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Publication Date

2012-08-15

CO prompt emission as a CO₂ marker in comets and planetary atmospheresKonstantinos S. Kalogerakis,^{a*} Constantin Romanescu,^{a,b} Musahid Ahmed,^c Kevin R.Wilson,^c and Tom G. Slinger,^a

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Pages: 21

Figures: 5

Tables: 0

Proposed Running Head: CO prompt emission in comets and planetary atmospheres

19 **Abstract**

20 Observations of CO emissions in the visible and near-infrared (NIR) have been rare for
21 comets, and no measurements from orbiters are currently available in the visible for the
22 dayglows of Mars or Venus. Analysis of the ultraviolet CO(*a-X*) Cameron bands from
23 Mars Express dayglow observations supports the conclusion that these bands have very
24 high rotational temperatures, some thousands of kelvins. The most plausible source for
25 the CO rotational excitation is its generation by CO₂ photodissociation. Recent laboratory
26 measurements investigating the photodissociation of CO₂ in the extreme ultraviolet
27 (EUV) reveal strong emissions in the visible and NIR region by the triplet CO(*a'*, *d*, *e*)
28 states, which we take to be a primary source for the UV CO(*a-X*) Cameron bands. Thus,
29 detection of visible emissions from the triplet CO states in planetary dayglows and
30 comets provides an upper limit to the CO₂ density. The presence of CO high rotational
31 excitation along with the intense visible and NIR band emissions should be considered as
32 a practical way by which planetary dayglow and cometary spectra provide information on
33 the presence of CO₂. Finally, we report on existing observations of cometary atmospheres
34 and estimate the altitude for the emitting layer of the CO triplet states in Mars and Venus.

35 *Icarus* Keywords: Mars atmosphere, Venus atmosphere, spectroscopy, photochemistry,
36 Comets

Introduction

CO₂ is the dominant species in the atmospheres of Mars and Venus. It can also be a significant component in comets and in the atmospheres of extrasolar planets.

Therefore, the details of CO₂ photochemistry are critical in interpreting the airglows of these bodies. A great deal is known from relevant laboratory investigations, but several issues have not yet been addressed by atmospheric observations, either in ground-based studies or those from orbiters.

A major problem is that space observations are typically designed to view UV and IR emissions to the exclusion of visible spectra. In principle, part of the reason for this is that the visible spectral region can be investigated from ground-based studies, which are not blocked by ozone in the UV and by water and other components in the IR. However, this is an inadequate rationale, because only the Venus nightglow can be studied from the ground. Dayglows require orbital observations, as is also true for the Mars nightglow. Because Mars' orbit is exterior to that of Earth, its nightglow is practically inaccessible from the ground.

There are common emissions in the terrestrial atmosphere that must have their counterparts on Venus and Mars but have not yet been observed from orbit. Foremost among these are the green and red lines of the oxygen atom, at 557.7 nm and 630.0/636.4 nm, to which we can also add the 777.4 and 844.6-nm lines. In the case of the O(¹S-¹D) green line, there is the O(¹S-³P) surrogate at 297.2 nm, which has an intrinsic intensity that is weaker by a factor of 9.5 [Slinger *et al.*, 2006a, 2011a; Gattinger *et al.*, 2009, 2010]. This UV emission is well known in the Mars dayglow from information gained in both the Mariner and Mars Express missions.

The green line has been studied from the ground in the Venus nightglow [Slanger *et al.*, 2001, 2006b, 2011a], and it was a somewhat surprising addition to the Venus features because it did not appear in the Venera visible spectra [Krasnopolsky *et al.*, 1976, 1983], which was the only previous visible nightglow measurements of Venus. These early experiments have now been duplicated by Venus Express [Garcia-Muñoz *et al.*, 2009], still without the appearance of the green line. Based on several observations from the ground, the green line emission appears to be highly variable [Slanger *et al.*, 2006b, 2011b]. Slanger and Fox [2009] have recently proposed an ionospheric source for $O(^1S)$ that follows the solar cycle, accounting for the current lack of detection.

CO_2 photodissociation, in addition to giving excited atomic oxygen states, generates excited states of CO. The $CO(a-X)$ Cameron band emission, in the range 180-260 nm, has been known ever since the Mariner days. Lawrence [1972a] investigated the production of the Cameron bands from CO_2 photodissociation below 108 nm and characterized the yield as a function of the photon energy. However, at energies greater than 12.4 eV (photon wavelength less than 100 nm), other channels open up, and the ultimate source of the Cameron bands becomes complicated.

In the 11-14 eV region, photoabsorption by CO_2 is strong and very structured [Chan *et al.* 1993]. Photoionization starts at 13.8 eV, accounting for a rapid decrease in the absorption cross-section. Other important emissions in the UV Mars dayglow include the $CO_2^+(B-X)$ 0-0 band at 289 nm and the $CO_2^+(A-X)$ bands above 300 nm, which require 18.1 eV and 17.3 eV, respectively, for direct excitation. It has been suggested [Leblanc *et al.*, 2006] that at least part of the $CO_2^+(B)$ excitation comes from photoexcitation of $CO_2^+(X)$.

Production of the CO excited states begins near 11.5 eV, which corresponds to the threshold for CO(*a*) formation [Lawrence, 1972a]. The 10.5-13.8 eV region is dominated by two types of dissociation,

where CO* corresponds to the four triplet levels—*a* ³*II*, *a'* ³*Σ*⁺, *d* ³*Δ*, *e* ³*Σ*[−]. Emission from the *a'*, *d*, and *e* states down to *a* ³*II* are known as the Asundi, Triplet, and Herman bands, respectively, and have associated radiative lifetimes of a few microseconds. Thus, *a'*-*a*, *d*-*a*, and *e*-*a* emissions are prompt in planetary and cometary atmospheres. The radiative lifetime associated with the *a*-*X* Cameron bands is about three orders of magnitude longer than for the triplet bands. Thus the Cameron band intensity is sensitive to the altitude in planetary dayglow, which will not be true for the triplet bands. Both emissions are prompt in comets.

The O(¹*S*) yields from CO₂ photodissociation have been determined [Lawrence, 1972b], and the sum of the CO* and O(¹*S*) yields over the stated energy region is not far from unity, although for the O(¹*S*) case, Lawrence suggests that the accuracy may not be better than a factor of two. It is important to note that the instrumental resolution with which the measurements were made was much coarser than the structure in the CO₂ absorption spectrum. However, for the Cameron bands, Lawrence showed that there was no correlation between the spectral structure and the apparent yield—the latter was a smooth function of the wavelength alone, rising from zero at the threshold at 108 nm to 50–60% at 90 nm. The measurements for O(¹*S*) were much less extensive because of the weakness of the signal, but the absence of a yield dependence on the cross section for

CO(*a*) (including the higher triplet states) carries the implication that the same is true for O(¹*S*). The production of O(¹*S*) occurs in a low cross-section region, while the CO triplet bands are generated in a region of shorter wavelength and large cross section.

If we consider the product of the CO₂ absorption cross section and the solar flux, we can demonstrate that the most important region for solar photodissociation is at 90-110 nm [Huestis *et al.*, 2008], just the region where the CO(*a*) yield is highest [Lawrence, 1972a]. Noteworthy is the fact that the very strong Lyman-alpha (Ly-α) line at 121.6 nm is much less important than the shorter wavelength radiation.

Interest in CO₂ photodissociation in the solar system is not limited to the atmospheres of Mars and Venus. Cometary atmospheres contain substantial amounts of CO₂, and what we learn about the dayglows of Mars and Venus has direct application to cometary spectra—the photon source being, in both cases, the sun. Thus, comparisons among Mars spectroscopic results, those from comets, and those from relevant laboratory studies can help improve our understanding of these systems. Finally, we would expect similar principles to be applicable to CO₂ planetary atmospheres in other solar systems.

Evidence from Observations and Laboratory Experiments

Highly Rotationally Excited CO in the Mars Dayglow

UV spectra of Mars dayglow were initially obtained by the Mariner spacecraft [Barth *et al.*, 1971], and more recently by the Spectroscopic Investigation of the Characteristics of the Atmosphere of Mars (SPICAM) spectrometer on Mars Express [Leblanc *et al.* 2006]. SPICAM has a long wavelength cut-off near 310 nm, while the Mariner instruments made measurements to 400 nm.

An example of the SPICAM spectra is shown in Figure 1, where the three most important dayglow emissions are seen—the CO Cameron bands, the $\text{CO}_2^+(B-X)$ 0-0 band, and the $\text{O}(^1S-^3P)$ line. The Ly- α geocoronal line is a strong feature at shorter wavelengths. For both Mars and Venus, solar scattering from haze and clouds can affect the spectra, but for Mars it is not an issue for tangent ray heights greater than 130 km and for lower altitudes corrections can be made. For the Spectroscopy for Investigation of Characteristics of the Atmosphere of Venus (SPICAV) spectrometer on Venus Express, the problem is much more severe, and there are as yet no published data, although it is reasonable to expect that the same features will appear.

It was pointed out long ago [Conway, 1981] that the Mariner Cameron band spectra showed a very hot rotational distribution. The analysis gave a bimodal temperature, the best fit showing both 1600 K and 10,000 K. This is an extraordinary result and, in our recent analysis of results from the Mars Express SPICAM instrument, we found such a distribution.

Figure 2 shows a series of DIATOM™ [Huestis, 1994] simulations of the intensity distribution of the Cameron bands in the Mars dayglow. They are composed of the $v' = 0-2$ band sequences, using published Franck-Condon factors [Krupenie, 1966], with slight adjustments to improve the relative amplitudes. The calculations are carried out for single temperatures from 500 K to 10,000 K. The thick solid line is a representative SPICAM spectrum; overall, it falls between the 4000 and 6000 K lines. Thus, we concur with Conway's analysis, in which he also investigated whether the $\text{CO}^+(B-X)$ First Negative bands might be present in this region, thus filling in the intensity between the Cameron bands. He concluded this system was not present. The resolution of the

SPICAM instrument is demonstrated by the appearance of the 297.2 nm atomic line, which shows that the bands are much wider.

As noted, there are no Mars/Venus visible dayglow spectra against which to check for the presence of the three CO triplet sequences, but there are visible ground-based cometary spectra, and we can look for evidence of both hot CO(*a*) distributions and the triplet bands.

Laboratory Studies of CO Emission Following CO₂ Photodissociation

From laboratory experimental work, it becomes clear that the CO triplet systems can be useful ground-based markers for CO₂ in cometary atmospheres, so any high-resolution cometary study should include a search for these features. These states can be generated by direct excitation of CO by photons or electrons, although the $X \rightarrow a'$, d , e transitions are spin-forbidden. Thus, appearance of the visible bands cannot be taken as conclusive proof of the presence of CO₂. Their absence, however, should be interpreted as an indication that little or no CO₂ and CO are present.

Although CO Cameron band emission is the best-known product of CO₂ photodissociation in planetary atmospheres, these higher CO states can cascade into CO(*a*), the emitting Cameron band state. There is a limited early history on this topic [Judge and Lee, 1973; Lee and Judge, 1973], and it is clear that with increasing photon energy, these states become important. CO(*a*) is first produced at 11.46 eV, and the three higher-lying triplet levels that are nearby, a' , d , and e , have thresholds at 12.31, 12.97, and 13.35 eV, respectively. The optical transitions from these levels to the CO(*a*) state are fully allowed, and any population excited to these higher levels cascades to CO(*a*),

because the transition to the ground-state is not optically allowed, except for localized perturbations [Tilford and Simmons, 1972; Slanger and Black, 1970]. These cascading pathways generate both visible and NIR emission, and provide a diagnostic for the presence of CO₂.

Laboratory studies of the CO excited states have been carried out for a variety of reasons—for pure spectroscopy, for combustion chemistry, and to understand planetary atmospheres. In combustion research, Burke *et al.* [1996] discovered that both the CO Cameron bands and the visible triplet bands were formed from two separate reactions—that of oxygen atoms with acetylene and with the C₂O molecule. Normally, this should have little relevance to cometary and planetary issues but, in fact, the emission patterns in both the UV and the visible are indiscernible from what we recently observed in relevant laboratory studies on the EUV photodissociation of CO₂ (C. Romanescu, K.S. Kalogerakis, T.G. Slanger, L.C. Lee, M. Ahmed, and K. R. Wilson, manuscript in preparation, 2012) and, for the UV, from what was seen at Mars by the Mariner spacecrafts [Barth *et al.*, 1971] and by Mars Express [Leblanc *et al.*, 2006]. It is not clear why this should be so, but we can make use of the information to learn about the NIR region, where neither the planetary probes nor the laboratory experiments have provided results yet. In the work of Burke *et al.* [1996], the most intense band is the *a'*-*a* 2-0 band, at 1.08 μ, which ought to be a target for cometary and planetary dayglow observations. We have looked for this emission in a published spectrum of Comet West [Johnson *et al.*, 1983], and its absence may indicate that the coma contains very little CO₂.

To observe the visible CO triplet bands, the energetics require that we carry out CO₂ photodissociation measurements in the 11-14 eV range. Details of the experimental

apparatus and results are described elsewhere (*Romanescu, et al.*, manuscript in preparation, 2012), and only a brief account is reported here. As the required light source must operate in the “windowless” spectral region, we ran the measurements in a reaction cell that was coupled to the direct output of the undulator at the Chemical Dynamics Beamline (9.0.2) at the Advanced Light Source of the Lawrence Berkeley Laboratory (ALS). Because of the large pressure differential—some twelve orders of magnitude between the ring and the reaction cell—it was necessary to build a series of differential pumping sections, so that the pressure in the reaction cell region could be made compatible with the ring pressure of 10^{-10} Torr. The beam flux entering the cell is nominally 10^{16} photons per second per 2.5% bandwidth, or 4×10^{15} photons per second per nm at a wavelength of 100 nm. The gas samples consisted of either 0.1% CO₂ in He (Matheson, Certified mixture grade) or pure CO₂ (Matheson, 99.995%).

Two principal types of measurements were carried out: excitation spectra and fluorescence spectra. In an excitation spectrum, we choose a detection wavelength and pressure, and scan the photon energy, to determine how the signal intensity behaves. This is determined by a combination of photoabsorption cross sections, photon flux, and fluorescence yields, all as a function of wavelength. The visible and UV emissions from the cell were measured simultaneously with filtered photomultiplier tubes (PMT). For the Cameron bands, we used a 10-nm full-width half-maximum (FWHM) interference filter centered at 214 nm, i.e., the position of the CO(*a-X*) 0-1 band. For the visible emission, we employed a 520-nm long-pass filter, so that all emission was collected out to the photomultiplier tube (PMT) cut-off (~850 nm), although much of the emission is from longer wavelengths. In Figure 3, we show two excitation spectra for a mixture containing

~4 mTorr CO₂ in 2 Torr He, one for the Cameron bands, and the other for emission in the 520 to 850-nm range. The intensities are normalized to the peak.

The spectra show different behavior, because the threshold for direct Cameron band production is ~1 eV lower than the triplet band threshold. Furthermore, the various triplet bands will not be registered at their threshold, because the emission will first appear in the IR, where our detector is not sensitive. With increasing photon energy, the emission moves into the visible and is recorded. From Figure 3, we can see that the Cameron band signal becomes large in line with the visible signal, indicating that the cascading contributions are a major Cameron band source.

After having determined that the maximum signal at both wavelength regions is at a photon energy of 13.4 eV (92.5 nm), we recorded fluorescence spectra using a monochromator and photon counting arrangement. The spectra were calibrated utilizing the phototube sensitivity and the monochromator grating efficiency, both to set the photon fluxes on a comparable scale with respect to the two spectral regions, and to carry out an extension into the IR. Because the phototube is not sensitive in the IR region, where much of the triplet emission is found, we can use the calibrated IR spectrum [Burke *et al.*, 1996] to extend the spectrum. In this manner, we can evaluate how much of the light is missing from the UV and visible region. By using the 785-nm *a'-a* 5-0 band—common to both spectra—it is possible to make this comparison.

Figure 4 shows the complete calibrated spectrum, from the UV to the IR, corrected for phototube sensitivity and grating efficiency, and extended into the IR by digitizing and adding the Burke *et al.* [1996] spectrum beyond 785 nm. The bands are tabulated elsewhere (Romanescu, *et al.*, manuscript in preparation, 2012), and higher

resolution data would be helpful in clarifying ambiguities. It is intriguing that the UV portion of the spectrum of Figure 4 has most of the features of the Mars dayglow, which further supports the notion that the visible/IR portion reproduces the as-yet-unobserved dayglow spectrum in that region.

The spectrum of Figure 4 and its extension into the IR to 1.4 μm shows that there is much more visible/IR emission than Cameron band emission for the excitation energy of 13.4 eV. For the studied mixture of ~ 6 mTorr CO_2 in 4 Torr He, the integrated [triplet]/[Cameron] intensity ratio is approximately 9. This factor depends on the CO_2 density. With decreasing density, the Cameron bands become larger relative to the $a'-a$ and $d-a$ bands, as the $\text{CO}(a)$ radiating efficiency increases. We can thus conclude that the visible/IR CO triplet bands must be a major emission feature in the Mars/Venus dayglows, where there is no question of the importance of CO_2 photoabsorption. In comets, the triplet bands will be significant if CO_2 is an important atmospheric component.

If the triplet bands were produced exclusively at 13.4 eV, and then cascaded to the $a^3\Pi$ state, the production rates in the two regions would be equal. However, the UV and visible/IR *intensities* will not be equal, because the Cameron bands are quenched by CO_2 , whereas the triplet bands are not. Thus, the fact that the Cameron bands are nine times weaker than the triplet bands in Figure 4 is an indication of this effect. The single $a'-a$ Asundi 2-0 band at 1.08 μ is twice as intense as the entire Cameron band system.

With regard to laboratory observations in condensed media, Gudipati and Kalb [1998] have carried out experiments in which CO/Ar mixtures were irradiated near 155 nm, while Wagner et al. [2000] did the same in CO_2 /Ar mixtures. In both cases the

visible/near IR CO triplet transitions were observed, preceding the Cameron bands. In the study on CO₂, CO was initially produced, which was then excited. Interesting to note is that in the CO study the strongest triplet feature is the *a'-a* 2-0 band, just as seen in Figure 4.

CO Emissions in Cometary Spectra

We now examine previously reported observations of cometary spectra in light of the information presented above. Since CO₂ in the cometary and planetary environments will interact similarly with solar radiation, we expect to see a hot distribution in the case of comets if CO₂ is a significant component. Weaver et al. [1994] and Feldman et al. [1997] have studied this and, although the Cameron bands could be detected in the observed comets, there was little indication of the hot distribution reported by Conway [1981]. On this basis, they concluded that the Cameron bands were not formed from CO₂ photodissociation, but more likely were the product of direct photoelectron excitation of CO. These observations provide further evidence that CO₂ is not a major component in most cometary atmospheres and, in fact, it is generally accepted that the [CO₂]/[H₂O] ratio is 0.05-0.1, based on IR absorption measurements [M. A'Hearn, private communication, 2008].

In addition to the UV Cameron bands, there are a number of claims to observations of the three CO triplet sequences in comets. Discussions of the presence of these systems rarely go beyond noting their identification, and much of this identification is suspect. There are several papers by the group of K.I. Churyumov [1997, 2003] claiming identifications of the Asundi and Triplet systems in comet C/1989 Y1

Skorichenko-George. They are far from convincing. Not only are bandhead positions up to 0.5 nm away from “theoretical” positions, but the latter are merely rather inaccurate laboratory measurements from earlier times. Additionally, the spectra shown in these papers do not convey to the viewers that the bands are real. A recent article by Picazzio et al. [2007] presents data that suffer from the same problems.

The most convincing identification of the triplet bands comes from spectra of Comet Bradfield [*Cosmovici et al.*, 1982]. There are several candidates between 630 and 740 nm, in the region of strong Asundi and Triplet bands. However, at longer wavelengths, where the Asundi/Triplet bands in our spectra get stronger, there are no clear identifications in the cometary spectrum.

Cochran and Cochran [2002] have published an extensive list of emission lines seen in Comet 122P/de Vico—more than 16,000 lines were found, of which 12,000 could be identified. None of these lines were identified as belonging to the CO triplet systems.

Overall, positive observations of CO visible emissions from comets are not at all common in the literature, a fact that highlights the relative scarcity of CO₂ in cometary composition.

CO Triplet Band Intensity Estimates in Comets

We can combine our laboratory data with models for cometary Cameron band emission to make approximate predictions of the intensity of the CO bands in the visible and near-infrared regions. Raghuram and Bhardwaj [2012] have recently published a model of CO Cameron band emission associated with Comet 1P/Halley. They have made the claim that the Cameron band source is not limited to CO₂ photodissociation, as

in earlier models [*Weaver et al.*, 1994; , *Feldman et al.*, 1997], but that photoelectron collisions on CO₂ is actually the more important mechanism. Still, they assign 20-30% of the Cameron band production to the CO₂ + hν process, although they do not invoke cascading from the CO(*a'*, *d*, *e*) levels as a source of CO(*a*).

For P1/Halley, the values given for the total slit-averaged brightness for the Cameron bands measured by the International Ultraviolet Explorer (IUE) is of the order of several hundred Rayleighs [*Raghuram and Bhardwaj*, Table 3]. If we take 25% as a value for the fraction of Cameron bands coming from CO₂ photodissociation, then the intensity from this source is on the order of 100 R. As we make the claim that most of the observed Cameron band emission arising from CO₂ photodissociation is preceded by cascading from the CO(*a'*, *d*, *e*) states, then the visible/near-IR emission from these states is predicted to be of this same magnitude, ~100 R, spread over the 600 to >1400 nm range shown in Figure 4. Because of reduced sensitivity of detectors in the IR, probably the best band to view in a search for the triplet emissions is the *a'-a* 5-0 band (the shortest wavelength head of the quintuple-headed band lies at 783 nm [*Krupenie*, 1966]), where an estimated intensity for this band alone is about 10% of the total, i.e. ~10 R.

However, the 75% fraction of the Cameron bands that are claimed to arise from photoelectrons on CO₂ [*Raghuram and Bhardwaj*, 2012] do not exclude similar CO products, considering that the energy threshold for CO(*a*) production from CO₂ is 11.5 eV, whereas that for CO(*a'*) production is 12.3 eV. Therefore the 10 R estimate for the intensity of the *a'-a* 5-0 band is a lower limit, an upper limit being larger by a factor of four.

Altitude of the CO Triplet Band Emission in Venus and Mars

Although we can conclude that the CO triplet bands are produced with high efficiency in CO₂ photodissociation at energies around 13.4 eV, it is necessary to consider how photons are absorbed in the CO₂ atmospheres, which sets constraints on the observations. The crux of the matter is that 13.4 eV photons are blocked by CO₂ at relatively high altitudes. Above such altitudes, the Cameron and triplet bands will have comparable intensities, but at the altitude where the Cameron band profile peaks, typically near 120 km in the Mars dayglow [Simon *et al.*, 2009], the unity optical depth (1/e absorption) for 13.4 eV photons will be higher. To quantify the photoabsorption process, it is useful to calculate the altitude of unity optical depth. This has been done for the Venus atmosphere [von Zahn, 1980], but not at the resolution of the CO₂ absorption cross sections presented in Figure 1. For the calculation, we integrate a CO₂ altitude profile from the top of the atmosphere downwards and use the photoabsorption cross section as a function of wavelength [Chan *et al.*, 1993],

$$1 = \alpha(\lambda) \int N_{\text{CO}_2}(h) dh \quad (3)$$

where $\alpha(\lambda)$ is the wavelength-dependent cross section and $N_{\text{CO}_2}(h)$ is the number density as a function of altitude. In Figure 5, the calculation is performed for both the Mars and Venus atmospheres, for a vertical sun, using the profiles given by Fox and Dalgarno [1979] and Fedorova *et al.* [2009] for Mars, and Krasnopolsky and Parshev [1983] for Venus. We see that for 13.4 eV photoexcitation, unity optical depth is reached at 137 km for Venus and 131 km for Mars. Therefore, for the case of Mars, the CO triplet band

emission generated by CO₂ photodissociation for 1/e absorption will lie only 11 km higher than the 120 km Cameron band peak seen by SPICAM [Simon *et al.*, 2009].

When cascading from the upper triplet levels is the dominant source of the Cameron bands, most of the emission comes from the $a(v = 0)$ level, because a large fraction of the visible/IR emission terminates on that level. We can estimate a quenching factor for $a(v = 0)$ from its radiative lifetime and the CO₂ removal rate coefficient. The latter has been measured, with a range of $(1.2\text{--}1.7) \times 10^{-11} \text{ cm}^3\text{s}^{-1}$ [Slanger, 1971; Taylor and Setser, 1971; Wysong, 2000]. The radiative lifetime of the $a^3\Pi$ state is dependent on rotational level; the most recent value for the CO($a^3\Pi_1$, $v = 0$, $J = 1$) level is about 3 ms [Gilijamse *et al.*, 2007]. Thus, the CO₂ density for which the collisional quenching and radiative rates are equal is about $2.2 \times 10^{13} \text{ cm}^{-3}$. For Mars, this corresponds to an altitude of ~80 km, and for Venus, ~120 km. Thus, for the 1/e penetration depths shown in Figure 5, quenching is unimportant for the CO(a) state and non-existent for the higher triplet states for photon energies above the CO(a) threshold of 11.45 eV. Emission from higher altitudes should have the signature of approximately equal contributions from the Cameron and visible-IR systems. However, as the altitude decreases, there are competing factors; lower energy photons will lead to increasing production of nascent CO(a) that is unaccompanied by triplet emission, and increasing density will preferentially quench CO(a).

Conclusions

CO₂ photodissociation in the extreme UV is of particular interest to our understanding of cometary spectra and of the Mars and Venus dayglows. The UV CO

Cameron bands are well-known features of these systems, but there have been essentially no attempts to observe other CO emissions that lie in the visible and NIR spectral regions. Because these emissions can be a source of the Cameron bands *via* cascading, it is important to evaluate their yields.

At the peak of the CO₂ absorption region, near 13.4 eV photon energy, the yields of visible/NIR emissions are essentially equal to the Cameron band yields. It follows that most of the Cameron band intensity originates with cascading from higher levels at that photodissociation energy, rather than from direct excitation. The visible/NIR emission is strongest at wavelengths longer than 1.0 μm . Detection of this emission in cometary atmospheres and in the planetary dayglows provides an upper limit to the CO₂ density. The presence of CO high rotational excitation along with the intense visible and NIR band emissions should be considered as a reliable indicator of the presence of CO₂ in planetary and cometary atmospheres. A search for CO triplet band emission in the Mars/Venus dayglows should be conducted at altitudes somewhat above the peaks in the Cameron band emission.

Acknowledgements

This work was performed under grant NNX06AB82G from the NASA Outer Planets Research Program to SRI International. Partial support from NSF grants AST-0709173 and AST-1109372 is also acknowledged. We are grateful to W.L. Dimpfl of Aerospace Corp. for providing laboratory spectra from their flow discharge studies, to the staff at ALS for technical support, and to our colleagues D. L. Huestis and L. C. Lee for helpful advice and discussions. M. Ahmed, K.R. Wilson, and the ALS are supported by

the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract No. DE-AC02-05CH11231.

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Figure Captions

Figure 1. SPICAM Mars dayglow spectrum. Orbit 947; tangent ray height, 111 km; latitude, 6 degrees N; SZA, 43 degrees (courtesy F. Leblanc).

Figure 2. DIATOM simulations of the CO Cameron bands in the region 190–240 nm for $T = 500\text{--}10,000\text{ K}$, compared to SPICAM data (solid black line), resolution 1.6 nm.

Figure 3. ALS excitation spectrum for CO_2 photodissociation of a mixture containing 4 mTorr CO_2 in 2 Torr He. The combs show the vibrational level positions of the four CO triplet states, with the arrows indicating the location of the $v = 0$ level.

Figure 4. Emission spectrum of CO triplet bands produced by CO_2 photodissociation of a mixture containing ~ 6 mTorr CO_2 in 4 Torr He at 13.4 eV photon energy. The region between 350 and 550 nm is not shown, as it only contains second order spectra of the Cameron bands. The IR portion beyond 870 nm originates with the data of Burke et al. [1996]. The spectrum has been corrected for variations in detector sensitivity as a function of wavelength.

Figure 5. Unity optical depth for solar radiation as a function of photon energy in CO_2 atmospheres (Mars and Venus) for a vertical sun.

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552 **Figures**

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