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Atmospheric Carbon Tetrafluoride: A Nearly Inert Gas

Abstract. An analysis of existing thermodynamic, photochemical, and kinetic data indicates that the dominant sinks for atmospheric carbon tetrafluoride (CF₄) are in and above the mesosphere. Theoretical calculations predict an atmospheric residence time for CF₄ of over 10,000 years, about 100 times that for dichlorodifluoromethane (CF₂Cl₂) and monofluorotrichloromethane (CFCl₃). It is predicted that CF₄ will be well mixed through the stratosphere and mesosphere; only one or two parts of hydrogen fluoride in 10¹² are predicted in the high stratosphere as a result of the decomposition of CF₄. Although natural sources of CF₄ cannot be ruled out, there are several likely industrial sources that may account for its present concentration. The principal environmental effect of CF₄ could be the trapping of outgoing planetary infrared energy in its intense bands near 8 micrometers.

Carbon tetrafluoride (CF₄) was detected in the air of several European countries by Gassman in 1973 (1) and in both hemispheres of the troposphere by Rasmussen et al. (2) in 1978. This compound is probably the most stable fluorocarbon gas. In this report I examine the potential of atmospheric and environmental processes to decompose CF₄ and conclude that it has an atmospheric lifetime of over 10⁸ years. Its principal sinks are vacuum ultraviolet (UV) radiation in the high mesosphere and ionosphere, possible (but unlikely) reactions with electronically excited oxygen atoms and with vibrationally excited (v = 9) OH molecules in the stratosphere and above, several ionospheric processes, and pyrolysis in high-temperature combustion. Its dominant sources are uncertain, but I identify several likely industrial processes. Such a long lifetime (residence time) ensures that relatively small sources will increase the atmospheric CF₄ burden and that CF₄ will remain ubiquitous in the atmosphere.

In an effort to understand the atmospheric behavior of CF₄ as quantitatively as possible, I have used available data on its chemical properties, estimated certain unknown parameters, and performed numerical calculations to simulate its atmospheric transport and photochemistry. Table 1 lists possible CF₄ sinks and the reaction rate parameters I adopted. Solar vacuum UV photons with wavelength λ < 103 nm photodissociate and photoionize CF₄ (3). Although no absorption has been observed for λ > 103 nm (3), I have performed calculations with photodissociation cross sections, σ, of 3 × 10⁻¹⁰ and 3 × 10⁻²⁰ cm² at λ = 122 nm because of the intense solar 121.6-nm line and with σ (122 nm) = 0. These data yield photodissociation rates, J (per second) as follows (3): the total J above the entire atmosphere (altitude, z = ∞) is 6.8 × 10⁻⁷ due to absorption over all wavelengths, that is, 122 nm and 60 nm < λ < 103 nm. With the maximum σ at 122 nm, that is, 3 × 10⁻¹⁹ cm², J (122 nm) = 10⁻⁷ at z = ∞. As a result of absorption by O₂ and N₂, the only significant photodissociation below an altitude of 90 km is due to the solar lines at 122 and 103 nm. With the maximum σ, J (122 nm) = 4.7 × 10⁻³, 2.6 × 10⁻³, 1.5 × 10⁻³, and 3.6 × 10⁻¹⁴ at 90, 80, 70, and 60 km, respectively, when averaged diurnally; J (103 nm) = 9 × 10⁻⁷, 3 × 10⁻¹¹, and 1.2 × 10⁻¹⁵ at z = 90, 90, and 80 km, respectively. Consequences of these rates are discussed below.

Chemical reactions between CF₄ and atmospheric constituents are limited by C-F bond strengths. I estimated upper limit bimolecular rate constants k₁ through k₁₀ in Table 1 as follows. Reaction 1, an atom insertion, should be slower than the observed (upper limit) rate (4) for O + CF₃H, an H abstraction.

I assumed an Arrhenius expression of the form A exp(−Eₐ/Rₜ), where A is a constant, Eₐ is the activation energy, R is the gas constant, and T is the temperature. For a generous upper limit on k₁, I took Eₐ for O + CF₃H and O + CF₄ as their respective ΔH (enthalpy of reaction) values (5), although generally Eₐ > ΔH. Multiplying this maximum k₁ by concentrations of O at each altitude from 10 to 110 km, one finds that the maximum product, 10⁻¹¹ sec⁻¹, occurs near the stratopause (50 km) (6).

The only exothermic reaction of CF₄ with O(D) other than quenching to O(Π) is the insertion reaction in Table 1; for O(Sₕ), two exothermic paths exist. In my calculations I let k₁, k₆, and k₉ = 0 and 10⁻¹² cm³ sec⁻¹ separately (7). Reaction with H atoms, although exothermic, requires at least 10 kcal per mole of activation energy (8). Reactions of ground-state OH with CF₄ are strongly endothermic and thus negligible. vibrationally excited OH (ν = 1, 2, · · · 9) is present in the stratosphere and mesosphere (9). It is possible for CF₄ to react with OH (ν = 9); I estimated reaction rates k₁ and k₉ in Table 1. Dissociative electron capture by CF₄ is strongly endothermic (10) so that free electrons in the lower ionosphere are insignificant. Above 150 km ionospheric photoelectrons with energies > 2 eV would dissociate CF₄, but this process would be very slow globally because the CF₄ available for attack there is 10⁻¹⁰ of that in the troposphere.

The nonphotochemical processes in Table 1 were evaluated as follows. If all rainfall is saturated with CF₄ with respect to its atmospheric partial pressure, pCF₄, and 1 m of water falls annually, the ratio of annually precipitated CF₄ to the atmospheric content is 2 × 10⁻⁶ for any pCF₄, according to its solubility (5). Moreover, because the rate of hydrolysis of CF₄ is immeasurably small (11), the capacity of the oceans to assimilate CF₄ is limited by its solubility; if all ocean waters (surface and deep) were saturated with CF₄, less than 0.2 percent of the atmospheric burden of CF₄ at any time would be in the oceans. The removal time due to pyrolysis in Table 1 is based on annual O₂ consumption rates in high-temperature combustion (11). Finally, there are no indications of biological processes that can break C-F bonds in CF₄ (12).

With the photochemical reactions of Table 1, I performed numerical calculations (13) for the time and altitude dependence of CF₄ concentrations. A constant ground-level source of CF₄ natural...
ly leads to an eventual steady-state atmospheric equilibrium vertical concentration profile. A source of $2.4 \times 10^{10}$ g year$^{-1}$ (10$^{10}$ cm$^{-2}$ sec$^{-1}$) gives a steady-state CF$_4$ concentration, $f_s$ (mole fraction), of 20 parts per billion (ppb) ($2 \times 10^{-8}$) when all photochemical losses are maximized as in Table 1. In this case the atmospheric residence time, $\tau$, defined as (total atmospheric CF$_4$ content)/(CF$_4$ input flux), is 14,000 years. With the same source and maximum photodissociation but $k_1, k_2, \ldots, k_{13}$ are 0, $\tau$, is 38,000 years and $f_s$ is 56 ppb. When $\sigma$ (122 nm) = $3 \times 10^{-30}$ cm$^2$, that is, 0.1 times maximum photodissociation and $k_1, k_2, \ldots, k_{13}$ are maximized, $\tau$, is 23,000 years and $f_s$ is 34 ppb. Taking $\sigma$ (122 nm) = 0 and $k_1, k_2, \ldots, k_{13}$ = 0, one finds $\tau$, = $17 \times 10^{6}$ years, but this is unrealistic because non-photochemical processes such as combustion would limit the CF$_4$ residence time (at least until fossil fuels are depleted).

I also performed calculations in which a time-varying, presumably industrial CF$_4$ source was used. Figure 1 shows altitude profiles of the CF$_4$ mole fraction at four dates. All photochemical destruction rates for CF$_4$ in Fig. 1 were the maximum values of Table 1. The present atmospheric burden of CF$_4$, about $10^{12}$ g (mole fraction = $6 \times 10^{-11}$), could have materialized thus. Because the CF$_4$ sinks are in the mesosphere and above except for O($D$) and OH$^+$ (minor compared to 122-nm photodissociation), only about $10^{-3}$ to $10^{-2}$ of the atmospheric CF$_4$ is exposed to the sinks at any time. The local photochemical removal processes have characteristic time constants of over 100 years, and $\tau$, = 14,000 years. Thus the CF$_4$ concentration increases with time, and the altitude profile approaches a straight line. At steady state, the ratio of the 99-km mole fraction to the 0-km mole fraction is 0.97. Thus the release of four F atoms in CF$_4$ decomposition leads to a very little HF (Fig. 1). The dominant organic F compound in the stratosphere and mesosphere should be HF (14). If CF$_4$ is a recent addition to the air, its mole fraction, $f_s$, will be less in the stratosphere and above than at $z$, = 0, for example, the 1980 profile in Fig. 1. If, instead, CF$_4$ was injected into the air over 100 years ago, it should be well mixed (like the A.D. 2105 profile). In any case, an atmospheric residence time of $>14,000$ years implies that, even with no sources, a given CF$_4$ profile will decay by only 7 percent in 1000 years ($e^{-14}$), as I have confirmed by additional numerical computations.

With such a long atmospheric lifetime, CF$_4$ concentrations will grow because CF$_4$ has industrial sources, for example, CF$_4$ released in the electrolytic reduction of alumina (15). Indeed, the liberation of CF$_4$ is not entirely limited to relatively brief anode-effect intervals. Japanese studies (15) suggest that the estimate of Rasmussen et al. (2) of $6 \times 10^{10}$ g of CF$_4$, per year released during electrolytic cell anode effects is supplemented by CF$_4$ released during normal cell operation. Release of as much as $10^{10}$ g year$^{-1}$ is easily possible, but changing industrial practices, technology, and output imperils such estimates; direct measurements are needed. Several other industrial processes are likely sources of CF$_4$, either because CF$_4$ has been detected in the process or because C, F, and heat are available: the electrolytic generation of F$_2$, especially in carbon or graphite electrode systems, the analogous reduction of UF$_4$, or UF$_6$ (16), the use of fluorospar in steelmaking (17, p. 298; 18) (although CF$_4$ production from CaF$_2$ seems disfavored thermodynamically), the burning of polyfluoroethylenes, rocket fuel combustion (18), and inadvertent production in fluorocarbon manufacture. Direct, intentional industrial production of CF$_4$ amounts to only 10 to 60 tons per year.

Sources of CF$_4$, especially anthropogenic, require measurements to quantify, as does the possible CF$_4$ photoabsorption at 122 nm. With these data, more accurate predictions of CF$_4$ concentrations and effects will be feasible.

*Note added in proof:* A recent stratospheric measurement by Goldman et al. (19) found $7.5 \times 10^{-11}$ (mole fraction CF$_4$) at 25 km, as is roughly predicted by the curve for 1980 in Fig. 1.

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References and Notes


**Table 1. Bimolecular rate constants (in cubic centimeters per second) and process rates for the decomposition of atmospheric CF$_4$.** Additional reactions between CF$_4$ and NO, NO$_2$, NO, HO, OH, O$_3$, SO$_2$, ClO, HOCl, other gases, and positive ions were considered but no exothermic paths exist. Although the reaction H$_2$ + CF$_4$ + H + CF$_3$ is exothermic, it is expected to have a prohibitive activation energy as is the case for NO$_2$ + CF$_4$ + NO$_2$ + CF$_3$. Other natural sinks, for example, solar x-rays, ionospheric photoelectrons, lightning discharges, and surface reactions with atmospheric aerosols are active but unimportant quantitatively (11).

<table>
<thead>
<tr>
<th>Candidate reaction or process</th>
<th>$\Delta H_{298}$ (kcal mole$^{-1}$)</th>
<th>Adopted reaction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum UV photodissociation</td>
<td>Bond dissociation energy is 129 kcal mole$^{-1}$ ($\lambda = 220$ nm)</td>
<td>$\sigma (\lambda)$ for $\lambda &lt; 103$ nm</td>
<td>(3)</td>
</tr>
<tr>
<td>$O + CF_4 \rightarrow CF_2O + F_2$</td>
<td>+10.8</td>
<td>$k_1 &lt; 2.0 \times 10^{-18}$ exp(-5000/T)</td>
<td>(4, 5, 7)</td>
</tr>
<tr>
<td>$O + CF_4 \rightarrow FO + CF_3$</td>
<td>+77.1</td>
<td>$k_2 = 0.6 \times 10^{-12}$</td>
<td>(4-6)</td>
</tr>
<tr>
<td>$O(D) + CF_4 \rightarrow CF_3O + F_2$</td>
<td>+137.1</td>
<td>$k_3 = 0.0$</td>
<td>(5-7)</td>
</tr>
<tr>
<td>$O(S) + CF_4 \rightarrow FO + CF_3$</td>
<td>-34.4</td>
<td>$k_3 = 0.0, k_4 = 10^{-12}$</td>
<td>(5-7)</td>
</tr>
<tr>
<td>$O(S) + CF_4 \rightarrow F_2 + CF_3O$</td>
<td>-19.1</td>
<td>$k_5 = 0.0, k_6 = 10^{-12}$</td>
<td>(5-7)</td>
</tr>
<tr>
<td>$H + CF_4 \rightarrow HF + CF_3$</td>
<td>-85.4</td>
<td>$k_7 = 3.0 \times 10^{-13}$ exp(-5000/T)</td>
<td>(8)</td>
</tr>
<tr>
<td>$OH + CF_4 \rightarrow FO + CF_3H$</td>
<td>-6.6</td>
<td>$k_8 = 7.3 \times 10^{-11}$</td>
<td>(5)</td>
</tr>
<tr>
<td>$OH + CF_4 \rightarrow FO + CF_3$</td>
<td>-70.2</td>
<td>$k_9 = 0.0$</td>
<td>(5)</td>
</tr>
<tr>
<td>$OH + CF_4 \rightarrow$ other products</td>
<td>$&gt; 77$</td>
<td>$k_{10} = 0.0$</td>
<td>(5)</td>
</tr>
<tr>
<td>$OH^+(v=9) + CF_4 \rightarrow FO + CF_3H$</td>
<td>-3.1 $\pm 10$</td>
<td>$k_{11} \leq 10^{-12}$</td>
<td>(6)</td>
</tr>
<tr>
<td>$OH^+(v=9) + CF_4 \rightarrow HO + CF_3$</td>
<td>-5.9 $\pm 10$</td>
<td>$k_{12} \leq 10^{-11}$</td>
<td>(6)</td>
</tr>
<tr>
<td>Thermal $e + CF_4 \rightarrow F + CF_3$</td>
<td>70</td>
<td>$k_{13} = 5.0 \times 10^{-7}$ exp(-25,000/T)</td>
<td>(10)</td>
</tr>
<tr>
<td>Removal time, 5000 years</td>
<td>None</td>
<td>Removal time, $&gt; 50,000$ years</td>
<td>(11)</td>
</tr>
<tr>
<td>Rainout in the troposphere</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Bioreactivity or microbiological consumption</td>
<td></td>
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<tr>
<td>Pyrolysis in high-temperature combustion</td>
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</table>
Deciphering the Scattering Code Contained in the Resonance Echoes from Fluid-Filled Cavities in Solids

Abstract. From the echoes of elastic waves incident on inclusions in solids, one may extract certain resonance features. These 'spectral lines' and their widths form a code identifying the material composition of the inclusion in a way that resembles spectroscopy. This idea finds applications in geophysics, materials science, and any field dealing with materials containing inclusions.

The amplitudes of backscattered waves returned by inclusions in viscoelastic solids, when plotted as a function of frequency, exhibit many rapid oscillations and complicated features that until very recently it was not possible to extract the physical information contained in them. The amplitudes of these waves can be analyzed in light of our new resonance theory of scattering from cavities in solids (1, 2) and can be used to identify, for a given shape of the cavity, the material composition of the filler material. When a (spherical) filler is set into oscillation by elastic (say, compressional) waves incident upon it, a set of modal resonances (fundamental and overtones) get excited in it; these resonances characterize the filler as if they were its signature. Since incident shear waves excite the same resonances in the filler, we will limit this analysis to elastic wave amplitudes. From the usual spectral plots of the backscattered wave amplitudes versus inelastic frequency 

\[ f_{\text{scat}}(\theta) = \sum_{n=0}^{\infty} A_n P_0(\cos \theta) \]

where the coefficients \( A_n \) are given by ratios of two \( 3 \times 3 \) determinants whose elements contain products of the fillerto-matrix density ratio (that is, \( \rho_r/\rho_b \)) with various spherical Bessel and Hankel functions and their derivatives, of arguments \( k_0 a \) and \( k_0 a_0 \), and of order \( n \). These elements are determined from the boundary conditions of the problem and are given in (1). In the backscattering direction \( \theta = \pi \), the Legendre polynomials are simplified by means of the relation

\[ P_n(\cos \pi) = (-1)^n \]

Figure 1 shows the plot of the modulus of this summed backscattered amplitude for a cavity filled with ethyl alcohol in an aluminum matrix. This is the "echo," containing the rapid oscillations and complex features mentioned above.