Keeping Mars warm with new super greenhouse gases

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Our selection of new super greenhouse gases to fill a putative "window" in a future Martian atmosphere relies on quantum-mechanical calculations. Our study indicates that if Mars could somehow acquire an Earth-like atmospheric composition and surface pressure, then an Earth-like temperature could be sustained by a mixture of five to seven fluorine compounds. Martian mining requirements for replenishing the fluorine could be comparable to current terrestrial extraction.

Greenhouse gases may be of some use in making Mars habitable, or at least in sustaining its habitability if otherwise achieved. Previously suggested gases include the chlorofluorocarbons (CFCs; refs. 1 and 2), SF_6 (2), and C_nF_{2n+2} (2, 3). Recent detailed calculations for C_2F_6 and the CFCs (3) have led to optimism about terraforming. Probably some means other than greenhouse gases must be used for the initial warming, even though a few heavy gases may absorb strongly (4) at current Martian pressure (600 Pa). They are unlikely to cover the low-frequency half of the emission spectrum. We introduce some new candidate gases, and we frame our inquiry by asking what mixture of trace gases could sustain an Earth-like temperature if Mars were endowed somehow with an Earth-like atmospheric composition and surface pressure. We suggest that a 70-K greenhouse effect might be maintainable with as little as 5×10^{22} m^{-2} column amount of a mixture of "designer" greenhouse molecules. This molecular column corresponds to about 240 parts per billion by volume in Earth's atmosphere. Our argument begins with a simple energy balance (5) arising from a two-stream approximation.

$$\sigma \theta_g^4 = F_S(1 + 3\tau/4) \qquad [1]$$

Here, σ is the Stefan–Boltzmann constant, θ_g is the temperature at the planet's surface, F_s is the downward solar flux, and τ is the gray optical thickness. To obtain τ directly from θ, we must assume no absorption of incoming solar radiation, but our assumption about a window implies the presence of much water, hence of some absorption in the interval 1 to 3 μm, and also the presence of water clouds. The cooling or warming effect of clouds depends in a complex way on their distribution in altitude and latitude (6), so we prefer not to address it.

If we ignore absorption of incoming solar radiation, a fractional increase in θ_g is a simple function of τ. Taking the present gray opacity on Mars to be nearly zero, Eq. **1** implies that a gray opacity near $\tau = 3$ should increase the surface temperature to 280 K from the current 210 K. If Mars can acquire an Earth-like atmosphere somehow, the transmission of outgoing radiation at frequencies below 700 cm^{-1} and above 1,400 cm^{-1} will be just a few percentage points as on Earth. We therefore direct our attention to filling the window.

In the interval between 700 and 1,400 cm^{-1}, we approximate the spectral transmission of the Earth's atmosphere at a crude resolution (7). We then double the spectral optical thicknesses, because the lower gravity of Mars requires 2.6 times Earth's column airmass to achieve 100 kPa pressure at the surface. Next, we seek to add a mixture of greenhouse gases that will lower the overall transmission through the window to 5% ($= e^{-3}$).

We considered 21 fluorine compounds, some of which were not previously synthesized, observed, or documented. Fluorine in the bulk composition of Mars has been estimated at 32 ppm by mass vs. 19.4 ppm for the Earth (8). Abundances of the other elements are more than sufficient for our purposes. We performed *ab initio* calculations to find vibrational fundamental frequencies and band intensities. After estimating bandwidth and selecting five of the candidate molecules, we stepped along the window spectrum at intervals of 1 cm^{-1} to calculate spectral transmission and derive gray opacity. Then we iterated with the aim of minimizing the required number of molecules of manufactured gas.

Finally, we will demonstrate that Earth-like ozone and oxygen, if present, would shield all of the selected molecules effectively against rapid photolysis, such that their continuous replenishment by synthesis on Mars then might be feasible.

Infrared Quantum-Mechanical Calculations

Gases considered for the special purpose of maintaining warmth on Mars are shown in Table 1. To determine the structure and vibrational spectra of each gas, all calculations were performed by using the GAUSSIAN 98 suite of programs (9). All geometries were optimized fully with no constraints to better then 0.1 pm (for bond lengths) and 0.1° (for angles). The calculations were done with two kinds of basis sets: (*i*) the medium size double ζ-split valence basis set, 6–31G(d); and (*ii*) the large 6–311 ++G(3df,3pd) basis set. Optimizations were performed with the Becke nonlocal three-parameter exchange (10) and correlation functional was performed with the Lee-Yang-Parr method (B3LYP) with these basis sets (11). In all cases, harmonic vibrational frequency calculations were done with the optimized geometries. Structures giving rise to imaginary vibrational frequencies were rejected, because these structures are not global minimum structures. To determine the reliability of the various methods for predicting the vibrational frequencies for the super greenhouse gases, 10 other gases were selected as calibrants, because the fundamental vibrational modes are experimentally well characterized. These gases are CO_2, $CFCl_3$, CF_2Cl_2, CF_2CFOCF_3, CH_3OCH_3, CHF_2OCF_3, CHF_2OCHF_2, CH_3OCF_3, SF_6, and NF_3. Usually, vibrational frequencies calculated with lower levels of theory are found to overestimate experimental frequencies by 5–10%, so a popular approach has been to use scale factors (12). However, in the present work no scaling factors were applied. A comparison of observed and calculated frequencies for our calibration set of gases showed that calculations performed at the B3LYP/6–311 ++G(3df,3pd) level of theory produced frequencies within an rms error of 3% of experimental vibrational frequencies. Recent studies have

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Table 1. The 21 fluorine compounds considered for super greenhouse warming

CF_3CF_3	$CF_3CF_2CF_3$	CF_3NF_2
$CF_3CF_2NF_2$	CF_3NFCF_3	SF_5CF_3
CF_3OCF_3	CF_3SCF_3	$SF_4(CF_3)_2$
$CF_3OCF_2CF_3$	$CF_3SCF_2CF_3$	$SF_3(CF_3)_3$
$CF_3OCF_2NF_2$	$CF_3SCF_2NF_2$	$SF_2(CF_3)_4$
$CF_3OCF_2OCF_3$	$CF_3SCF_2SCF_3$	$SF(CF_3)_5$
$CF_3OCF_2SCF_3$	$CF_3OCF_2NFCF_3$	$S(CF_3)_6$

Of 10 calibrants (see text), only SF_6 was chosen as an optimal warmer.

found that the B3LYP method offers the best performance in computing intensities (13). As a further test of the reliability of the calculations, the infrared spectra from the *ab initio* frequencies were simulated and compared with the experimental spectra. We found that the simulated spectra showed reasonable agreement with the experimental spectra of each calibrant gas.

Required Greenhouse Columns

After examining the calculated spectra, we selected five gases in an attempt to minimize remaining windows. These five gases' strong vibrational bands in the range of 670–1,400 cm^{-1} are listed in Table 2. Although some of these gases have been synthesized or observed elsewhere (e.g., SF_6 in ref. 4 and SF_5CF_3 in ref. 14), we use B3LYP outputs for all of them to work with a consistent set of statistics.

Based on various analogs such as fluorinated ethers (15), the Earth's 9.6-μm band of ozone, or the calibrations described above, we estimate bandwidths for the super greenhouse gases to have full-width half-max between 16 and 30 cm^{-1}. Rather than use Lorentzian band shapes and give ourselves the benefit of far wings that may not exist, we model all bands as triangles. We do not increase bandwidths with gas amount, so that the equivalent width of any given band has an upper-limit independent of concentration. In this way we hope to avoid crediting a saturated band with filling in nearby windows.

For a first guess at column amounts, we identified a constraining band of each gas not overlapping strong absorptions of any of the other gases. Because the band intensities are calculated at standard temperature and pressure (STP), we are not accounting for the reduction of pressure in the Martian upper troposphere and stratosphere properly; however, we note that the 9.6-μm ozone band in the Earth's atmosphere contributes an optical thickness comparable to the product of its STP band intensity and its column density divided by its bandwidth, even though most of Earth's ozone is not in the troposphere. We doubled the spectral optical thickness of terrestrial gases, because Mars's lower surface gravity (0.38 that of Earth) requires increased airmass to achieve 100 kPa at the surface. We added spectral optical thicknesses of the five selected super greenhouse gases to the spectral opacity of the doubled terrestrial gases. Without regard to the variation of the Planck function, we then stepped through the spectrum 700 to 1,400 cm^{-1} at 1-cm^{-1} intervals adding optical thicknesses and calculating spectral transmission. We iterated with the intent of minimizing the total number of special greenhouse molecules within the constraint that the gray optical thickness be at least 3.

The minimum column amounts resulting when bandwidth (full-width half-max) is estimated as 30 cm^{-1} are given as the second column in Table 3. The total molecular column density of the mixture is less than 5×10^{22} m^{-2}, which would be about 240 parts per billion by volume (ppbv) of Earth's atmosphere. If the bandwidth is estimated as 16 cm^{-1}, achieving $\tau = 3$ would require the addition of some NF_3 and CF_3NF_2 to the five gases

Table 2. Strong bands in the spectral region of interest, for the selected super greenhouse gases

	v	S
$SF_4(CF_3)_2$	1,249	540
	1,246	533
	1,113	459
	816	249
	815	250
	679	383
$CF_3CF_2CF_3$	1,341	7
	1,309	147
	1,237	589
	1,236	389
	1,188	98
	1,174	46
	1,146	180
	1,000	231
	726	51
$CF_3SCF_2CF_3$	1,309	129
	1,214	224
	1,200	201
	1,178	399
	1,165	287
	1,131	160
	1,120	167
	1,071	133
	948	309
	761	21
	750	45
SF_5CF_3	1,243	289
	1,239	282
	1,134	319
	868	319
	867	319
	859	307
	746	115
SF_6	916	1,236
	743	6

v = frequency, inverse cm; S = intensity at standard temperature and pressure, km/mol. All isotopes are included.

in Table 2 and a total molecular column of 1.7×10^{23} m^{-2} (about 810 ppbv of Earth's atmosphere).

Fig. 1 shows spectral absorption through the 700–1,400 cm^{-1} window when the gas mixture of Tables 2 and 3 is added (solid curve) to the spectrally doubled terrestrial gases. The dotted curve represents absorption by the super greenhouse gases only. The three humps just to the left of the deepest trough may be identified roughly with bands of $SF_4(CF_3)_2$, SF_5CF_3, and SF_6 seen in Table 2. The contribution of ozone accounts for the difference between the two curves in the interval between 1,000 and 1,080 cm^{-1}. Other humps are hybrid absorptions of several gases. It's worth noting that experiments on SF_6 (4) show its peak absorption between 940 and 950 cm^{-1}, which would make our problem a little easier to solve.

Photolysis

For four of the five selected gases, we computed photolytic lifetimes in the Earth's present atmosphere. For SF_6, we use the lifetime reported in ref. 16. Because the super greenhouse gases have no multiple bonds or hydrogen atoms that would make them readily susceptible to atmospheric degradation, the primary loss mechanism for these gases will, in general, be photolysis. Chemical losses by reactions with $O(^1D)$ in the atmo-

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Table 3. Column amounts to raise grey opacity of a doubled terrestrial atmosphere to 3; lifetimes in present terrestrial atmosphere

Gas	Suggested column per m^2	Lifetime against photolysis, yr
CF$_3$CF$_2$CF$_3$	1.1×10^{22}	$>1 \times 10^8$
CF$_3$SCF$_2$CF$_3$	1.4×10^{22}	8950
SF$_6$	5.2×10^{21}	3200*
SF$_5$CF$_3$	1.0×10^{22}	4050
SF$_4$(CF$_3$)$_2$	8.0×10^{21}	3070

*Includes reaction with mesosphere's free electrons.

Fig. 1. The solid curve is fractional absorption by the gas mixture of Table 3 when added to a spectrally doubled terrestrial atmosphere. The dotted curve is the absorption of the super greenhouse gases by themselves (but at standard temperature and pressure).

sphere will probably be less important than photolysis (16), and OH is not expected to attack this class of molecules.

To estimate the UV-excited state spectra for the super greenhouse gases, vertical excitation energies were calculated by using the configuration interaction singles method (17). This method allows for systems with a large number of atoms and large number of basis functions to be investigated with reliability. The success of this method in predicting excited states depends on the choice of basis set, so we used the large 6–311 ++G(3dp,3pd) basis set. The UV absorption cross sections then were estimated, assuming that they have the same spectral shape as that of CF$_2$Cl$_2$, shifted to the proper wavelengths, and scaled by the oscillator strengths. The resulting spectra then were used to generate photolytic lifetimes by using the one-dimensional Caltech/Jet Propulsion Laboratory photochemical model for the terrestrial mesosphere and lower thermosphere (18, 19). The times for e^{-1} folding are shown in Table 3. Given the crude way the lifetimes were computed, they must be regarded as order-of-magnitude results. The lifetime of the reference molecule CF$_2$Cl$_2$ computed by our model is 96 years.

Discussion

The initial warming of Mars and volatilizing its polar caps remains a major problem. Investigators have suggested engineering solutions such as a large reflecting solar sail over the Martian north pole (see reviews in refs. 1 and 2).

Relative to the difficulty of increasing the volatiles on the Martian surface, the task of maintaining them at an Earth-like temperature would seem easy. Our work should be refined with a multilayered radiative-transfer model, and specific absorption line-spacings and -strengths used. If we have overestimated bandwidths, the strategy of choice would not be to increase column amounts but to include another gas with a strong vibrational fundamental near 10.25 μm (the clearest spectral region in the presence of a terrestrial atmosphere and "our" gas mixture).

Although the lifetimes in Table 3 look long, they imply that the greenhouse gases considered here would require replenishment at a rate of nearly 400 kilotons per year to offset photolysis. Because the lifetimes in Table 3 were modeled at 1 astronomical unit from the sun, it would be plausible to multiply those lifetimes by 2.3, reducing the annual requirement to 170 kilotons. In either case, the rate compares very favorably with the 3-teraton annual rate of CFC production mentioned in ref. 1, which was based on a recognition that CFCs would destroy any ozone layer.

Fluorine on Mars would have to be mined locally. For comparison, South African export of acid-grade fluorspar was 470 kilotons in 1980 but then receded somewhat because of weak commodity markets (20). It takes 2.2 tons of acid-grade fluorspar to produce a ton of HF, and the majority of the weight of the gases we are discussing is the fluorine weight. Even though
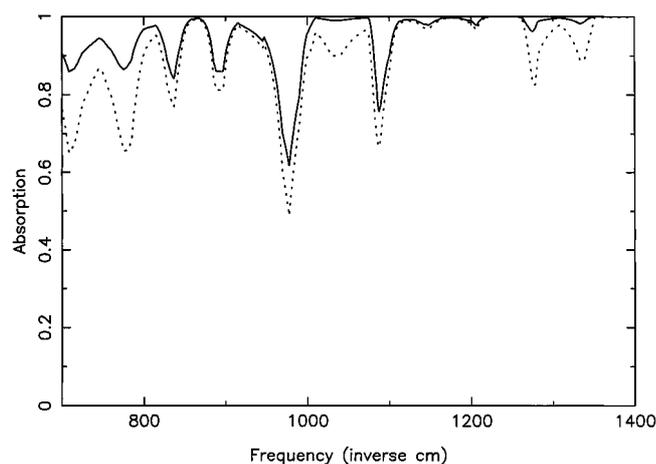
the bulk composition of Mars may be richer in fluorine than that of Earth's (8), whether the element can be found there in sufficient concentrations is unknown.

Considering the likely 3% rms error in band-center frequencies, our solution is presented as an example, not a prescription. During the course of our own calculations, we had selected some other gases at various times as members of our optimal subset (CF$_3$SCF$_3$, CF$_3$OCF$_2$OCF$_3$, CF$_3$SCF$_2$SCF$_3$, CF$_3$OCF$_2$NFCF$_3$). With our final set, a judicious shift of just two strong band centers by 30 cm^{-1} in opposite directions increases the manufacturing requirement by almost 15%. Here again, the best response to an unexpected window in the true spectrum of the gases, when all have been synthesized, would be to identify an additional gas to fill the window.

A secondary implication of our findings is a reminder that the current terrestrial warming scare or controversy may be too fixated on the likelihood of CO$_2$ doubling, when the greater danger may be from new trace gases with strong absorption bands in the window such as SF$_5$CF$_3$, which is observed in the Earth's atmosphere (14).

A more speculative corollary is that advanced extrasolar civilizations, if they exist, already may have engineered planetary environments in zones we would consider inhospitably cold. Therefore, searches for extraterrestrial intelligence, which now mainly seek radio waves, should perhaps include looking for spectra of manufacturable molecules such as those mentioned here.

Speculations on planetary environmental engineering have considered most often materials found in nature or materials already engineered for some terrestrial purpose. We have taken the next step by including consideration of some materials not found in nature and not previously manufactured. Our methods of investigating these materials are not in themselves novel; nor would we want them to be, preferring to build our argument on accepted foundations.

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