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Reports

Carbon Monoxide on Jupiter and Implications for Atmospheric Convection

Abstract. A study of the equilibrium and disequilibrium thermochemistry of the recently discovered carbon monoxide on Jupiter suggests that the presence of this gas in the visible atmosphere is a direct result of very rapid upward mixing from levels in the deep atmosphere where the temperature is about 1100 K and where carbon monoxide is thermodynamically much more stable. As a consequence the observed carbon monoxide mixing ratio is a sensitive function of the vertical eddy mixing coefficient. We infer a value for this latter coefficient which is about three to four orders of magnitude greater than that in the earth’s troposphere. This result directly supports existing structural and dynamical theories implying very rapid convection in the deep Jovian atmosphere, driven by an internal heat source.

Carbon monoxide (CO) was recently detected in the atmosphere of Jupiter by Beer (1), utilizing ground-based observations with a high-resolution Fourier transform interferometer-spectrometer in the 5-μm wavelength region. This detection has now been confirmed by Larson et al. (2), using similar instrumentation on the Kuiper Airborne Observatory. Both observers estimate that the volume mixing ratio for CO is about 10^-9 if they assume that the gas is well mixed, but this assumption has been questioned because it implies a rotational temperature of roughly 2100 K for CO (3). The discovery of CO is of considerable interest for, like the earlier discoveries of C2H2, C2H4, and PH3 (4, 5), it provides direct evidence for chemical dissociation of Jovian water vapor is essentially inhibited because photons capable of dissociating H2O do not penetrate down to levels where there are significant H2O concentrations (10). Without somewhat arbitrarily assuming convective injection of Jovian water cloud particles into the upper atmosphere or an extra-Jovian source for upper atmospheric H2O, production of OH by photolysis of H2O therefore appears to be inhibited. Dissociation of H2O lower in the atmosphere by hot H atoms which are produced by H2S photodissociation (11) or by lightning and thunder shock waves are two other possible OH sources. However, Jovian H2O still has very low concentrations at the levels where the hot atoms are being produced, and the hot atoms themselves are almost immediately quenched by collisions with H2 and He (12). In addition, in analogy with our own atmosphere, the vertical energy flux associated with lightning and thunder on Jupiter is only about 0.1 percent of the solar ultraviolet flux and a significant fraction of this flux is ineffectual in the breaking of chemical bonds (13).

Another mechanism for producing CO in the visible atmosphere—one which we will demonstrate is, in fact, adequate—involves very rapid vertical mixing in the hot lower atmosphere. This allows the CO formed by thermochemical oxidation of CH4 at high temperatures to be mixed up to visible levels (12). We argue here that the observation of CO, assuming it is well mixed, can be used to make a quantitative estimate of the strength of vertical mixing in Jupiter’s atmosphere. If the CO is not well mixed our analysis will apply only to the well-mixed component.

Before discussing the details of the latter mechanism we must establish what
An adiabatic temperature lapse rate (16), as implied by radiative-dynamical equilibrium calculations (17), was assumed below the 1-bar level. Earth-based and spacecraft data indicate a temperature at the latter level of 175 °K (18). We are interested here in the results of this study for the important carbon-containing compounds CO, CO₂, CH₂O, CHO, CH₄, C₂H₂, CH₃, and C₂H₂ and also for H, OH, and H₂O. The computed concentrations of these various species are shown in Fig. 1 along with the relationship between altitude, pressure, and temperature used in the model atmosphere.

If we assume that CO is well mixed we expect a rotational temperature of about 210 °K for the observed CO on Jupiter. In comparison, the volume mixing ratio for CO in thermochemical equilibrium at the 210 °K level is 6 x 10⁻⁴⁸, or some 36 orders of magnitude less than the observed value. Clearly, the observations imply the existence of a potent disequilibrating mechanism.

In developing our explanation for the appearance of CO in the visible atmosphere we must obtain a rough estimate for the rate of irreversible reduction of CO to CH₄ on Jupiter. The high-temperature kinetics of mixtures of CO, H₂, and O₂ and of CH₄ and O₂ have been studied in some detail by combustion chemists (19). Reaction paths in the hydrogen-rich but oxygen-deficient Jovian atmosphere will, of course, differ from those in the latter studies, but the rate constants of all the elementary reactions will remain the same.

In our study of the expected reaction paths on Jupiter we have found it convenient to divide the abundant carbon-containing compounds into two distinct families: oxidized carbon, comprising those with a carbon-oxygen bond (such as CHO, CO, CO₂, and CH₂O), and reduced carbon, comprising those without (such as CH₄, CH₂O, CH₃, and C₂H₂). Using measured rate constants (19, 20) and the concentrations shown in Fig. 1, we find that conversions within each family are generally very rapid at temperatures at or above 1100 °K. For example, in the oxidized carbon family the reactions

\[ \text{CO + H}_2 + \text{M} \rightarrow \text{CH}_2\text{O} + \text{M} \]
\[ \text{CH}_2\text{O} + \text{M} \rightarrow \text{CO} + \text{H}_2 + \text{M} \]
\[ \text{CO} + \text{H} + \text{M} \rightarrow \text{CHO} + \text{M} \]
\[ \text{CHO} + \text{M} \rightarrow \text{CO} + \text{H} + \text{M} \]
\[ \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \]
\[ \text{CO}_2 + \text{H} \rightarrow \text{CO} + \text{OH} \]

where M is another atom or molecule, enable conversions between CO, CO₂, CH₂O, and CHO to occur on time scales shorter than any feasible time scales for vertical transport. Thus the relative concentrations of these four species should always closely approximate their thermochemical equilibrium values. Similarly, the reactions

\[ \text{CH}_4 + \text{M} \rightarrow \text{CH}_3 + \text{H} + \text{M} \]
\[ \text{CH}_3 + \text{H} + \text{M} \rightarrow \text{CH}_4 + \text{M} \]
\[ \text{CH}_4 + \text{M} \rightarrow \text{CH}_3 + \text{CH}_3 + \text{M} \]
\[ \text{CH}_3 + \text{CH}_3 + \text{M} \rightarrow \text{CH}_4 + \text{H}_2 + \text{M} \]

permit sufficiently rapid conversions between CH₄, CH₃H₂, and CH₄ in the reduced carbon family (20).

In contrast to this situation, we have found that conversions from one carbon family to the other are a good deal slower. Available kinetic data (19) imply that oxidized carbon will be converted to reduced carbon on Jupiter by the reactions

\[ \text{H}_2 + \text{CH}_2\text{O} \rightarrow \text{OH} + \text{CH}_3 \] (1)
\[ \text{H} + \text{CH}_2\text{O} \rightarrow \text{O} + \text{CH}_3 \] (2)
\[ \text{OH} + \text{CH}_2\text{O} \rightarrow \text{O}_2 + \text{CH}_3 \] (3)

We have computed the rate constants for these three reactions, using the measured rate constants for the reverse reactions (19) together with their appropriate equilibrium constants (14). Reaction 1 is much more important than reactions 2 and 3 because of the large excess of H₂. The rate constant k computed for reaction 1 is

\[ k = 2.3 \times 10^{-10} \exp \left( \frac{-36,200}{T} \right) \text{ cm}^3 \text{ sec}^{-1} \]

Since CO and CH₄ are, respectively, the dominant forms of oxidized and reduced carbon, the rate of conversion of CO to
CH$_4$ can be equated with the rate of reaction 1. Thus the lifetime $t_{\text{chem}}$ of CO in an air parcel containing a large excess of CO over its equilibrium value (21) can be expressed as

$$t_{\text{chem}} = \frac{[\text{CO}]}{[\text{H}_2][\text{CH}_4]}$$

where the square brackets denote the number concentrations of the particular molecules. To compute these $t_{\text{chem}}$ values we use the fact that the relative concentrations of CO and CH$_4$ will be close to their equilibrium values.

We are now in a position to discuss the effects of vertical mixing on CO concentrations. To facilitate this discussion we have divided the atmosphere into two regions. One lies below the altitude $z = 0$, and all species in this lower region are assumed to be in thermochemochemical equilibrium. In practical terms, $z \leq 0$ will imply that $t_{\text{chem}} \leq t_{\text{conv}}$, where $t_{\text{conv}}$ is the time constant for vertical mixing. The other region lies above $z = 0$, and in this upper region we can conveniently write the CO destruction rate as

$$[\text{CO}] = \frac{[\text{CO}]_0}{t_{\text{chem}}(0)^{-1} \exp\left(-\frac{z}{t_{\text{chem}}}ight)}$$

where the "chemical scale height" $h_{\text{chem}}$ is given by

$$h_{\text{chem}} = -\left(\frac{d}{dz} \ln([\text{CO}]_0 t_{\text{chem}}^{-1})\right)^{-1}$$

To predict the CO volume mixing ratio $f_{\text{CO}}$ in the region above $z = 0$, we must solve the following equation, which expresses the continuity of mass for CO

$$d\frac{dz}{dz} \exp\left(-\frac{z}{H}\right) = \frac{f_{\text{CO}}(0)}{t_{\text{chem}}(0)^{-1} \exp\left(-\frac{z}{t_{\text{chem}}}ight)}$$

Here $H$ is the atmospheric "density scale height" and $K$ is the vertical eddy diffusion coefficient. The two boundary conditions necessary for solution of this continuity equation are $f_{\text{CO}} = f_{\text{CO}}(0)$ at $z = 0$ and $f_{\text{CO}}$ finite and positive as $z$ approaches infinity. Noting that $t_{\text{chem}}(0) = t_{\text{conv}}$ and that $t_{\text{conv}}$ is given approximately by

$$t_{\text{conv}} = \frac{H^2}{K}$$

the resultant expression for $f_{\text{CO}}$ when $0 < t_{\text{chem}} < H$ is (22)

$$f_{\text{CO}} = f_{\text{CO}}(0)\left(1 - \frac{h_{\text{chem}}^2}{H^2} \times \frac{1}{1 - \exp\left(-\frac{1}{h_{\text{chem}} H}\right)}\right)$$

Since $h_{\text{chem}} \ll H$ (23), this equation tells us that $f_{\text{CO}}$ in the visible atmosphere (that is, at $z >= H$) is not much less than at $z = 0$. In essence, once $t_{\text{chem}} \approx t_{\text{conv}}$, vertical mixing results in CO in an air parcel being chemically quenched by rising a distance from $z = 0$ which is considerably less than $H$.

If we regard $K$ as an unknown quantity we can identify the level $z = 0$ for each $K$ value by finding where $t_{\text{chem}} = H^2/K$. We can then obtain $f_{\text{CO}}(0)$ at this same level from the thermochemochemical equilibrium calculations presented in Fig. 1. In this manner we obtain the $f_{\text{CO}}(0)$ value corresponding to each $K$ value. The results are illustrated in Fig. 2. Since the observed $f_{\text{CO}}$ value is approximately $f_{\text{CO}}(0)$, Fig. 2 demonstrates the dependence of the observed CO concentrations on the $K$ value in the deep atmosphere. From observations (1, 2) $f_{\text{CO}} = 10^{-6}$, which implies $K = 2 \times 10^8$ cm$^2$ sec$^{-1}$. The corresponding temperature at $z = 0$ is 1004K. By way of comparison, $K = 10^8$ cm$^2$ sec$^{-1}$ in the terrestrial troposphere. In view of the several assumptions and approximations we have made, we caution that this result should be regarded only as indicating the order of magnitude of $K$ in the deep atmosphere. A detailed laboratory study of the high-temperature reduction of CO to CH$_4$ by H$_2$ will be necessary before better accuracy can be obtained.

Recent measurements from Pioneer 10 (24) confirm earlier earth-based observations (25) suggesting that Jupiter emits at thermal wavelengths about twice the energy it receives from the sun at visible wavelengths. The internal heat source implied from these observations has been used to argue that Jupiter is a convective fluid throughout most of its interior (26). The required $K$ value can be calculated from theories for free convection and is about $10^7$ to $10^8$ cm$^2$ sec$^{-1}$ in Jupiter’s deep atmosphere (27). Considering the approximations we have made, the agreement between our deduced $K$ value and the latter theoretical values must be regarded as surprisingly good. The observation of CO on Jupiter has thus provided independent evidence for very rapid vertical mixing in its deep atmosphere.

The mechanism proposed here for producing nonequilibrium concentrations of CO in the atmosphere should also apply to a large number of other molecules. This mechanism has already been used to explain the observation of PH$_3$ (27). It has been advanced for GeH$_3$ (12), which has also recently been observed (5). If CO$_2$ has a chemical time constant similar to that of CO, then its observed mixing ratio should be roughly that at the 1100K level, which from Fig. 1 is 5 x 10$^{-12}$. Larson et al. (2) place an observational upper limit on CO$_2$ of 67 times the observed CO value. A complete list of the mixing ratios of abundant species in chemical equilibrium in the region between 800° and 1500°K on Jupiter is given elsewhere (14). Since some or all of these species may be transported up to visible regions of the atmosphere, they could be observable by remote spectroscopy or by an entry-probe mass spectrometer.

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References and Notes
4. We note that some of the lines with high values of the rotational quantum number J that are expected for well-mixed CO with a rotational temperature of about 2100K are not discernible in their recent spectra. They suggest that CO is therefore not well mixed but is concentrated in the stratosphere with a resultant rotational temperature of 125K. However, Larson et al. (2) note that there is evidence for some of these high-J lines in their spectra and they therefore prefer the well-mixed interpretation.
17. Heat capacity data for computing lapse rates were taken from the Handbook of Chemistry and Physics (Chemical Rubber Co., Cleveland, Ohio, 1961), p. 3232.

21. Our estimate of $t_{th}$ will be too small if partial reformation of CO by reactions such as the reverse of reaction 1 is appreciable. Since CH₄ and CO have very short lifetimes for conversion to CH₄ and CO₂, their concentrations should be close to their equilibrium values. Consequently, in an excess of CO the reformation of CO by the reverse of reaction 1 will be much slower than the forward reaction and can thus be ignored. On the other hand, our estimate of $t_{th}$ will be too large if other CO-to-CH₄ conversion mechanisms (such as heterogeneous reactions on Fe particles) exist. We are concerned here primarily with the order of magnitude of $t_{th}$, which we expect to be less sensitive to the exact details of the kinetics.

22. Because $K_{eq}(0) = M^p$, the influence of $K$ in this expression is not immediately apparent. Its influence is, in fact, considerable since it determines the level $z = 0$ and thus the value for $f_{cd}(0)$.

23. From its definition we compute $k_{ran} > 25$ km at the 1100 R level, where $H = 220$ km. Thus $k_{ran}^2/H = 0.013 < 1$.


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Minimum Size of Mammalian Homeotherms:
Role of the Thermal Environment

Abstract. The minimum size of a mammalian homeotherm appears to be related to the animal's maximum rate of endogenous heat production, the ambient thermal environment, and the animal's ability to be a facultative homeotherm.

Many additional data now have been accumulated on the minimum metabolic rates of small mammals (Fig. 1). The relationship between minimum metabolic rate and body size in thermoneutrality is essentially linear ($r^2 = .42$), although a power function provides a slightly better fit ($r^2 = .48$; see Fig. 1 for regression). The smallest (about 7 g) adult mammals (excluding shrews and bats) have metabolic rates that are only one-third the rate reported (2) for the masked shrew. The metabolism-body mass relationships for most homeotherms do not show the dramatic increase in metabolism near the minimum size of mammalian homeotherms that has been reported for shrews (1). This is partly because the metabolic data for shrews were all determined for animals held at 24°C, which is lower than the thermal neutrality for all shrews (2). Thus, the experimental conditions were cold enough that the animals responded with elevated metabolic rates to maintain homeothermy. Because the amount of cold stress to the shrews is related inversely to body size, smaller and smaller shrews had higher and higher metabolic rates. However, it is not so clear that very small shrews would necessarily have extraordinarily high metabolic rates if subjected to conditions of thermal neutrality, and, indeed, there are some data showing that British shrews have metabolic rates (at rest and during activity) that are not different from those of similarly sized mice (4).

For several reasons related to heat transfer from organisms (namely, that the surface area/body mass ratio of homeotherms is greater in smaller animals, and that the convective boundary layer of still air around any animal is thinner for smaller animals), smaller body size (with all other things held constant) is usually related to greater heat losses from animals. That the minimum metabolic rates (heat production) relative to body size for small mammals do not show a dramatic increase as body size becomes smaller (5) indicates that very small mammals need not have extraordinarily high rates of metabolic heat production to remain homeothermic. However, the range of thermal environments in which an animal can maintain a minimum metabolic rate at constant body temperature becomes smaller for smaller animals, such that an infinitely small animal can maintain a constant body temperature only in a perfectly constant thermal environment. Thus, a very small animal can be homeothermic if (i) it has the capacity for extraordinarily high heat production (6), or (ii) it has the capacity for precise body temperature regulation through nanoclimatic selection and possibly the ability to be facultatively homeothermic. The former seems to describe endothermic mammals and birds, and the latter tends to describe numerous reptiles and insects.

How, then, can one predict the minimum size of endothermic homeotherms? The answer is that it is not possible to predict the smallest size of endothermic homeotherms without also specifying the environment in which the animal exists. Homeotherms theoretically can be infinitely small (in thermoneutral environ-