

Observations of CO in the atmosphere of Mars in the (2–0) vibrational band at 2.35 microns

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Abstract. Following our high-resolution infrared observations of CO in the atmosphere of Mars in 1988 and 1989 at $4.7\mu\text{m}$ (Billebaud et al., 1992), we recorded new spectra of CO: one covering the whole disk of the planet in 1990 and 4 spectra corresponding to 4 different locations on the planet in 1991. All these spectra were recorded in the (2–0) vibrational band at $2.35\mu\text{m}$. These data allow us to measure the CO abundance and to search for possible middle-scale spatial variations of this abundance in the case of the 1991 spectra. The CO mixing ratio derived from the 1990 data is in good agreement with the values we obtained in 1988 and 1989 (Billebaud et al., 1992), showing a great stability over a period of 3 years, with a value of the CO mixing ratio remaining in the range of $4.2\text{--}8.5 \times 10^{-4}$. The results we obtained with the 1991 data also seem to comfort the stability of the CO mixing ratio, although the possible range is somewhat larger ($5.5\text{--}11.5 \times 10^{-4}$). This common CO mixing ratio range for the four locations on the planet then tends to exclude the presence of any significant horizontal variations of the CO mixing ratio, even if, from our data, we cannot firmly rule them out.

Key words: planets and satellites: individual: Mars – infrared: solar system

1. Introduction

Although studied for long, the problem of the stability of the CO₂-dominated martian atmosphere remains a topical question. It was raised when it was noticed that the photolysis of CO₂ by solar light penetrating deeply in Mars tenuous atmosphere might have led to an accumulation of CO and O₂ giving an abundance for these two constituents of up to 10%. Indeed, this would have been possible as the spin-forbidden inverse reaction (CO + O → CO₂) is very slow. However, observational evidences

show that the amount of CO and O₂ remains very modest (approximately 0.08% and 0.12% respectively) and that therefore CO₂ is somehow efficiently recycled. McElroy and Donahue (1972) and Parkinson and Hunten (1972) showed that oxydation of CO to CO₂ can occur through a process involving the OH radicals. These two models differed in the source of OH radicals (HO₂ in the case the of McElroy and Donahue model, HO₂ and H₂O₂ in the case of the Parkinson and Hunten one) and in the required value of the eddy diffusion coefficient K. In fact both models failed in matching the reality, the first one because it required too high values of K in the middle atmosphere and the second one because it needed too high an amount of water in the atmosphere. More recently, Krasnopolsky (1993a) and Atreya and Gu (1994) proposed models taking into account the temperature dependence of CO₂ cross-sections, for which pure gas-phase chemistry resulted in slightly too low predicted CO amounts. Along with Anbar et al. (1993a), they thus showed that the CO₂ stability problem could even be reversed ! It appeared so that there was a need for a sink of HO_x radicals, which could be provided by heterogeneous processes. However, Anbar et al. (1993b) suggested that revising the rates associated to the reactions involving HO_x, which are not precisely known, could be enough to balance the CO₂ production and loss rates, and Nair et al. (1994) demonstrated not only that heterogeneous chemistry would be inadequate to bring the CO abundance back into agreement with the observations, but also that there was no need to invoke it when reasonable modifications in a homogeneous gas-phase model can provide satisfactory agreement. Krasnopolsky (1995) reached agreement as well with the observed CO abundances assuming a reduced photolysis of water vapor due to either a temperature effect of the cross section near 1900 Å or the possible effect of impurities on the measurements of the H₂O cross sections made by Thompson et al. (1963) near 1900 Å.

However, frequent and disk-resolved observations are necessary to assess the existence or non-existence of spatial and temporal variations of the carbon monoxide abundance. Clancy et al. (1983) have not seen clear evidence for a significant change of the CO abundance over a timescale of about 5 years, although

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their data allow a range of CO variability of 0 to 100%. Nair et al. (1994) suggest that, given the variability of the water vapour abundance and the critical role played by odd hydrogen in the abundances of CO and O₂, these could vary on time scales of the order of their photochemical lifetimes. This presumes that the variability of CO is comparable with the variability of the global-mean water vapour abundance averaged over a period of 5 years and the expected effect is very low. Krasnopolsky (1993b) has also shown that the solar cycle could have an effect on the CO mixing ratio, inducing a variation which could reach 35%. In all cases, the problem remains however of the apparent lack of variation of the O₂ abundance, which makes it difficult for the CO abundance to vary. Concerning the question of possible spatial variations of the CO abundance, Lellouch et al. (1991), from millimetric observations, have shown that spatial variations, if any, could not exceed 40% on spatial scale comparable to a martian radius. However, few spatially-resolved observations are available at present. In 1992, using data obtained with the instrument ISM (an infrared imaging spectrometer) onboard the Phobos spacecraft, Rosenqvist et al. (1992) found a possible depletion by a factor of about 3 above the high volcano region. But this result remained controversial, especially after Hunten (1993) showed that a small instrumental error might be at the origin of this result and also because a variable CO might be confused with a variable presence of an absorbing mineral on the surface.

In order to investigate the presence of possible temporal and spatial CO abundance variations, we have conducted a four year observation programme of CO in the atmosphere of Mars, starting in 1988. The 1988 and 1989 data have already led to CO abundance measurements from the (1–0) band at 4.7 μm (Billebaud et al., 1992). The next step was to record one new spectrum in 1990 and then four spectra in 1991, corresponding to four different points on the planet, in order to test both the short-term stability of the CO abundance and the possibility for middle-scale spatial variations. These new data were recorded in the (2–0) vibrational band of CO at 2.35 μm. This band was preferred to the (1–0) one because, as it is located in the solar reflected component of the planetary emission, the analysis of the data is much less sensitive to the atmospheric thermal profile.

The observations are described in Sect. 2. The model is presented in Sect. 3 and the discussion and conclusions are given in Sect. 4.

2. Observations

The observations were made using the Fourier Transform Spectrometer of the Canada-France-Hawaii 3.6 meter telescope located at the Mauna Kea Observatory (Hawaii). This instrument is a dual-input-dual-output interferometer, equipped with two InSb detectors operating between 0.9 and 5 μm (Maillard & Michel, 1982). The filter (4100–4500 cm⁻¹) was chosen in order to select the CO (2–0) vibrational band centered at 2.35 μm.

The 1990 spectrum was recorded on May 31. The aperture was 8" so that the entire disk of the planet (6.8") could be observed. The solar longitude was L_S=231° and the subearth point

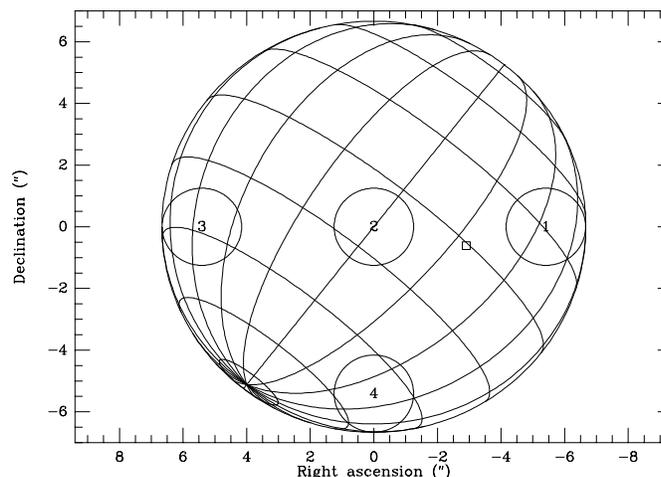


Fig. 1. Geometry of Mars and the four positions of the aperture on the planet for the 1991 data.

located at 24°S, with a local time around 3 p.m. The spectral resolution was 0.017 cm⁻¹ and the Doppler shift was around 0.14 cm⁻¹ (at 4280 cm⁻¹ = central wavelength of the useful portion of the filter). The useful portion of the spectrum (i.e. the portion of the spectrum corresponding to the best filter transmission: 4240–4320 cm⁻¹) exhibits 25 ¹²CO absorption lines, well separated from the corresponding telluric ¹²CO lines. The spectrum however contains solar CO lines that could be mixed with martian CO lines. For this reason, a Moon spectrum was recorded at the same time and with the same spectral resolution. The Moon spectrum was corrected for Doppler shift with respect to the Mars spectrum, so that the solar CO lines be at the same wavelength position in the two spectra. The Mars spectrum was then divided by the rescaled Moon spectrum. This allowed us to remove the solar contribution to the martian CO lines, although this resulted in the telluric lines (water lines in particular) to appear twice (in emission and in absorption), as they were thus shifted in one spectrum with respect to the other. But this effect has no influence on our ¹²CO martian lines.

On January 2, 1991, we recorded four spectra corresponding to four points on the disk of the planet (Fig. 1). The aperture was 2.5" while the planet was 13.5". This thus gives an average spatial resolution of about 1260 km at the centre of the disk. The spectral resolution was 0.049 cm⁻¹ for the four spectra and the Doppler shift was about 0.18 cm⁻¹ (at 4280 cm⁻¹). The solar longitude was 358.5° and the subearth point was located at 13°S with a local time around 10.5 a.m. The geometry of the disk is shown on Fig. 1. The latitude, longitude and local time of the central point of the four positions are, respectively: 22°N, 251°, 1.5 p.m. for position 1; 13°S, 311.6°, 10.5 a.m. for position 2; 37°S, 358.5°, 7 a.m. for position 3 and 48°S, 275.7° and 2 p.m. for position 4. No Moon spectrum could be recorded at the time the 1991 data were taken.

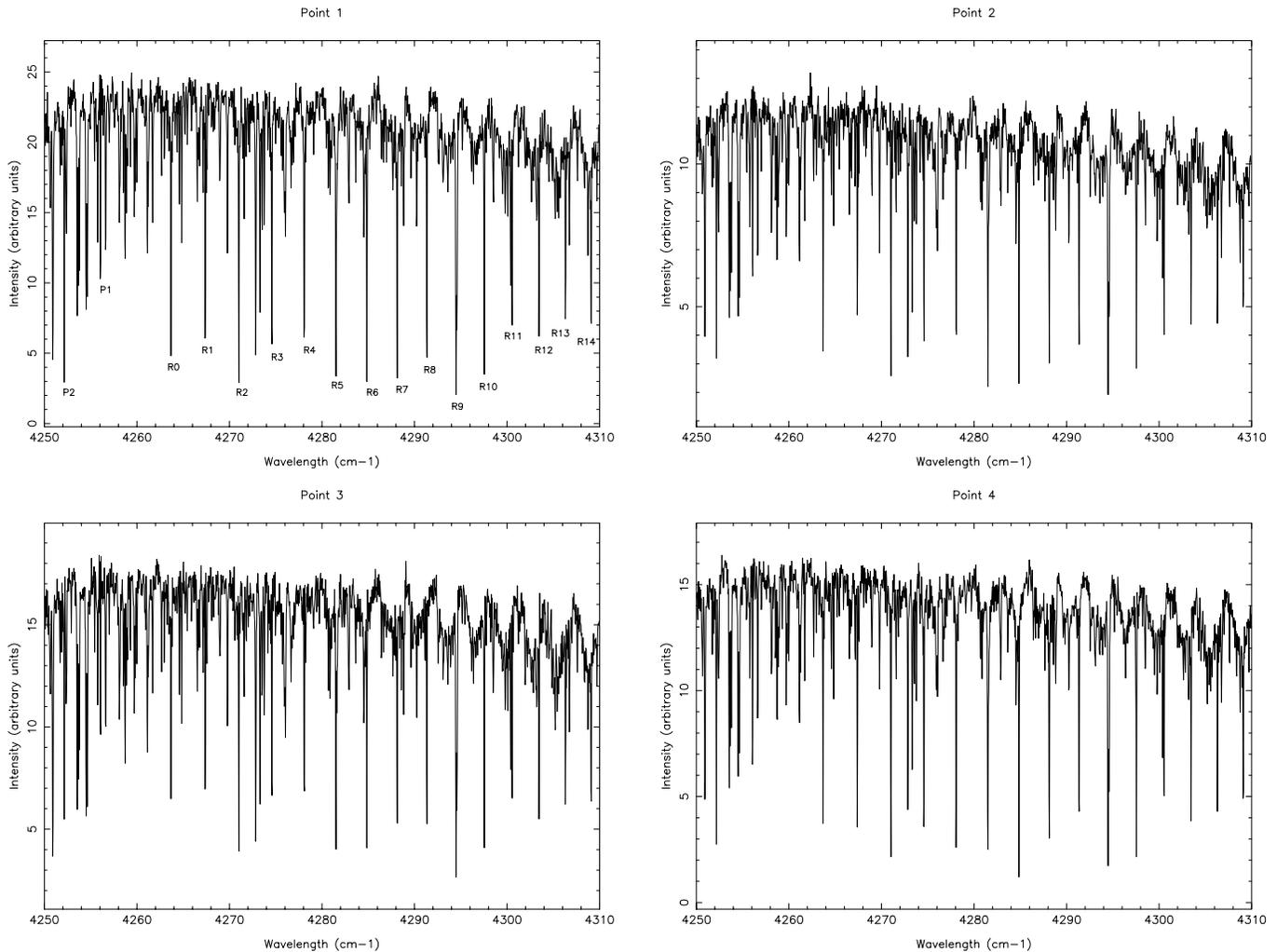


Fig. 2a–d The four 1991 spectra. The line identifications are given for Point 1. All are raw data.

3. Data analysis and modelling

3.1. Data calibration and determination of the line characteristics

The full transmission level of the spectra exhibits instrumental low frequency ripples. These were locally removed by fitting a Spline function to the continuum. As no absolute calibration of the data was available, the lines were rescaled to the continuum level, i.e. expressed as a fraction of the continuum, which is itself rescaled to its calculated value.

However it should be noticed that although not calibrated in absolute, the relative flux levels of the four 1991 spectra are consistent with the average albedos taken for the four different Mars areas sampled (see Sect. 3.2). About 30 ^{12}CO lines were detected in the spectra. We selected among these lines those which were located in the parts of the spectra that have the best transmission level. We selected 25 such lines in the case of the 1990 spectrum, which all fall in the 4245–4330 cm^{-1} region, and 17 for the four 1991 spectra (Fig. 2), which all fall in the 4250–4310 cm^{-1} region. No isotopic CO lines were detected in the useful parts of the spectra (which is to be expected given our spectral resolution).

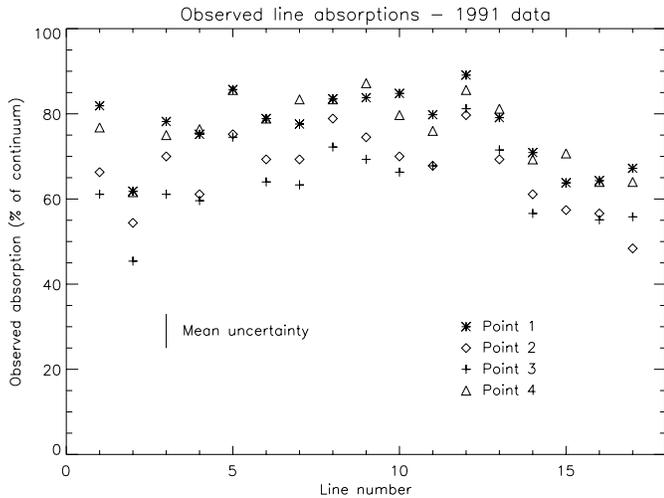
The very high spectral resolution of the 1990 data allowed us to use three parameters to fit the 1990 lines: the depth at the center of the line, the depth at one FWHM (Full Width at Half Maximum) and the depth at two FWHMs. In the case of the 1991 data, the lower spectral resolution of the spectra resulted in the line widths to be entirely defined by the instrumental function. For this reason we fitted the 1991 data using the line depths only (Fig. 3). The estimated uncertainty on the measured line depths is given by the noise level as measured outside the filter plus the uncertainty on the position of the continuum level. We estimate its value to be of 10% of the continuum. This uncertainty on the line depths results in an equivalent uncertainty on the line FWHMs.

3.2. Modelling of the 2.35 μm spectrum of Mars

At 2.35 μm , the emission of Mars is entirely dominated by its solar reflected component. The model used is quite comparable to the one we developed for the lines at 4.7 μm (Billebaud et al., 1992): it consists of a multilayer radiative transfer code which generates synthetic CO lines. A major complication, however, is that at 2.35 μm , the effects of light scattering by atmospheric

Table 1. Local characteristics for the four points on the planet – 1991 data.

Parameter \ Point	Point 1	Point 2	Point 3	Point 4
Albedo	0.3 ± 0.02	0.18 ± 0.02	0.26 ± 0.02	0.23 ± 0.02
Altitude	-0.9 ± 0.8 km	$4.0 -0.5 +0.2$ km	$0.5 -0.7 +0.8$ km	$-0.2 -0.4 +0.5$ km
Pressure	$8.4 -0.8 +0.2$ mbar	5.4 ± 0.3 mbar	7.4 ± 0.6 mbar	$7.8 -0.6 +0.4$ mbar
Local time	1.5 pm	10.5 am	7.0 am	2.0 pm
Mean latitude	22deg N	14deg S	37deg S	48deg S
Mean longitude	251 deg	312 deg	358 deg	276 deg

**Fig. 3.** Observed line absorptions for the 1991 data. The observed absorption (expressed as a percentage of the continuum level) is given as a function of line number (number 1 is for P2, number 2 is for P1, number 3 is for R0 and then number 4 to 17 are for R1 to R14).

dust are significant. Therefore, a complete scattering model, previously developed by Rosenqvist et al. (1992), was used to estimate the influence of the suspended dust on the depths and widths of the martian lines. It is a doubling–adding model consisting in 150 sublayers of 0.5 km thickness which finally provides the reflection coefficient of the total atmosphere. Conversely, the effects of scattering by ice clouds are neglected for two reasons: (i) their contribution is very small because the optical depth of these clouds is lower than 0.03 (Chassefière et al., 1992), (ii) the ice clouds are dispersed and small in dimension. Three main parameters define the scattering process: i/ the single scattering albedo a ; ii/ the phase function and iii/ the total opacity. The single scattering albedo of the dust (0.9) was taken from Drossart et al. (1991), using results on the atmosphere of Mars obtained by the ISM instrument onboard the Phobos spacecraft. This value is also consistent with those from Pollack et al. (1977, 1979). The phase function is derived from Drossart et al. (1991). It can be described by a double Henyey–Greenstein function (Henyey and Greenstein, 1941; Rosenqvist, 1991) with a positive asymmetry parameter of 0.7 and a negative one of 0.5. These parameters are valid for the period of the Phobos observations (1989), but they can be extended to the period of our observations (January 1991), as the atmosphere of Mars did not exhibit large modifications (like global storms) between 1989 and 1991 (James et al., 1994). The surface reflectance property

Table 2. Relative effects of the parameter variations on the equivalent area (area multiplied by FWHM) of a line.

Parameter	Variation	Relative variation of the equivalent area of a line
Surface pressure	1 mbar	10 %
$T(0$ km)	20 K	3 %
Single scattering albedo	0.05	0.5 %
Parameter of asymmetry	0.05	1 %
Minnaert coefficient	0.05	1 %
Dust opacity	0.1	10 %
CO mixing ratio	1×10^{-4} (around 6.5×10^{-4})	4 %

is assumed to be described by the Minnaert law with a coefficient of 0.85. The scale height of the dust (≈ 6 km) was taken from Chassefière et al. (1992) and Chassefière et al. (1995).

In the case of the 1990 data, we assumed an average surface pressure on the whole disk of the planet of 6 mbar. Concerning the 1991 data, for each spectrum (i.e. for each point on the planet), we determined a local average altitude, using the two available orographic datasets: the Consortium and the Digital Terrain Model. The altitude was then used to determine the surface pressure, under the assumption of a temperature profile, using Viking data (Seiff and Kirk, 1977). The pressures were compared to those obtained with the General Circulation Model (GCM) of Laboratoire de Météorologie Dynamique which accounts for local conditions, seasonal and diurnal variations as well as for the impact of atmospheric dynamics on the surface pressure distribution (Hourdin et al., 1993, 1995). The GCM pressures systematically lie in between the extreme values obtained by extrapolation of the Viking data. The albedos were taken from Kieffer et al. (1977) in order to check out the consistency with the flux levels (see 3.1). The temperature of the atmospheric level just above the surface was directly taken from the GCM simulations.

This temperature is 210 ± 10 K for the four points and was used to compute a Viking-type thermal profile (Seiff, 1982), which is then used to calculate a CO absorption coefficient. It should be noted however that, as we work within the reflected component of the planetary emission, it is not required that the thermal profile be precisely determined. The local characteristics of the four points on the planet are given in Table 1. The effects of variations of the parameters on the integrated intensity of a typical line are given in Table 2. The CO spectroscopic data were taken from the GEISA databank (Husson et al., 1986) and the collisional broadening coefficients from Varanasi (1975). A

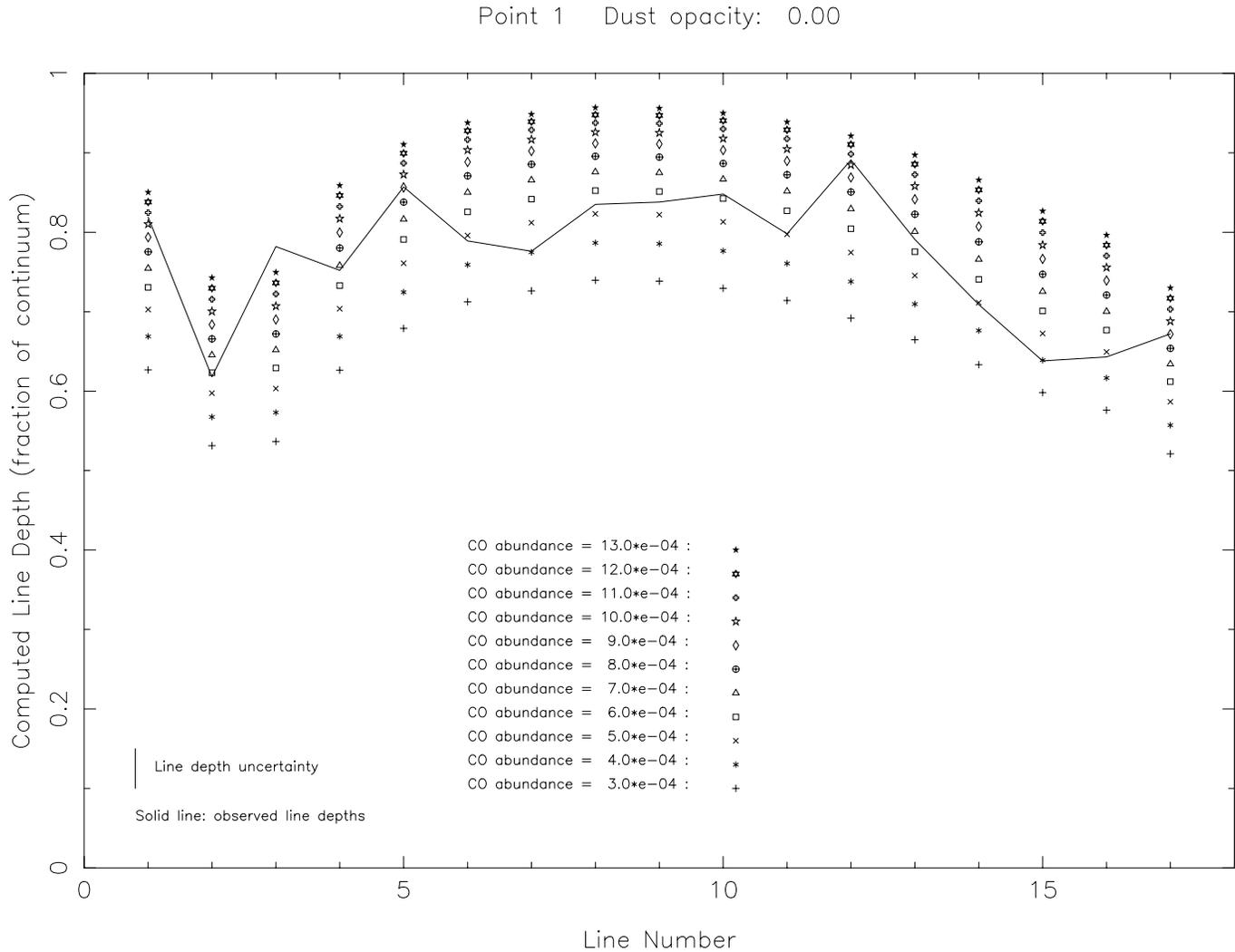


Fig. 4. Examples of fits of the line depths with various CO mixing ratios for a dust optical depth of 0.0 (no dust) in the case of the Point 1 (calculations done with the minimum value of the pressure), 1991 data.

Voigt profile was used to account for the simultaneous collision and Doppler broadening.

3.3. Results

The two unknowns in the model are the dust optical depth and of course the CO mixing ratio. We varied the dust optical depth within the 0.0 to 0.6 range, higher values being unrealistic (James et al., 1994) during periods without dust storms, as it was the case at the time of our observations. For the CO mixing ratio, we used values ranging from 3×10^{-4} to 13×10^{-4} for the 1990 data and from 3×10^{-4} to 20×10^{-4} for the 1991 data, by step of 1×10^{-4} (see examples of fits with various CO mixing ratios on Figs. 4 and 5). Again, smaller or larger values are not realistic in the frame of what we presently know about the CO mixing ratio.

The presence of atmospheric dust complicates the analysis. Indeed, all the lines that we could use are strong CO lines. The prime effect of the dust is thus that the bottom of the lines is

rising when the amount of dust is increased. As on the contrary, an increase in the CO mixing ratio deepens the lines, we see that the effects of the dust and of the CO mixing ratio go in opposite directions. The result of that is that we obtain domains of possible solutions that are not strongly constrained in the case of the 1991 data. For the 1990 data, as we could fit the line with three points (one at the center of the line and two in the wings, see Sect. 3.1) and as the effect of the dust scattering is different on the line core and line wings, the domain of solutions is narrower. In order to determine the domains of solutions, we made χ^2 tests. The result of this test with a $2\text{-}\sigma$ confidence level in the case of the 1990 data gives a value of the dust optical depth between 0.13 and 0.23 and a value of the CO mixing ratio between 4.5×10^{-4} and 8.5×10^{-4} (which gives a column density of $1.0 \times 10^{20} \text{ cm}^{-1}$ to $2.0 \times 10^{20} \text{ cm}^{-1}$), stressing that not any combination of dust opacity and CO abundance is possible (see Fig. 6).

The domains of solutions obtained after the χ^2 tests ($2\text{-}\sigma$ confidence level) for the four 1991 spectra are presented on

1990 data – Line R14

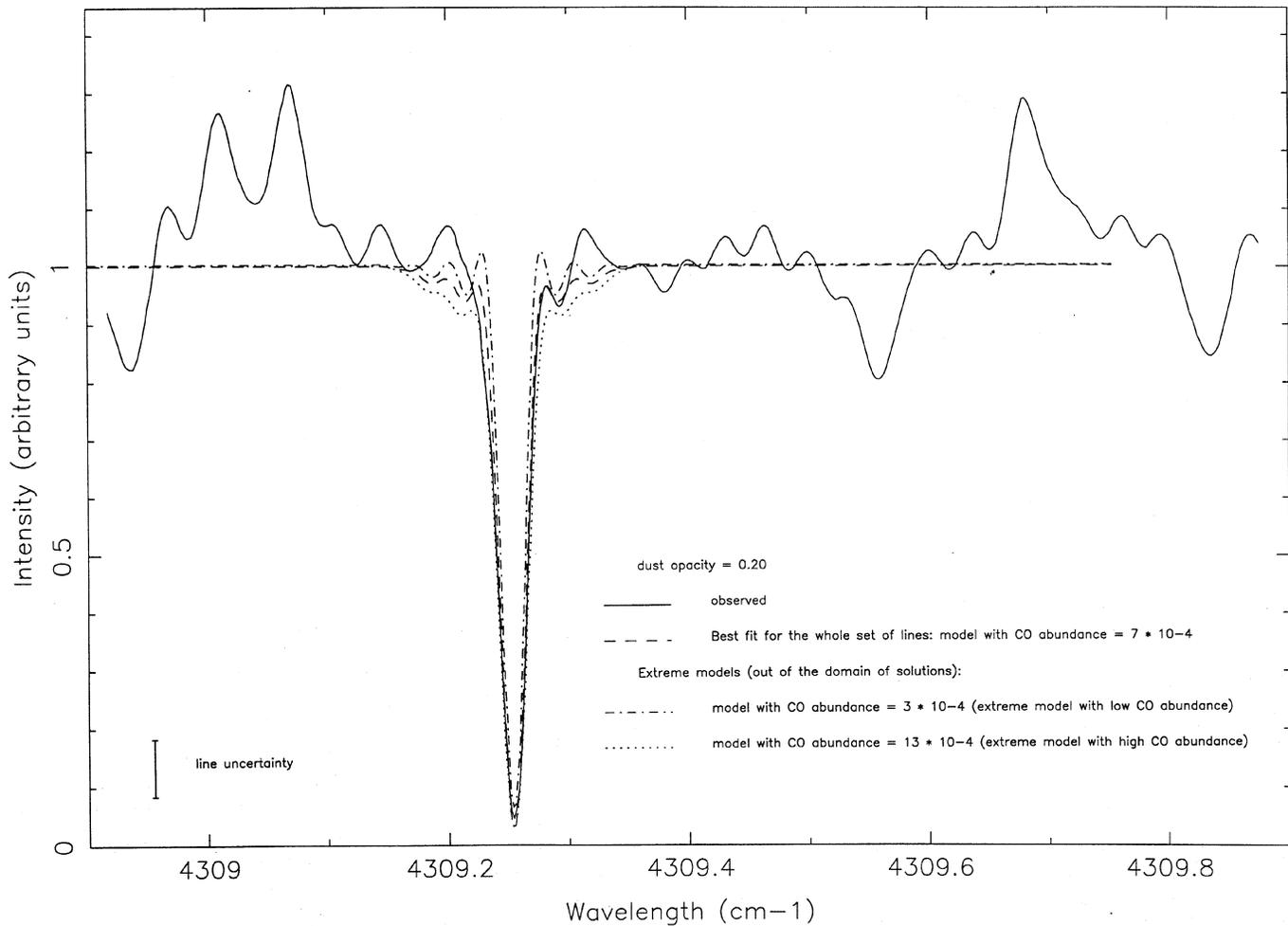


Fig. 5. Examples of fits of the R14 line of the 1990 data, with the best model and two extreme models (which are outside the domain of solutions) with the same dust opacity of 0.20.

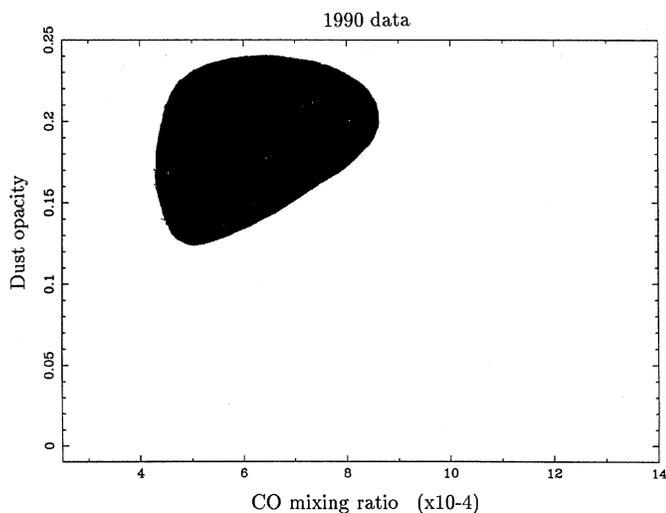


Fig. 6. Domain of solutions for the 1990 data.

Fig. 7 (note on Figs. 6 and 7 how the CO mixing ratio and dust optical depth appear to be correlated). They show that the CO abundance can take any value between 3.5×10^{-4} and 20.5×10^{-4} (column density of 1.3 to $6.5 \times 10^{20} \text{ cm}^{-1}$) for Point 1 and between 5.5 to $20. \times 10^{-4}$ (column density of 1.3 to $4.2 \times 10^{20} \text{ cm}^{-1}$) for Point 2. In fact, the upper limit is artificial and corresponds to the highest value we introduced into the model, so we could have gone higher, as shown by the shape of the domains obtained for these two points. But as we said previously, this would not be realistic. The domains of solutions for the two other points give us a value of the CO abundance that can range from $3.$ to 17.5×10^{-4} (column density of $8.5 \times 10^{19} \text{ cm}^{-1}$ to $4.8 \times 10^{20} \text{ cm}^{-1}$) for Point 3 and from $3.$ to 18.5×10^{-4} (column density of $8.9 \times 10^{19} \text{ cm}^{-1}$ to $5.4 \times 10^{20} \text{ cm}^{-1}$) for Point 4. Concerning the dust opacity, it never exceeds 0.08 for Points 3 and 4 and can take any value for Point 1 and 2. However, again, as shown on Fig. 7, not any combination of CO mixing ratio and dust opacity is possible. Fig. 8 represents the intersection of the previous domains. It shows that a CO

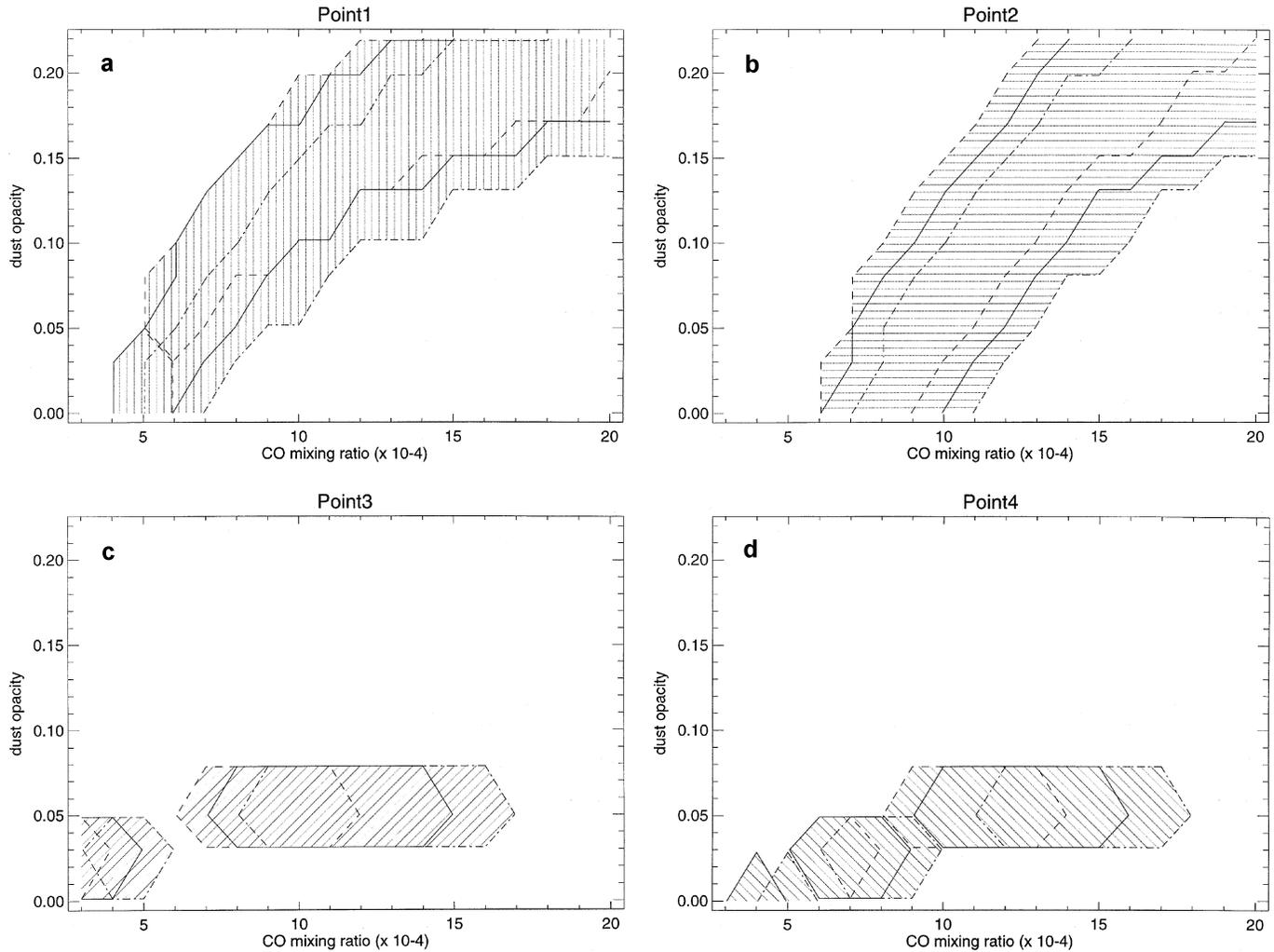


Fig. 7a–d Domains of solutions for the four points of 1991. The solid, dotted, dash-dotted lines indicate respectively the limits of the domains of solutions obtained with the optimum, minimum and maximum values of the pressure. The sharpness of the contours is due to the discretization and therefore has no real meaning. This is also the case for the gap between the two domains of solution obtained for Point 3.

mixing ratio ranging from 5.5 to 11.5×10^{-4} and a dust optical depth ranging from 0.03 to 0.08 provide a satisfactory fit to the ensemble of observations.

4. Discussion and conclusion

The values of the CO mixing ratio that we have derived from the 1990 data are in good agreement with the values obtained previously with the 1988 and 1989 data (Billebaud et al., 1992), even if our error bars allow for some small variations (of the order of 50%). This would not necessarily be in contradiction with the photochemical models, as present models admit that, considering the high sensitivity of the CO abundance to the presence of water, this abundance could fluctuate over a timescale of a few years (Nair et al., 1994; see also Sect. 1).

The results we obtain with the 1991 data are more uncertain. It is indeed possible to find values of CO mixing ratios which would be compatible with all the points. Such values would be

in the range from 5.5×10^{-4} to 11.5×10^{-4} . And the dust opacity would then remain very small on all four locations: between 0.03 and 0.08 . This range in CO mixing ratios is compatible with our previous determinations, therefore it has our preference, as in this case there is no need to invoke the presence of temporal or spatial variations of the CO abundance. However, from our results, it is not possible to firmly exclude the presence of possible variations, especially horizontal ones, over a scale of a few thousand kilometers, which corresponds to the resolution of our data. This is especially true as there could exist some variations of the dust optical depth. Indeed, Viking data showed that the dust optical depth is not constant all over the planet (Clancy and Lee, 1991). And as shown from our results (Fig. 7), a change in the dust optical depth results in a change in the CO mixing ratio. A comparison with the Rosenqvist et al. (1992) results would have been interesting, but it is unfortunately difficult, because we do not have the same spatial resolution (there is a difference of roughly a factor 3 between our resolution and the size

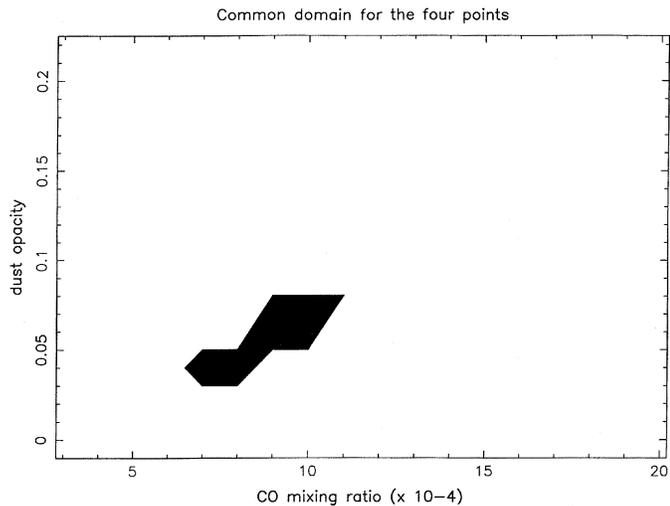


Fig. 8. Intersection of the domains obtained for the four points of 1991.

of the high volcano regions). As mentioned previously, heterogeneous chemistry could account for some spatial variations of the CO mixing ratio, but the complexity and the uncertainties introduced by such a chemistry led several authors (Anbar et al., 1993b; Nair et al., 1994; Krasnopolsky, 1995) to exclude it from their models as long as the need to introduce it is not clearly justified. In all cases, in order to obtain a firm conclusion on this issue, new observations would be necessary, and in particular it would be interesting to resolve the high volcanoes (a spatial resolution of the order of 100 km should be enough).

We consider that we have reached the limits of 1D infrared spectroscopy concerning the monitoring of species such as CO. Choosing to make observations in the thermal and solar reflected components of the planetary emission field allowed us to experience both the advantages and drawbacks of the two. The thermal component near $5\mu\text{m}$ had the advantage to be unaffected by dust scattering, but one has to carefully take the atmospheric thermal profile into account; in contrast, the solar reflected component is essentially independent from the thermal profile, but not from the presence of dust. Both components are very sensitive to the pressure, which is a key-parameter not easy to determine, especially for wide areas. In the case of observations performed in the solar reflected component of the planetary emission, a high spectral resolution and the availability of intrinsically strong and weak lines, not affected in the same way by the presence of dust, would be necessary to facilitate the interpretation of the data. The need for spatial resolution also implies to use 2D spectroscopy in order to investigate the possibility of spatial variations; and in addition, a higher spatial resolution would facilitate the determination of the average local pressure on a smaller area. Such observations, which depend on the availability of efficient spectro-imaging instruments will be performed as soon as possible.

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