

Fig. 1 Six IR bursts from the source Liller I/MXB1730 – 333, the rapid burster. Note the composite structure of burst number 6; the two components are designated a and b. The ordinate numbers are in units of  $10^{-16}\,W\,cm^{-2}\,\mu m^{-1}.$ 

output was linearly integrated for 6 s. The measurements reported here were made with an H-filter (λ peak 1.6 μm, half width 0.3 µm, maximum transmission ~75%). Several standard IR sources were observed before the observation of Liller I.

The steady IR flux from Liller I was observed and its magnitude calculated as  $m_{\rm H} = 7.5 \pm 0.4$  using a nearby star IRC-30317 for calibration. Kleinmann et al. have reported  $m_{\rm H} = 6.4$ for Liller I using 24 arc s beam size and 90 arc s chopper throw. The present measurement has (1) a smaller beam and (2) a smaller chopper throw. Taking the flux distribution of Liller I as given by Kleinmann et al.<sup>7</sup> we estimate that our measurement will be higher by  $m_{\rm H} = 0.54$ . After accounting for (1) and (2) above and subtracting 0.54 from our  $m_{\rm H}$  value, it is still higher by  $0.56 \pm 0.4$  than the flux value given by Kleinmann et al.<sup>7</sup>.

Six IR bursts detected during the 2.5 h observing time are shown in Fig. 1. The details of the time of occurrence, rise time, duration, FWHM, peak intensity and energy in the bursts are summarised in Table 1. Kleinmann et al.<sup>7</sup> have given interstellar extinction in the K-band  $A_k = 1.1$  mag for Liller I. Assuming an inverse wavelength dependence for extinction, we estimate  $A_{\rm H} = 1.4$  mag. While calculating peak luminosity and energy we have subtracted  $A_{\rm H} = 1.4$  mag from observed  $m_{\rm H}$  values. The energy in the bursts is estimated by integrating the area under the burst profiles and assuming a distance of 10 kpc to the object3. Note the close similarity of the various characteristics of the successive IR bursts. They seem to rise rapidly in a time period of nearly 2 s and decay gradually over time of about 30 s. Note that burst number 6 is composed of two bursts, the characteristics of which are separately given in Table 1. The occurrence of burst numbers 3, 4 and 5, 6 in rapid succession  $(\sim 150 \text{ s})$  may be significant.

The remarkably close similarity of the rise time, duration and gradual decay of intensity of the IR bursts with the corresponding characteristics of type-I X-ray bursts<sup>3,4</sup> strongly indicate the

association between the two. The low rate of occurrence of the IR bursts accords with this association.

The observed IR emission from the bursts is unlikely to be of black body type. If a region of 2 light seconds in size is assumed then the peak burst luminosity implied a brightness temperature of  $7 \times 10^7$  K at 1.6  $\mu$ m if the radiation were thermal. This is greater than the X-ray burst temperature and would imply a much greater total luminosity.

The observations of the rapid burster at the X-ray and IR wavelengths suggest that there could be emission of burst radiation at all intermediate wavelengths. It is likely that in spite of large interstellar extinction the optical bursts from the rapid burster would be detected. It will also be interesting to observe other X-ray burst sources at different IR wavelengths.

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> P. V. KULKARNI N. M. ASHOK

Physical Research Laboratory, Ahmedabad 380009, India

> KRISHNA M. V. APPARAO S. M. CHITRE

Tata Institute of Fundamental Research, Bombay 400005, India

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## Possible chemical impact of planetary lightning in the atmospheres of Venus and Mars

THE importance of lightning as a source of trace gases in the Earth's atmosphere has long been recognised. In 1827, von Liebig proposed lightning as a source of atmospheric fixed nitrogen1 and recent investigations have supported this hypothesis<sup>2-7</sup>. In the Earth's pre-biological atmosphere lightning may have produced organic molecules, such as HCN, which led to the evolution of life8. After life evolved, but before photosynthesis and biological nitrogen fixation developed, lightning may have provided an abiotic source of organic C and fixed N to the growing biota<sup>9,10</sup>. The presence of cloud layers on Venus<sup>11</sup> and synoptic scale dust storms on Mars<sup>12</sup> suggest that lightning may also occur on these planets, and indeed there have been reports of lightning being detected on Venus by American and Soviet spacecraft. The implications for atmospheric chemistry of lightning on Venus and Mars are discussed here.

The production of gases by an electrical discharge involves high-temperature chemical reactions in and around the discharge channel<sup>13</sup>; the air around the channel is heated by the radially propagated shock wave. As the temperature, T, of the heated air decreases at some rate characterised by a cooling time,  $\tau_T(T)$ , a species X may attain a final concentration in

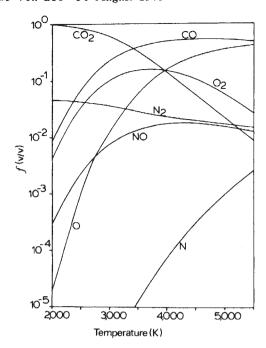


Fig. 1 Equilibrium mixing ratios of CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, O, NO and N as a function of temperature in heated Cytherean air. To obtain these results, the equilibrium abundances of the 24 species previously listed plus S, S<sub>2</sub>, S<sub>2</sub>O, SO, SO<sub>2</sub>, SO<sub>3</sub>, COS, CS<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> were determined as a function of temperature using the thermochemical data from the JANAF tables <sup>14</sup>. Ambient conditions were chosen for an altitude of 55 km, the lower cloud region; ambient  $T=310~{\rm K}$  (ref. 15), ambient CO<sub>2</sub>=0.66 atm, N<sub>2</sub>=0.032 atm, SO<sub>2</sub>=1.4×10<sup>-4</sup> atm, O<sub>2</sub>=4×10<sup>-5</sup> atm, H<sub>2</sub>O=4×10<sup>-4</sup> atm, and  $\rho=1.2~{\rm kg~m}^{-3}$  (ref. 16).

excess of its ambient value, thus leading to a net production of X. The final concentration of X is approximated by the equilibrium concentration  $f_{\mathbf{x}}^{\mathbf{x}}(T_{\mathbf{F}}(X))$  (v/v) at  $T_{\mathbf{F}}(X)$ , the 'freeze-out' temperature for X.  $T_{\mathbf{F}}$  is given by the temperature at which

$$\tau_{\mathbf{x}}(T_{\mathbf{F}}(X)) = \tau_{\mathbf{T}}(T_{\mathbf{F}}(X)) \tag{1}$$

where  $\tau_x$  is the chemical lifetime of species X. When  $T > T_F$ , then  $\tau_x < \tau_T$  and the chemical reactions are sufficiently rapid to keep X in thermochemical equilibrium. However, for  $T < T_F$ ,  $\tau_x > \tau_T$  and chemical reactions are too slow to adjust to the rapidly decreasing T; X, therefore, 'freezes-out' with mixing ratio  $f_x^\circ(T_F(X))$ . While a lower abundance in X is favoured thermodynamically at low T, the kinetics are too slow for readjustment. P, the net yield of X due to this process, is approximated by

$$P(X) \simeq \frac{f_{x}^{\circ}(T_{F})M(E_{0}, T_{F}(X))}{E_{0}} \quad \text{(molecules J}^{-1}\text{)}$$
 (2)

where M is the number of molecules per metre heated to or above  $T_F$  in the region where X is being produced, and  $E_0$  is the discharge energy (in J m<sup>-1</sup>). Generally,  $T_F$  is between 1,000 and 5,000 K.

Figure 1 illustrates the thermochemical equilibrium concentrations of several species of interest for air in the cloud layer of Venus heated to temperatures of 2,000-5,500 K, for  $A=\rho/\rho_0=1$  where  $\rho$  is the mass density within the heated air and  $\rho_0$  is the ambient mass density. The variation of martian equilibrium composition with temperature is quite similar to that of Venus. For both planets we find significant enhancements of CO, O<sub>2</sub>, NO and O for T>2,000 K, indicating that these species may be produced by lightning on Venus and Mars. Production of these gases by lightning could have significant implications for the

chemistry and evolution of the atmospheres of Venus and Mars and needs, therefore, to be investigated.

Whether lightning does, in fact, produce trace species depends on the cooling characteristics of the discharge; an estimate of the source rates requires knowledge of the energy properties and the frequency of planetary lightning. Thus, a reliable prediction of the chemical impact of lightning on Venus and Mars will have to await appropriate observations. However, we estimate the source rates by assuming that lightning of Venus is similar to that on Earth, as an illustration.

The source rates of CO, O2, NO, and O on Venus with Earth-like lightning are estimated using an earlier reported method<sup>7</sup>;  $\tau_T(T)$  and  $M(T, E_0)$  are calculated from Lin's<sup>17</sup> differential equations describing a cylindrical shock wave. Yields predicted by this method for NO, N2O and CO in discharges in present atmospheric conditions have compared favourably with laboratory experiments<sup>4,7,18</sup>. The shock wave differential equations are solved with a specific heat ratio,  $\gamma = 1.16$ , appropriate to a CO<sub>2</sub> atmosphere at temperatures between 1,500 K and 5,000 K<sup>19</sup>. As these equations indicate that, for the temperature region of interest,  $1 \le A = \rho/\rho_0 \le 10$ ,  $f_x^{\circ}$  and  $\tau_x$  are determined for A=1 and 10 as limiting values. Finally, as CO<sub>2</sub>, which comprises about 95% of the ambient atmosphere, is significantly dissociated at temperatures above 2,000 K, stoichiometrically it follows that virtually all O atoms in our system must originate from CO2 dissociation and we therefore require that  $P(CO) = P(NO) + 2P(O_2) + P(O)$ .

Using the earlier method

$$\tau_{\rm T}(T) \sim \left(\frac{1}{T(R)} \frac{{\rm d}T(R)}{{\rm d}t}\right)^{-1} = \frac{5.7 \times 10^{-5} E_0^{1/2}}{\rho_0^{1/2} T}$$
 (s) (3)

for  $\gamma=1.16$ , where R is the shock front radius, and t is time. For  $E_0\sim 10^5~\rm J~m^{-1}$ , as on Earth<sup>20</sup>, and  $\rho_0=1.2~\rm kg~m^{-3}$  at 55 km, the lower portion on Venus' cloud layer,  $\tau_{\rm T}\sim (5-7)\times 10^{-6}~\rm s$  for  $2,500\leqslant T\leqslant 5,000~\rm K$ , as depicted in Fig. 2. Figure 2 also shows  $\tau_{\rm CO}$ ,  $\tau_{\rm O2}$  and  $\tau_{\rm NO}$ . Using equation (1) to determine  $T_{\rm F}$ , Fig. 2 indicates that CO freezes-out first; for A=1,  $T_{\rm F}({\rm CO})=5,500~\rm K$  with  $f_{\rm CO}^{\rm c}(5,500~\rm K)=0.5$  and for A=10,  $T_{\rm F}({\rm CO})=3,500~\rm K$  with

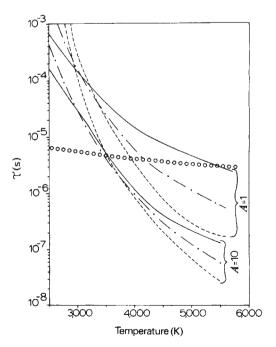


Fig. 2 Temperature dependence of the cooling time,  $\tau_{\rm T}$  (OO), and chemical lifetimes;  $\tau_{\rm CO}$  (———),  $\tau_{\rm O2}$  (—·—); and  $\tau_{\rm NO}$  (-——) for A=1 and 10 where  $A=\rho/\rho_0$ . The chemical lifetimes were determined from densities taken from the thermochemical equilibrium calculations and the appropriate kinetic data  $^{21.22}$ .

Table 1 Estimated production rates for Earth-like lightning on Venus

Species	$f_{\mathbf{x}}^{\circ}(T_{\mathbf{F}}(X))^*$ $(\mathbf{v}/\mathbf{v})$		$P(X)$ (molecules $J^{-1}$ )		$S(X)^{\dagger}$ (molecules cm <sup>-2</sup> s <sup>-1</sup> )	
	A = 1	A = 10	A = 1	A = 10	A = 1	A = 10
CO O <sub>2</sub>	0.50 0.16	0.26 0.12	$1.4 \times 10^{17}$ $4.5 \times 10^{16}$	$1.1 \times 10^{17}$ $5 \times 10^{16}$	$1.4 \times 10^{10}$ $4.5 \times 10^{9}$	$1.1 \times 10^{10}$ $5 \times 10^{9}$
NO O	0.018 0.16	0.013 0.018	$5 \times 10^{15}$ $4.5 \times 10^{16}$	$6 \times 10^{15}$ $0.8 \times 10^{16}$	$5 \times 10^{8}$ $4.5 \times 10^{9}$	$6 \times 10^{8}$ $0.8 \times 10^{9}$

\* For cooling time characterised by  $E_0=10^5$  J m $^{-1}$ ,  $\rho=1.2$  kg m $^{-3}$ . † For  $10^{-7}$  W cm $^{-2}$  dissipated by lightning.

 $f_{CO}^{\circ}(3,500 \text{ K}) = 0.26$ . For  $\gamma = 1.16$ , Lin's quations yield

$$M(T_{\rm F}, E_0) = \frac{1.55 \times 10^{21}}{T_{\rm F}} E_0 \quad \text{(molecules m}^{-1}\text{)}$$
 (4)

and, substituting equation (4) into equation (2),  $P(CO) \sim (1.1 1.4)\times10^{17}$  molecules J<sup>-1</sup>

The yields of O<sub>2</sub>, NO and O are controlled by the CO kinetics. As CO<sub>2</sub> dissociation is the only source of O atoms, O<sub>2</sub>, NO and O cannot be produced outside the CO-producing region. In the CO-producing region, the equilibrium abundances and chemical lifetimes of  $O_2$ , NO and O below  $T_F(CO)$  may be determined from the thermochemical calculations with the CO abundance set at  $f_{CO}^{\circ}(T_{F}(CO))$ . The final number of  $O_{2}$ , NO and O molecules or atoms produced is then given by their respective freezeout abundances multiplied by  $M(T_F(CO), E_0)$ , the numbers of molecules heated to or above  $T_{\rm F}({\rm CO})$ . We find that  ${\rm O}_2$  and NO freeze-out at approximately the same temperature; for A = 1,  $T_F(O_2) \sim T_F(NO) \sim 4{,}000 \text{ K}$ , and for A = 10,  $T_F(O_2) \sim$  $T_{\rm F}({\rm NO}) \sim 3{,}300~{\rm K}$ . The final concentration of O, which freezesout at a lower T, is determined by conservation of oxygen. Table 1 summarises the estimated final abundances of the species and their yields, and also indicates the resulting global source rates, S, obtained by assuming that lightning on Venus, as on Earth, dissipates about 10<sup>-7</sup> W cm<sup>-2</sup>

Before this study it was believed that O, O<sub>2</sub> and CO were produced exclusively above the clouds by photochemistry<sup>23,24</sup>. Downward transport is thought to supply the lower atmosphere with O<sub>2</sub> and CO and thereby fuel the conversion of S and SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O particles and SO<sub>2</sub> to liquid S, components of the clouds of Venus<sup>25-29</sup>. Photochemical models<sup>23</sup> estimate downward fluxes at 62 km of  $1.4 \times 10^{12}$  CO molecules cm<sup>-2</sup> s<sup>-1</sup> and  $5.5 \times 10^{11}$  O<sub>2</sub> molecules cm<sup>-2</sup> s<sup>-1</sup>. Comparison with the numbers in Table 1 indicates that, if lightning on Venus were similar to that on Earth, it would contribute a small, additional, local source of CO and O<sub>2</sub> to augment the upper atmospheric source. However, if lightning on Venus were 100 times more energetic or frequent, and this is certainly a possibility, the CO and O<sub>2</sub> discharge sources would be comparable with the downward transport source and thus could have a key role in maintaining the clouds. If in the 55 km region SO<sub>2</sub> is about 100 p.p.m. (ref. 16), the major sink for lightning-produced O is probably  $O + SO_2 + M \rightarrow SO_3 + M$ , further augmenting  $SO_4^{2-}$  production.

While we predict 2-3 times more CO production than O<sub>2</sub> production by lightning, Oyami et al. 16 found at least 60 times more O2 than CO in the lower atmosphere of Venus. However, note that the abundance of an atmospheric constituent is a function of both the loss and source terms. In the terrestrial atmosphere, for example, CO is considerably more reactive than O<sub>2</sub> and thus, while the O<sub>2</sub> source is only 100 greater than that of CO<sup>30,31</sup>, the O<sub>2</sub> abundance is 10<sup>6</sup> greater than the CO concentration. While a similar effect may cause the apparent enhancement of O<sub>2</sub> relative to CO on Venus, complete photochemical model calculations which include all the relevant sources and sinks are needed to explain the observed composition of the atmosphere of Venus.

The production of NO by lightning may result in the formation of HNO<sub>2</sub> and HNO<sub>3</sub> and thus imply the trace presence of  $NO_2^-$  and  $NO_3^-$  in the clouds. The  $NO_2^-$  and  $NO_3^-$  are probably removed in precipitation and may either be recycled back to N<sub>2</sub> or remain on the surface. For the NO yield obtained, the time to

consume atmospheric N<sub>2</sub> is about 5 billion years and thus, in the absence of recycling, roughly equal amounts of nitrogen would reside in the atmosphere and lithosphere. A similar effect on Mars could help to explain the apparent deficiency of nitrogen on this planet relative to Earth. However, on Mars we find rather low yields for lightning with energies of 10<sup>5</sup> J m<sup>-1</sup> and cooling rates of about  $10^{-6}$  s; the thin martian atmosphere leads to slow chemical reaction rates, high freeze-out temperatures, and low chemical yields. For lightning on Mars to lead to significant chemical production cooling times of 0.01-1.0 s are required which, according to equation (3), would imply extremely energetic discharges.

We find that lightning, if present, may produce CO, O<sub>2</sub>, NO and O in the atmospheres of Venus and Mars. Calculations for lightning on Venus indicate that this process could conceivably influence the atmospheric nitrogen budget and the sulphur chemistry that maintains the Venus cloud layer. A final determination of the chemical role of planetary lightning, however, will have to await systematic observations of the presence and properties of electrical discharges on Venus and Mars.

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Note added in proof: Since completion of this work, documentation of the evidence for lightning on Venus gathered by American and Soviet spacecraft has appeared<sup>32,33</sup>, further emphasising the potential importance of planetary lightning.

W. L. CHAMEIDES

Department of Physics and Astronomy, University of Florida, Gainesville, Florida 32611

J. C. G. WALKER

National Astronomy and Ionosphere Center, Arecibo, Puerto Rico 00612

A. F. NAGY

Department of Atmospheric and Oceanic Science, University of Michigan, Ann Arbor, Michigan 48109

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