CO IN THE SOLAR SYSTEM

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1. Introduction

The CO molecule is the most common gaseous species found in the Solar system. In addition to the Earth's atmosphere, CO is found in Mars and Venus; it has been detected in three giant planets, Jupiter, Saturn, and Neptune, and in Titan's atmosphere; CO ices were detected on the surface of Triton and Pluto; CO has been detected, in variable abundances, in most of the comets. The presence of CO in all these objects is remarkable, taking into account the wide diversity of their global atmospheric compositions; in all cases, CO appears to be a minor constituent relative to the dominant atmospheric compound (Table 1). Its abundance, relative to CH_4, is an indicator of the conditions and processes which prevailed at the time of the formation of these objects from the surrounding primordial nebula.

2. The Formation of Solar-system Objects and the Abundance of CO

2.1. THE CONDENSATION SEQUENCE

How do we understand the formation of planets? The currently proposed scenario, based on the condensation sequence of the various species is the following. It is generally accepted that all Solar-system objects were formed after the collapse of the primordial solar nebula into a disk. This nebula, with all its elements in their cosmic abundances, cooled down rapidly, with decreasing temperatures from the inner part to the outer edge of the disk. At the end of this cooling phase, expected temperatures were in the range of a few hundreds K within the first 3 AU (i.e., where the terrestrial planets are found today), but were significantly lower (about 100K or less) beyond 5 AU, in the region where giant planets are now found. Within 3 AU, the species which were able to condense were only the heavy elements, in particular metals and silicates, with, under some conditions, water and carbon dioxide. In contrast, beyond 5 AU, most of the molecules had to be condensed in ices: first H_2O and CO_2, then NH_3, CH_4, H_2S, etc.

All planetary bodies are believed to have formed from the accretion of solid particles, the "planetesimals". These planetesimals were made from the species which were present in condensed form. Below 3 AU, the cores which would lead to the formation of the terrestrial planets could only use metals and silicates. In contrast, beyond 5 AU, they could make use of all the ices which, according to the cosmic abundances, constitute most of the mass of the nebula, if we exclude hydrogen and helium. Theoretical models (Mizuno 1980) show that, in this case, the nuclei formed in this process are expected to be about 10 times more massive than the ones formed below 3 AU (which have about 1 terrestrial mass). Once nuclei of 10 terrestrial masses are built, they become able to bind gravitationally the surrounding nebula, mostly composed of hydrogen and helium. This process is likely to have led to the formation of the giant planets. In contrast, the terrestrial planets were not able to retain the surrounding nebula; their mass is basically the mass of their solid body, and their atmospheres were probably later generated, through outgassing and meteoritic impacts. This simple scenario shows that the condensation sequence gives a natural explanation for the two classes of planets which we observe, the terrestrial ones and the giants; we may reasonably expect to find the same basic classification in any other stellar system.

2.2. THE CO/CH_4 RATIO

In order to interpret the relative abundance of CO in the various Solar-system objects, we need to understand in which form the carbon was present in the primordial solar nebula. This question refers to an earlier step of the Solar system formation, before the cooling of the nebula and the condensation sequence.

Under the conditions of thermochemical equilibrium, the forms in which carbon and nitrogen appear are indicated respectively by the two following reactions:

$$CH_4 + H_2O \quad \leftrightarrow \quad CO + 3H_2 \tag{1}$$

$$2NH_3 \quad \leftrightarrow \quad N_2 + 3H_2 \tag{2}$$

which evolve toward the right-hand side at high temperature, and toward the left-hand side at low temperature. CO, once formed, reacts again with H_2O to form CO_2:

$$CO + H_2O \quad \leftrightarrow \quad CO_2 + H_2 \tag{3}$$

In addition, the dynamical factor has to be included in the process (Prinn & Fegley 1988). The solar nebula is not static, but cools rapidly, at a rate which is fast enough for the CO formed at high temperature, at the beginning of the cooling phase, to be quenched. As a result, significant abundances of CO and N_2 can be found even at low temperature, at the end of the cooling process. Thermochemical calculations show that an object formed within the solar nebula is expected to have its carbon basically in the form of CO. In contrast, for an object formed within a "Jovian" subnebula (where the temperature is lower), CH_4 is dominant. In a similar way, N_2 is found to be dominant for objects formed within the solar nebula, while NH_3 should be dominant for objects formed in a "Jovian" sub-nebula.

At first order, reactions (1) to (3) seem to account, at least qualitatively, for the observed compositions of Solar-system objects (Table 1). Indeed, at high temperatures CO, CO_2, and N_2 are formed, as observed in the atmospheres of Venus and Mars; H_2 escapes, as it is too light to be gravitationally retained by the terrestrial planets. CH_4 and NH_3 are formed at low temperatures, as observed in the atmospheres of Jupiter and Saturn; the case of Neptune is more puzzling, as will be discussed below. The CO abundance in comets is also compatible with this scenario, but the apparent depletion of cometary N_2 remains to be explained. The case of the outer satellites is also puzzling. In the case of Titan, both N_2 and CH_4 are present. It has been suggested that both CH_4 and NH_3 might have been formed first in the vicinity of the Saturnian sub-nebula; in a subsequent evolution, NH_3 would have been later transformed into N_2 (Atreya 1986). For Triton and Pluto, precise information is still lacking. In conclusion, the relative abundance of CO in the various Solar-system objects is understood at first order, but several questions are still unsolved, especially for the objects of the outer Solar system. In particular, an accurate measurement of the CO/CH_4 ratio in Triton, Pluto, and in comets will provide an important constraint upon their formation scenarios.

3. Heterodyne Spectroscopy Measurements of CO in the Solar System

In the case of a planetary atmosphere where the molecular lines are pressure-broadened, the typical width of a line (FWHM) is about 3 GHz per atmosphere. As the typical bandwidth of a heterodyne receiver is about 0.5 GHz, such lines are too broad to be observed by this technique in the tropospheres of the planets. They can only be observed at pressure levels in the range 0.01-10 mb.

3.1. VENUS AND MARS

The atmospheres of Venus and Mars have similar compositions, but completely different structures. The atmosphere of Venus is extremely dense and hot (surface pressure of 93 bar, surface temperature of 730 K), while the Martian atmosphere is tenuous and cold (surface pressure of 7 mb, average surface temperature of 230 K). As a result, only the Venus mesosphere can be probed ($z = 70 - 110$km), while the Martian atmosphere can be probed down to its surface. As the temperature decreases with increasing altitude, the lines are usually observed in absorption.

In the case of both planets, the CO (1–0) line was monitored in order to retrieve the vertical distribution of CO and the thermal profile in the probed region. In the case of Venus, evidence was found for diurnal variations in the CO mesospheric vertical distribution (Clancy and Muhleman 1985). In the case of Mars, the CO (l–0) and (2–1) transitions were monitored, leading to a temporal monitoring of the Martian thermal profile (Clancy et al. 1990). A remarkable result has been the study of the dynamics in the upper atmospheres of Mars and Venus from the use of CO millimeter lines. Recent observations of the CO (l–0) and (2–1) transitions over the disks of Venus and Mars respectively have led to the determination of wind speeds, through an accurate measurement of the line Doppler shifts (Lellouch et al. 1991; 1994); the precision is about 10–20 m/s. One should mention that there is no other method allowing study of the dynamics of the upper atmospheres of Venus and Mars.

3.2. THE GIANT PLANETS

In contrast with the atmospheres of Venus and Mars, the atmospheres of the giant planets are characterized by a temperature inversion, occuring at the tropopause level (pressure level in the range 100–300 mb). As mentioned above, only stratospheric features can be detected by heterodyne spectroscopy; they are expected to appear in emission.

3.2.1. *CO and HCN in Neptune*

A recent exciting result has been the unexpected detection of CO and HCN in the stratosphere of Neptune (Marten et al. 1991; 1993; Rosenqvist et al. l992). CO was found to be constant with altitude, with a mixing ratio of about 10^{-6}; for HCN, which has to condense at the tropopause level, a mixing ratio of about 10^{-9} was derived in the stratosphere. Another surprise was the lack of detection of CO and HCN in the stratospheres of the three other planets. CO, however, had been previously detected, from infrared observations, in the deep tropospheres of Jupiter and Saturn, with a mixing ratio of about 10^{-9}. The detection of CO and HCN in Neptune raised two major questions: (1) why are these species so abundant in Neptune? (2) why are Uranus and Neptune different?

A CO mixing ratio close to 10^{-9} was found in the case of Jupiter and Saturn, in good agreement with the photochemical models; an external CO origin from meteoritic oxygen was also suggested (Atreya 1986), but more recent data seem to favor the tropospheric origin of CO. In this case, CO, like other disequilibrium species (PH_3, GeH_4...), is brought up by a strong vertical mixing from the deep levels where it is stable (T = 1100 K) into the upper troposphere where it becomes observable. However, there is a discrepancy by a factor of about 1000, presently unexplained, between the expected and the observed value of the CO mixing ratio in Neptune.

The presence of HCN, probably formed from a reaction between CH_3 and nitrogen atoms, requires a source for these atoms. Two origins are possible, either due to an escape of N atoms from Triton, or due to the presence of N_2 in the Neptune troposphere. It has been suggested that nitrogen, within the Neptune troposphere, could be in the form of N_2 rather than NH_3; a N_2 mixing ratio of 0.1–1% could also explain the HCN measurement (Gautier et al. 1995).

Regarding the difference between Uranus and Neptune, there is no clear explanation either. However, it has been noticed that this difference could be connected to the absence of internal energy from Uranus, while Neptune, has a strong internal source. In the case of Uranus, convection could be inhibited, leading to the absence of upward transport from the interior (Gautier et al. 1995).

3.2.2. *CO in Jupiter after the SL9 Collision*

With a mixing ratio of about 10^{-9}, CO is not abundant enough to be detectable in the Jupiter stratosphere by millimeter heterodyne spectroscopy. However, this observation became feasible just after the collision of comet Shoemaker-Levy 9 with Jupiter, in July 1994, due to the large amount of CO formed in the Jovian stratosphere after the explosion (Lellouch et al. 1995). The CO millimeter lines, as well as other newly observed transitions (CS, OCS, HCN), became maximum after the brightest impact. These started to decrease a few days later and turned into absorption lines, which remained detectable for more than six months after the impact, yielding information about the evolution of the thermal profile. These observations are the only ones which provided information on the long-term response of the Jovian stratosphere.

3.3. THE OUTER SATELLITES AND PLUTO

3.3.1. *Titan*

With its nitrogen-dominated composition, its surface pressure of 1.5 bar, and its rich and complex chemistry, Titan's atmosphere might be favorable for the development of prebiotic chemistry. Its strong temperature inversion and the presence of many hydrocarbons make Titan a very good candidate for heterodyne spectroscopy observations. Indeed, several molecules have been detected from this technique: CO, HCN, HC_3N and CH_3CN.

CO was first detected in Titan's troposphere, from near-infrared spectroscopy, with a mixing ratio of $6\ 10^{-5}$. At the same time, CO_2 was detected in Titan's stratosphere with a mixing ratio of about 10^{-8}, from the Voyager-IRIS infrared spectra. Both detections were unexpected, as CH_4 was known to be the most abundant species after nitrogen and, possibly, argon.

The first stratospheric detection of CO was performed in the millimeter range at OVRO by Muhleman et al. (1984), who derived a CO mixing ratio of $6\ 10^{-5}$. This implied a constant CO mixing ratio throughout the atmosphere, which was expected in view of the long lifetime of CO. However, subsequent IRAM measurements led to a much smaller mixing ratio ($2\ 10^{-6}$) for the stratospheric CO. Recent measurements by Gurwell & Muhleman (1995) seem to solve the controversy in favor of Muhleman et al.'s first result. Using the OVRO interferometer and double-side band measurements, the authors were able to obtain an absolute calibration of the two sidebands, something which is not possible with single-dish observations. Gurwell & Muhleman (1995) derived a CO mixing ratio of 5 ± 10^{-5}, which implies a uniform vertical distribution of CO in Titan's atmosphere.

What is the origin of CO and CO_2 in Titan? The current interpretation is that there is an external source of H_2O coming from meteoritic impacts. H_2O reacts with CH_4 to form CO, and CO in turn reacts with H_2O to form CO_2. Photochemical models predict that a constant H_2O input corresponding to a mixing ratio of 10^{-9} in Titan's stratosphere would be able to account for the observed abundance of CO and CO_2. H_2O has not been observed in Titan yet, but this detection should be feasible with the spectrometers of the ISO mission.

3.3.2. *Io, Triton and Pluto*

Because of its proximity to Jupiter, Io is subject to strong tidal forces which lead to an intense volcanic activity. SO_2, first detected by Voyager-IRIS over a volcanic plume, was later detected in the millimeter range as the component of a stable atmosphere with a surface pressure in the range of 3 to 40 nanobars. Other gases have been searched for without success, including CO. The present upper limit, from the CO(1–0) line, is 5 nbar (Lellouch et al. 1992).

Triton and Pluto both have nitrogen-rich atmospheres, with surface pressures of 14 microbar and 3 microbar respectively. Ices of N_2, CO and CH_4 have been detected on Triton (Cruikshank et al. 1993) and Pluto (Owen et al. 1983), but the relative gaseous abundances of CO and CH_4 are very uncertain (Table l).

3.4. COMETS

As first suggested by Whipple (1950) and confirmed with observations of Comet Halley, the composition of comets is dominated by H_2O. Although a minor component, CO plays a key role because, due to its high volatility, it is the first molecule to be outgassed from the nucleus at high heliocentric distance.

CO has been detected on many comets, with variable abundances. Observations were performed in the UV and infrared, and recently in the submillimeter range, with the detection of the (3–2) CO transition in a distant comet, P/Schwassman-Wachmann 1 (Senay & Dewitt 1994). These last measurements allowed to derive the velocity of the CO jet (1 km/s) outgassed from the nucleus.

4. Perspectives and Future Plans

CO observations have been of great value for Solar-system studies: they provide clues for constraining formation and evolution models; they are tracers of the dynamics of the terrestrial planets; they are indicators of activity in distant comets. Future progress can be expected in several directions.

First, the extended use of interferometry will provide better spatial resolution for the wind measurements on the disks of Venus and Mars. As discussed above, interferometry is also precious as it provides an absolute calibration of the emission lines of Neptune and Titan. Second, the extension of the spectral range toward higher frequencies will allow the use of stronger CO transitions, leading to improved determination of the CO vertical distributions, and providing, in the case of Io, an improved upper limit. Third, it should be mentioned that the use of millimeter/submillimeter spectrometers with a resolving power of 10^3–10^4, like Fabry-Perot or Fourier-Transform spectrometers, will be very powerful for detecting tropospheric lines, in particular CO in Neptune.

Triton and Pluto appear too weak for CO to be detectable by heterodyne spectroscopy; the detection of gaseous CO, however, might be feasible in the near-infrared, using cryogenically cooled high-resolution spectrometers.

Finally, a millimeter instrument (MIRO) has been submitted to ESA as part of the instrumentation of the ROSETTA mission, devoted to the long-term exploration of a comet. The spacecraft is expected to follow a comet (P/Wirtanen) on its way to perihelion, during the first decade of the next century. The millimeter instrument includes two channels, around 230 GHz and 557 GHz, for the study of several molecules, including two CO transitions. If selected, it will be an ideal instrument for detecting the early activity of the comet, measuring relative abundances of the gaseous species and studying the thermodynamics of the coma.

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TABLE 1. Carbon and Nitrogen Atmospheric Composition of Solar-system Objects

Object	Major Constituent	Minor Constituents (Mixing Ratio) Carbon	Nitrogen	Other
Venus	CO_2	CO (10^{-3}–10^{-4})	N_2 (0.03)	H_2O,O_2,O_3 +...
Mars	CO_2	CO ($8\ 10^{-4}$)	N_2 (0.03)	H_2O,O_2,O_3 +...
Jupiter	H_2	CH_4 (10^{-3}) CO ($1.5\ 10^{-9}$)	NH_3 ($2\ 10^{-4}$)	He H_2O,PH_3, GeH_4,AsH_3.. C_2H_2,C_2H_6
Saturn	H_2	CH_4 ($2\ 10^{-3}$) CO ($2\ 10^{-9}$)	NH_3 ($2\ 10^{-4}$)	He PH_3,GeH_4, AsH_3 C_2H_2,C_2H_6..
Uranus	H_2	CH_4 (1–2 10^{-2})	?	He
Neptune	H_2	CH_4 (1–2 10^{-2}) CO (10^{-6})	N_2? (10^{-2}–10^{-3}) HCN (10^{-9})	He C_2H_2,C_2H_6
Titan	N_2	CH_4 (0.02) CO ($5\ 10^{-5}$) CO_2 (10^{-8})	HCN ($2\ 10^{-7}$) CH_3CN (10^{-9}) HC_3N C_2N_2	Ar? H_2O?
Triton (* ices)	N_2	CH_4 (10^{-4}) CO* ($2\ 10^{-4}$) CO_2*		
Pluto (* ices)	N_2	CH_4* (10^{-5}–10^{-3}) CO* ($2^{-20}\ 10^{-4}$)		
Comets	H_2O	CO (0.05) CO_2(0.03) H_2C0(0.04) CH_30H NH_3? (0.01) CH_4?(0.003) OCS?(0.002)	HCN (0.001) N_2? ($2\ 10^{-4}$) (10^{-3})	H_2S