CO_2^+ DAYGLOW ON MARS AND VENUS

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Abstract. Quantitative calculations are presented of the intensities of the CO_2^+ bands present in the dayglows of Mars and Venus and it is argued that fluorescent scattering by CO_2^+ ions and photoionization of CO_2 are the main sources of excitation. An estimate is made of the intensity of 3914 Å emission that would arise if the atmosphere contained N_2.

1. Introduction

The ground-based observations of Kozyrev (1954) indicate the occurrence of the $(\mathbf{X}^2\Pi_g - \mathbf{A}^2\Pi_u)$ emission bands of CO_2^+ in the dayglow of Venus (Polyakova *et al.*, 1963) and the Mariner 6 observations of Barth *et al.* (1969) have established that the $(\mathbf{X}^2\Pi_g - \mathbf{A}^2\Pi_u)$ and $(\mathbf{X}^2\Pi_g - \mathbf{B}^2\Sigma_u^+)$ emission bands are important components of the dayglow of Mars. The excited $\mathbf{A}^2\Pi_u$ and $\mathbf{B}^2\Sigma_u^+$ levels of CO_2^+ can be populated by direct photoionization of CO_2 by solar radiation

$$CO_2 + h\nu \rightarrow CO_2^+(\mathbf{A}^2\Pi_u, \mathbf{B}^2\Sigma_u^+) + e \tag{1}$$

by fluorescent scattering of solar radiation by pre-existing CO_2^+ ions

$$CO_2^+ (\mathbf{X}^2\Pi_g) + h\nu \rightarrow CO_2^+ (\mathbf{A}^2\Pi_u, \mathbf{B}^2\Sigma_u^+) \tag{2}$$

and by simultaneous excitation and ionization of CO_2 by photoelectron impact

$$e + CO_2 \rightarrow e + CO_2^+ (\mathbf{A}^2\Pi_u, \mathbf{B}^2\Sigma_u^+) + e. \tag{3}$$

In this paper we shall investigate each of the three mechanisms and calculate their contributions to the CO_2^+ dayglow on the planets Mars and Venus.

2. Photoionization of CO_2

Cross sections for the absorption of radiation by CO_2 have been measured by Tanaka *et al.* (1960), by Tanaka and Ogawa (1962), by Nakata *et al.* (1965), by Cook *et al.* (1966) and by Dibeler and Walker (1967).

Photons of wavelengths λ shorter than 902 Å can ionize CO_2 leaving CO_2^+ in its ground electronic state

$$CO_2 + h\nu(\lambda < 902 \text{ Å}) \rightarrow CO_2^+(\mathbf{X}^2\Pi_g) + e. \tag{4}$$

For $\lambda < 716$ Å, it is energetically possible to populate also the first excited state of CO_2^+ in a photoionizing transition

$$CO_2 + h\nu(\lambda < 716 \text{ Å}) \rightarrow CO_2^+(\mathbf{A}^2\Pi_u) + e \tag{5}$$

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and for $\lambda < 687$ Å the second excited state

$$CO_2 + h\nu(\lambda < 687 \text{ Å}) \rightarrow CO_2^+(\mathbf{B}^2\Sigma_u^+) + e. \tag{6}$$

For wavelengths shorter than 640 Å, it is possible to produce CO_2^+ ions in the third excited state

$$CO_2 + h\nu(\lambda < 640 \text{ Å}) \rightarrow CO_2^+ (\mathbf{C}^2\Sigma_g^+) + e. \tag{7}$$

The total photoionization cross sections for CO_2 have been measured by Nakata *et al.* (1965), by Cairns and Samson (1965), by Cook *et al.* (1966), and by Dibeler and Walker (1967), and the branching ratios appropriate to the $\mathbf{X}^2\Pi_g$, $\mathbf{A}^2\Pi_u$, $\mathbf{B}^2\Sigma_u^+$, and $\mathbf{C}^2\Sigma_g^+$ states of CO_2^+ have been measured by Bahr *et al.* (1969).

If we assume tentatively that the neutral components of the atmospheres of Mars and Venus are effectively pure CO_2, the total rates of population of the electronic levels of CO_2^+ by photoionization can be calculated directly from the cross section data and the incident solar flux. Our adopted solar flux is based on the 1967 measurements reported by Hinteregger (1970) for which the solar 10.7 cm flux was $F_{10.7} = 144$. We scaled these data appropriately for Mars and Venus and for the 10.7 cm flux $F_{10.7} = 162$, adjusted for burst, that was measured at the time of the Mariner 6 flight past Mars.

The results for Mars and for Venus are presented in Table IA and IB respectively for various solar zenith angles Z. The table contains the rates of population in a vertical column. If no deactivation or cascading occurred, the rates would be also the emission intensities in photons cm^{-2} sec^{-1}. Deactivation of the $\mathbf{A}^2\Pi_u$ and $\mathbf{B}^2\Sigma_u^+$ states is

TABLE IA

Total production rates of CO_2^+ states by photoionization on Mars in units of 10^9 cm^{-2} sec^{-1} at various solar zenith angles Z°

Z	$\mathbf{X}^2\Pi_g$	$\mathbf{A}^2\Pi_u$	$\mathbf{B}^2\Sigma_u^+$	$\mathbf{C}^2\Sigma_g^+$
0	6.3	2.8	4.9	1.5
30	5.5	2.4	4.2	1.3
50	4.1	1.8	3.2	0.9
60	3.2	1.4	2.4	0.7
70	2.2	1.0	1.7	0.5
80	1.1	0.5	0.9	0.3

TABLE IB

Total production rates of CO_2^+ by photoionization on Venus in units of 10^9 cm^{-2} sec^{-1} at various solar zenith angles Z°

Z	$\mathbf{X}^2\Pi_g$	$\mathbf{A}^2\Pi_u$	$\mathbf{B}^2\Sigma_u^+$	$\mathbf{C}^2\Sigma_g^+$
0	25.0	11.2	19.4	6.5
30	21.7	9.7	16.8	5.7
50	16.1	7.2	12.4	4.2
60	12.5	5.6	9.7	3.3
70	8.6	3.8	6.6	2.2
80	4.4	1.9	3.4	1.1

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negligible since the radiative lifetimes are about 10^{-7} sec (Schwenker, 1965; Anton, 1966; Hesser, 1968) but the $\mathbf{C}^2\Sigma_g^+$ state decays to both the $\mathbf{A}^2\Pi_u$ and $\mathbf{B}^2\Sigma_u^+$ states giving rise to emission in the red and infrared region of the spectrum.

We assume arbitrarily that the branching ratio for cascade into the $\mathbf{A}^2\Pi_u$ and $\mathbf{B}^2\Sigma_u^+$ states is 4:1. The predicted intensities in kilorayleighs of the $\mathbf{X}^2\Pi_g - \mathbf{A}^2\Pi_u$ and $\mathbf{X}^2\Pi_g - \mathbf{B}^2\Sigma_u^+$ emission systems are given in Table II.

TABLE II

Predicted intensities in kilorayleighs of the $\mathbf{X}^2\Pi_g - \mathbf{A}^2\Pi_u$ and $\mathbf{X}^2\Pi_g - \mathbf{B}^2\Sigma_u^+$ band systems resulting from photoionization on Mars and Venus at various solar zenith angles $Z°$

Mars			Venus	
Z	$\mathbf{A}^2\Pi_u$	$\mathbf{B}^2\Sigma_u^+$	$\mathbf{A}^2\Pi_u$	$\mathbf{B}^2\Sigma_u^+$
0	4.0	5.2	15.8	20.5
30	3.5	4.5	13.7	17.8
50	2.6	3.4	10.2	13.2
60	2.0	2.6	7.9	10.3
70	1.4	1.8	5.4	7.0
80	0.7	0.9	2.7	3.6

3. Fluorescent Scattering by CO_2^+

The rate of population for each molecular ion of CO_2^+ by fluorescent scattering is given by

$$g = 8.85 \times 10^{-21} If\lambda^2 \text{ sec}^{-1}, \tag{8}$$

where I is the solar continuum intensity at the absorption wavelength λ Å measured in photons sec^{-1} Å^{-1} and f is the band oscillator strength. For the lifetime of the $\mathbf{A}^2\Pi_u$ state, Schwenker (1965) has measured a value of 1.39×10^{-7} sec and Hesser and Dressler (1966) and Hesser (1968) a value of 1.1×10^{-7} sec. The values are in harmony with that derived by Anton (1966) from pressure quenching measurements. The system oscillator strength corresponding to a lifetime of 1.1×10^{-7} sec is $f = 1.5 \times 10^{-2}$. Taken in conjunction with the relative probabilities of Poulizac and Dufay (1967) and the solar fluxes at the band heads, this oscillator strength gives a g value for the $\mathbf{A}^2\Pi_u$ population of 1.1×10^{-2} at Mars and 4.9×10^{-2} at Venus.

For the $\mathbf{B}^2\Sigma_u^+$ state of CO_2^+, Hesser and Dressler (1966) and Hesser (1968) have measured a lifetime of 1.19×10^{-7} sec consistent with an absorption oscillator strength of 5.3×10^{-3}. The corresponding g value at Mars is 1.2×10^{-3} and the g value at Venus is 5.2×10^{-3}. In making these estimates of scattering efficiencies, Fraunhofer absorption has been ignored.

If we assume tentatively that the ionic components of the atmospheres are pure CO_2^+, the total rates of emission of the two CO_2^+ band systems can be calculated directly from the measured electron densities. For Mars, the total electron content derived from Mariner 4 occultation data was about 4.2×10^{11} cm^{-2} for a solar zenith angle of 67° (Fjeldbo *et al.*, 1966, Fjeldbo and Eshleman, 1968) and from Mariner 6 data it was about 1.2×10^{12} cm^{-2} for a solar zenith angle of 56° (Fjeldbo *et al.*, 1969). For Venus the total electron content derived from Mariner 5 occultation data was about 1.6×10^{12} cm^{-2} for a solar zenith angle of 33° (Kliore *et al.*, 1967).

The measured Venus ionization profile is consistent with a pure CO_2 atmosphere and dissociative recombination of CO_2^+ (McElroy, 1969). We have extended the equilibrium calculations of McElroy (1969) to other zenith angles and we obtain the total ionization contents of Table III, scaled linearly to that observed at 33°.

TABLE III

Total ionization content in 10^{11} cm^{-2} on Mars and Venus at various solar zenith angles Z°

Mars			Venus
Z	Mariner 4	Mariner 6	Mariner 5
0	6.4	15.1	17.7
30	6.0	14.1	16.8
50	5.2	12.4	14.7
60	4.8	11.2	13.2
70	3.9	9.4	11.2
80	3.0	7.3	8.4

We adopt a similar model for Mars, but scaled linearly to the observed total electron contents at 56° or 67°. The corresponding ionization contents on Mars at various solar zenith angles are included in Table III. The linear scaling procedure is an arbitrary one.

The contributions to the $\mathbf{X}^2\Pi_g - \mathbf{A}^2\Pi_u$ and $\mathbf{X}^2\Pi_g - \mathbf{B}^2\Sigma_u^+$ emission intensities from fluorescent scattering by CO_2^+ are given in kilorayleighs in Table IV.

TABLE IV

Predicted intensities in kilorayleighs of the $\mathbf{X}^2\Pi_g - \mathbf{A}^2\Pi_u$ and $\mathbf{X}^2\Pi_g - \mathbf{B}^2\Sigma_u^+$ band systems resulting from fluorescent scattering on Mars and Venus at various solar zenith angles Z°. The CO_2^+ contents are based upon the Mariner 5 and Mariner 6 data

Mars			Venus	
Z	$\mathbf{A}^2\Pi_u$	$\mathbf{B}^2\Sigma_u^+$	$\mathbf{A}^2\Pi_u$	$\mathbf{B}^2\Sigma_u^+$
0	15.9	1.8	86.7	8.8
30	15.3	1.6	82.3	8.4
50	13.9	1.5	72.0	7.3
60	12.3	1.3	64.6	6.6
70	10.2	1.0	55.2	5.7
80	7.6	0.9	41.1	4.2

4. Electron Impact Excitation

The photoelectrons produced by photoionization lose energy through excitation and ionization of CO_2 and by elastic collisions with the ambient electrons. Some fraction of the ionizations leaves CO_2^+ in excited states. Precise predictions would involve detailed studies of the energy degradation of the photoelectrons of the kind carried out for the earth by Green and Barth (1967) and by Dalgarno *et al.* (1969). We can easily demonstrate however that photoelectron impact is a comparatively small source of population of the $\mathbf{A}^2\Pi_u$ and $\mathbf{B}^2\Sigma_u^+$ states of CO_2^+ on Mars and Venus.

The thresholds for ionization to the $\mathbf{X}^2\Pi_g$, $\mathbf{A}^2\Pi_u$, and $\mathbf{B}^2\Sigma_u^+$ states occur at respectively 13.8 eV, 17.3 eV, and 18.1 eV. The energy flux of photoelectrons with energies greater than 17.3 eV is about 3.8×10^{11} eV cm^{-2} sec^{-1} on Mars and about 1.5×10^{12} eV cm^{-2} sec^{-1} on Venus for the sun at zenith. For fast electrons absorbed by CO_2 the mean energy per ion pair is about 35 eV, a value which must increase ultimately with decreasing initial electron energy. Thus the number of ionizations produced by electrons with energies in excess of 17.3 eV does not exceed 1.1×10^{10} cm^{-2} sec^{-1} on Mars and does not exceed 4.3×10^{10} cm^{-2} sec^{-1} on Venus. According to McConkey *et al.* (1968), the excitation functions of the $\mathbf{A}^2\Pi_u$ and $\mathbf{B}^2\Sigma_u^+$ states are similar in shape to the total ionization function (Rapp and Englander-Golden, 1965), the ratios being approximately 1/5 and 1/15 respectively. The corresponding upper limits to the $\mathbf{X}^2\Pi_g-\mathbf{A}^2\Pi_u$ and $\mathbf{X}^2\Pi_g-\mathbf{B}^2\Sigma_u^+$ emission intensities are respectively 2 kR and 700 kR on Mars and 9 kR and 3 kR on Venus, all values referring to $Z=0°$.

The actual intensities may be of the order of half the upper limits. The estimated intensities from photoelectron impact are given in Table V for various solar zenith angles.

TABLE V

Estimated[a] intensities in kilorayleighs of the $\mathbf{X}^2\Pi_g-\mathbf{A}^2\Pi_u$ and $\mathbf{X}^2\Pi_g-\mathbf{B}^2\Sigma_u^+$ band systems resulting from photoelectron impacts on Mars and Venus at various solar zenith angles $Z°$

Mars			Venus	
Z	$\mathbf{A}^2\Pi_u$	$\mathbf{B}^2\Sigma_u^+$	$\mathbf{A}^2\Pi_u$	$\mathbf{B}^2\Sigma_u^+$
0	1.1	0.4	4.3	1.4
30	0.9	0.3	3.7	1.2
50	0.7	0.2	2.8	0.9
60	0.5	0.2	2.1	0.7
70	0.4	0.1	1.5	0.5
80	0.2	0.1	0.7	0.2

[a] Upper limits are obtained by doubling the entries. The ratio of *any* pair of entries is much more accurate than the individual entries.

5. Comparison with Mars Observations

Table VI summarizes the contributions from the three sources for Mars at a solar zenith angle of 30°. Photoionization and fluorescence scattering are important sources for both transitions. Photoionization is more important for one system and fluorescence scattering for the other. Fluorescence scattering assumes a larger role for both planets with increasing solar zenith angle and it is relatively more important on Venus than on Mars.

Photoelectron impact contributes not more than 5% to either transition on either planet at any solar zenith angle. Barth *et al.* (1969) have remarked that their Mars

TABLE VI

Theoretical intensities in kilorayleighs of the $X^2\Pi_g - A^2\Pi_u$ and $X^2\Pi_g - B^2\Sigma_u^+$ band systems resulting from photoionization, fluorescence scattering and photoelectron impact on Mars at 30° solar zenith angle

System	$X^2\Pi_g - A^2\Pi_u$	$X^2\Pi_g - B^2\Sigma_u^+$
Photoionization	3.5	4.5
Fluorescence scattering	15.3	1.6
Photoelectron impact	0.9	0.3
Total	19.7	6.4

spectrum is similar to that produced in the laboratory by the bombardment of CO_2 with electrons of 20 eV energy. According to the cross section data of McConkey *et al.* (1968), the ratio of system intensities produced by 20 eV electrons is somewhat greater than 3 consistent with our predicted ratio on Mars at 30° of 3.1, produced by a combination of photoionization and fluorescence scattering.

Our ratio refers to the total intensities, whereas the measurements of Barth *et al.* (1969) give the intensities above particular altitudes. If we have correctly identified the excitation mechanisms, the ratio of the intensity of the $X^2\Pi_g - A^2\Pi_u$ system to that of the $X^2\Pi_g - B^2\Sigma_u^+$ system should increase with increasing altitude because photoionization decreases with the scale height of the neutral atmosphere and fluorescent scattering decreases with the scale height of the ionized component (if the major ion remains CO_2^+). A detailed study of the Mars data of Barth *et al.* (1969) may provide a test of the solar wind model of Cloutier *et al.* (1969).

The increasing importance of fluorescent scattering with increasing altitude should be reflected also in a changing vibrational distribution within the $X^2\Pi_g - A^2\Pi_u$ electronic transition.

6. Vibrational Distributions

Measurements of photoionization cross sections of CO_2 in which the individual vibrational levels of the product electronic state are resolved have been carried out by Turner and May (1967) and by Spohr and Puttkamer (1967) for a wavelength of 584 Å. The values for the $A^2\Pi_u$ state decrease more slowly with increasing ν' than do the theoretical Franck-Condon factors of Sharp and Rosenstock (1964).

Contributions to photoionization from autoionizing levels of CO_2 are significant in the region between 830 Å and 600 Å (Dibeler and Walker, 1967) and the vibrational populations in the atmosphere are modified by cascading. Despite the uncertainties, we proceed on the assumption that the 584 Å ratios of Table VII give the relative rates of population of the different vibrational levels by photoionization in the atmospheres of Mars and Venus.

The relative efficiencies with which fluorescent scattering populates the individual vibrational levels of the $A^2\Pi_u$ state can be computed from the solar flux intensities and the Franck-Condon factors for the $X^2\Pi_g\ (\nu''=0) - A^2\Pi_u(\nu')$ transitions. The

TABLE VII

Relative probabilities for populating vibrational levels v' of the $A^2\Pi_u$ state of CO_2^+ by photoionization, by fluorescent scattering and by electron impact

v'	Photoionization	Fluorescent scattering	Electron impact
0	0.08	0.30	0.09
1	0.18	0.35	0.21
2	0.20	0.25	0.20
3	0.22	0.07	0.23
4	0.16	0.015	0.21
5	0.12	0.005	0.06

results are included in Table VII as are the approximate relative efficiencies for electron impact that follow from the data of Nishimura (1966) and McConkey *et al.* (1968).

Individual band intensities resulting from the three sources of excitation can be calculated approximately by combining Table VII with the relative transition probabilities of Poulizac and Dufay (1967). The relative band intensities are listed in Table VIII together with the approximate wavelengths of the mean band heads for

TABLE VIII

Approximate relative intensities and wavelengths in Å of the bands of the $X^2\Pi_g - A^2\Pi_u$ transition of CO_2^+ produced by (1) photoionization of CO_2, (2) fluorescent scattering by CO_2^+ and (3) electron impact of CO_2

v''/v'		0	1	2	3	4	5
0	(1)	.030	.092	.092	.038	.008	.002
	(2)	.077	.125	.080	.009	.000	.000
	(3)	.028	.094	.082	.036	.007	.001
	λ (Å)	3508	3374	3250	3136	3031	2935
1	(1)	.043	.022	.035	.052	.043	.021
	(2)	.107	.031	.030	.011	.003	.000
	(3)	.041	.024	.031	.047	.051	.010
	λ (Å)	3669	3523	3392	3267	3154	3046
2	(1)	.024	.036	.062	.022	.043	.025
	(2)	.060	.051	.055	.006	.003	.001
	(3)	.023	.039	.055	.021	.051	.011
	λ (Å)	3845	3686	3540	3399	3280	3168
3	(1)	.013	.054	.013	.046	.017	.003
	(2)	.034	.076	.011	.010	.001	.000
	(3)	.013	.056	.011	.042	.021	.001
	λ (Å)	4038	3863	3704	3553	3420	3300
4	(1)	.006	.036	.032	–	.021	.010
	(2)	.017	.051	.045		.001	.000
	(3)	.006	.039	.028		.021	.004
	λ (Å)	4264	4059	3883		3573	3440
5	(1)	–	.011	.025	.024	–	–
	(2)		.016	.036	.006		
	(3)		.013	.022	.023		
	λ (Å)		4301	4102	3925		

$2\Pi_{1/2}$ and $^2\Pi_{3/2}$ final states. Table VIII shows that in the altitude region where CO_2^+ is the major positive ion bands originating in $\nu'=0$ and 1 become relatively more intense with increasing altitude than bands originating in $\nu'=2$.

7. Other Constituents

Molecular nitrogen may be a minor constituent of the atmospheres of Mars and Venus. Of the many emission band systems, the appearance of which would establish the presence of N_2, the 3914 Å band of the first negative system of N_2^+ may be the most sensitive. The $\mathbf{B}^2\Sigma_u^+$ level of N_2^+ can be excited by the same three mechanisms that we have studied for the CO_2^+ emissions.

The N_2^+ ions produced by photoionization can be removed by dissociative recombination

$$N_2^+ + e \rightarrow N + N \tag{9}$$

with a rate coefficient of about 3×10^{-7} cm^3 sec^{-1} (cf. Biondi, 1969) and by conversion into CO_2^+ through the reaction

$$N_2^+ + CO_2 \rightarrow N_2 + CO_2^+ \tag{10}$$

which has a rate coefficient of 9×10^{-10} cm^4 sec^{-1} (Fite, 1969). For illustrative purposes we have adopted model atmospheres for Mars containing 9% N_2 and 91% CO_2 with an exospheric temperature of 487° (McElroy, 1969). The atmosphere is assumed to be either completely mixed at all altitudes or such that diffusive separation begins at 120 km. The total abundance of N_2^+ ions lies in the range from 10^9 to 10^8 cm^{-2} and the fluorescent scattering intensity on Mars lies between 20 rayleighs and 2 rayleighs.

The contribution from simultaneous excitation and ionization in a direct photoionization process can be computed straightforwardly. It is 120 rayleighs for the diffusive model and 70 rayleighs for the mixed model.

The contribution from photoelectron impact can be estimated using arguments similar to those of Section 4. It is unlikely to exceed 50 rayleighs for the diffusively separated atmosphere or 20 rayleighs for the mixed atmosphere.

The intensity of 3914 Å emission that we predict for a CO_2–N_2 composition ratio of ten is accordingly two or three hundred rayleighs for the entire atmosphere. The predicted intensity could be substantially reduced by the presence of a lighter constituent such as atomic oxygen.

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