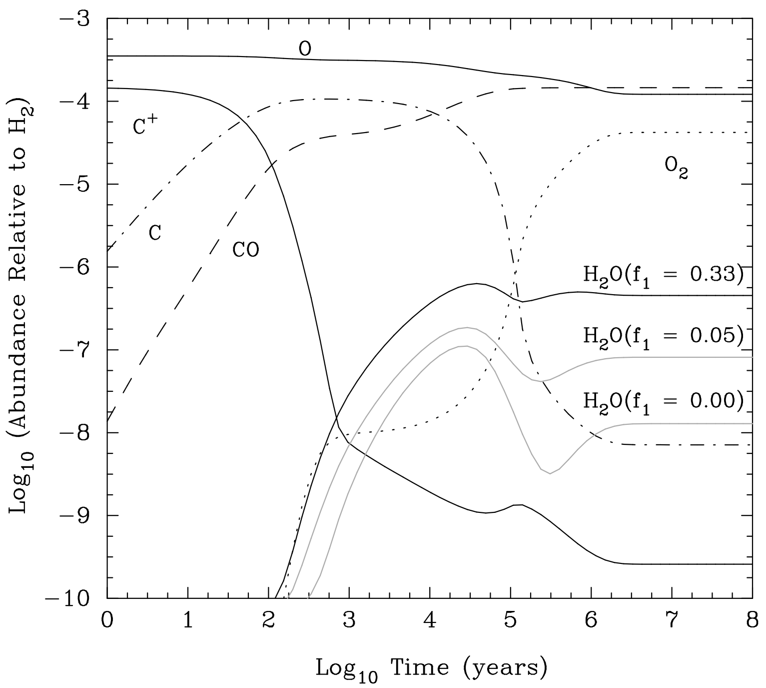

Fig. 1: Time evolution of chemical abundances relative to H_2 for a solar C/O ratio of 0.4 (Bergin et al. 2000). The evolution of H_2O abundance is shown for three different probabilities $f = 0.00$, 0.05 and 0.3, for the reaction of H_3O^+ with electrons to yield H_2O + H. The conditions assumed are $n(H_2) = 10^5\,\mathrm{cm}^{-3}$, a gas temperature of 30 K, and a shielding factor from the ambient radiation field corresponding to $A_V = 20$ mag.

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