# Predicting the infrared band profiles for CO2 cloud particles on Mars

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ABSTRACT

The present contribution describes the influence of the properties of potential martian CO2 cloud particles on their mid-infrared (IR) extinction spectra, with the goal to provide a reference for possible future IR extinction cloud studies on Mars. The focus lies on the understanding of the band shape of the antisymmetric stretching vibration at about 4.3 μm. For this purpose, modelling of particle spectra with the vibrational exciton model, the discrete dipole approximation, and density functional calculations are combined with experimental results recorded in a collisional cooling cell. The effect of particle size, shape, and architecture on IR extinction spectra is studied for pure CO2 particles, H2O–CO2 core–shell particles with and without a molecularly mixed interface, H2O particles partially engulfed by CO2 patches, and mineral dust–CO2 core–shell particles. The results show how IR extinction spectra might be helpful in the identification of the martian cloud properties in particular if other complementary data is available.

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## 1. Introduction

The formation of CO2 clouds on Mars and the properties of these cloud particles is an area of active study. The martian atmosphere is primarily composed of CO2 gas (about 95% by volume) (Owen et al., 1977). Generally, condensation of a planet's major atmospheric constituent is not a common occurrence, and thus the microphysics of such processes, including the formation of CO2 aerosols on Mars, are currently not well understood (Glandorf et al., 2002; Colaprete and Toon, 2003; Montmessin et al., 2007; Scholten et al., 2010; González-Galindo et al., 2011). In addition, CO2 clouds likely impact the martian climate, but to study these effects, a greater knowledge of cloud particle properties is required (Forget and Pierrehumbert, 1997; Mischna et al., 2000; Glandorf et al., 2002; Colaprete and Toon, 2003; Vincendon et al., 2011).

Despite data from numerous missions to Mars, the properties of CO2 cloud particles (e.g. size, shape) are currently not well known. A thorough summary of martian mesospheric CO2 cloud observations was compiled by González-Galindo et al. (2011). Several size estimates (effective radii) have been proposed for CO2 cloud particles, including <100 nm (Montmessin et al., 2006), 0.5–2 μm (Vincendon et al., 2011), 0.1–0.3 μm (Clancy and Sandor, 1998), 1–2 μm (Montmessin et al., 2007), 1–3 μm (Määttänen et al., 2010), and 0.1 or 1.5 μm (McConnochie et al., 2010). CO2 particle

size estimates have always been derived from Mie theory, which assumes spherical particles. While there are no direct observations of particle morphologies in the martian atmosphere, CO2 cloud particles are expected to be cubic or octahedral based on the cubic crystal structure of CO2 (Colaprete et al., 2003; Montmessin et al., 2007). Laboratory studies of CO2 deposition, either onto a bulk CO2 ice surface (Foster et al., 1998) or a cold specimen substrate at martian surface pressures (Erbe et al., 2003), resulted in formation of predominantly bipyramidal particles. Previous work in our group studying CO2 aerosols in a bath gas cooling cell resulted in particles with mainly truncated cubic morphologies (Bonnamy et al., 2005; Preston and Signorell, 2011). Although the condensation of CO2 in the martian atmosphere is not fully understood, it is generally accepted that homogeneous CO2 nucleation is less likely due to the extremely high supersaturations that would be required (Wood, 1999; Glandorf et al., 2000, 2002; Colaprete and Toon, 2003; Määttänen et al., 2005, 2007). Thus, CO2 cloud formation likely occurs via heterogeneous nucleation, with possible substrates including water, dust, and/or water-coated dust (Pollack et al., 1977; Gooding, 1986; Wood, 1999; Glandorf et al., 2000, 2002; Colaprete and Toon, 2003; Määttänen et al., 2005, 2007).

The analysis of infrared (IR) spectra of martian CO2 clouds from any future orbiter missions to Mars requires an understanding of how particle properties relate to spectra. We intend for the spectra presented in this paper to act as guide for the analysis of future occultation spectra (extinction spectra) of CO2 clouds in the martian atmosphere. For that purpose, we model IR extinction (absorption + scattering) spectra for possible CO2 cloud particles in the region of the $\nu_3$ antisymmetric stretching vibration ($\sim$2345 cm$^{-1}$ or $\sim$4.3 μm). The CO2 antisymmetric stretching motion was

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previously used as a marker for $CO_2$, for example, on several of Saturn's satellites (Cruikshank et al., 2010) as well as on Mars (Montmessin et al., 2007; Määttänen et al., 2010). The shape of this absorption band is highly sensitive to particle properties (Signorell, 2003a, 2003b; Signorell and Kunzmann, 2003; Bonnamy et al., 2005; Firanescu et al., 2006a; Signorell et al., 2006; Sigurbjörnsson et al., 2009a), and thus can provide insight into the physical characteristics of $CO_2$ cloud particles. We focus mainly on pure $CO_2$ particles, $H_2O$–$CO_2$ core–shell particles (a $H_2O$ particle completely surrounded by a $CO_2$ ice layer of even thickness), and $H_2O$–$CO_2$ particles where $CO_2$ forms patches on $H_2O$ cores rather than a complete shell. We consider the effect that particle size, shape, and architecture have on the shape of the $CO_2$ $\nu_3$ band. As well, we examine the effect of molecular mixing in the interface region of $H_2O$–$CO_2$ core–shell particles and we consider $CO_2$ particles with a dust core in place of the water core. These calculated extinction spectra can then be compared to IR spectra of $CO_2$ clouds in the martian atmosphere and give insight into which particle properties can be discerned on the basis of IR band shapes. Because the suggested cloud densities on Mars are very low, we do not consider multiple scattering in our calculations.

There exist numerous experimental studies of $H_2O$/$CO_2$ thin films in the IR (Bar-Nun et al., 1985; Gerakines et al., 1995; Andersson et al., 2004; Collings et al., 2004; Bernstein et al., 2005; Kumi et al., 2006; Öberg et al., 2007; Gálvez et al., 2007, 2008; Hodyss et al., 2008; Maté et al., 2008; Trainer et al., 2010). Many have found that molecular mixing can occur between $H_2O$ and $CO_2$, but this is highly dependent on sample temperature. Most of these studies were not performed with relevance to Mars. Experimental studies of $H_2O$/$CO_2$ aerosols with Fourier transform IR spectroscopy (FTIR) are limited (Fleyfel and Devlin, 1989; Taraschewski et al., 2005; Devlin et al., 2009) and none have reported formation of $H_2O$–$CO_2$ particles with a core–shell architecture. Both Devlin et al. (2009) and Taraschewski et al. (2005) concluded that $CO_2$ may form patches on the surface of $H_2O$ particles in their experiments. However, a thorough analysis of spectral features was not performed in either study. We have chosen to experimentally investigate the potential formation of $H_2O$–$CO_2$ core–shell aerosols in our bath gas cooling cell more carefully and compare our results to calculated spectra to support our conclusions.

## 2. Methods

### 2.1. Discrete dipole approximation

The discrete dipole approximation (DDA), as implemented in DDSCAT 6.1 (Draine, 1988; Goodman et al., 1991; Draine and Goodman, 1993), was used to model IR extinction spectra of possible $CO_2$ cloud particles. DDA can be applied to dielectric particles of arbitrary geometry (approximated by a cubic array of equally-spaced point dipoles) with sizes similar to or smaller than the wavelength of incident light (Purcell and Pennypacker, 1973). The light–particle interaction is described within the frame of classical electrodynamics and the complex refractive index of the bulk is used for the particle's optical properties.

DDA was used to model the $CO_2$ $\nu_3$ band to examine the effects of size, shape, architecture, and core material for particles ranging in size from 10 nm to 1 μm. The bulk refractive index data used as input in this work are for $H_2O$ ice (cubic, 150 K) (Mastrapa et al., 2009), $CO_2$ ice (Baratta and Palumbo, 1998), FeO (Henning et al., 1995), and $Fe_3O_4$ (magnetite) (Steyer, 1974). The applicability of DDA is limited by the availability of refractive index data and such data is rarely available for molecularly mixed substances. Additionally, the IR spectral features of particles less than 10 nm cannot be accurately reproduced using DDA. Thus, to consider each of these cases, exciton calculations were performed as outlined below.

### 2.2. Vibrational exciton calculations

The vibrational exciton model is described in detail elsewhere (Signorell, 2003b; Firanescu et al., 2006a, 2011; Sigurbjörnsson et al., 2009a). Briefly, it is a quantum mechanical model to calculate IR spectra of molecular nanoparticles. It was previously shown that resonant transition dipole coupling (exciton coupling) leads to highly structured IR band shapes that are strongly dependent on particle size, shape, architecture, and composition for vibrational bands with large transition dipole moments (>0.1 D) (Signorell, 2003b; Signorell and Kunzmann, 2003; Jetzki et al., 2004; Bonnamy et al., 2005; Firanescu et al., 2006a, 2006b, 2008, 2011; Signorell et al., 2006; Firanescu and Signorell, 2009; Sigurbjörnsson et al., 2009a, 2009b). In the exciton model, the calculation of IR absorption is reduced to this dominant interaction and the prediction of spectra for large molecular aggregates (tens of thousands of molecules) is tractable.

Calculations were performed for $CO_2$ particles ranging from 1 to 10 nm (i.e. the size range where DDA is no longer valid) for the $\nu_3$ band of $CO_2$ (transition dipole = 0.32 D). All calculations were convoluted with a 4 cm$^{-1}$ Voigt profile, unless otherwise noted. This accounts for additional broadening effects such as coupling to phonons. Note that these couplings have no significant influence on the band structure arising from the exciton coupling. The vibrational exciton model is a molecular approach which does not require refractive index data as input, and thus it is possible to analyze molecularly mixed systems. In core–shell particles, exciton calculations were used to investigate the influence of a molecularly mixed $H_2O$/$CO_2$ interface layer between the $H_2O$ core and $CO_2$ shell. Generation of these mixed $CO_2$/$H_2O$ interface structures is outlined below.

### 2.3. Mixed $H_2O$/$CO_2$ unit cells

To simulate spectra of $H_2O$–$CO_2$ core–shell particles with a molecularly mixed interface, mixed $H_2O$/$CO_2$ unit cell structures were required. A 32-molecule amorphous water cell was used as an initial structure and $H_2O$ molecules were replaced by $CO_2$ molecules to create mixed cells with $H_2O$:$CO_2$ ratios of 28:4, 24:8, 20:12, 16:16, 12:20, 8:24, and 4:28. Density functional theory (DFT), as implemented in SIESTA (Ordejón et al., 1996; Soler et al., 2002), was used to perform a relaxation of the geometry for each of the mixed cells to minimize unfavorable interactions between the molecules. These relaxed geometries were used to create the structures to model $H_2O$/$CO_2$ mixing in vibrational exciton calculations of core–shell particles.

### 2.4. Experiments

Aerosol particles were generated in a bath-gas cooling cell, which is described in detail elsewhere (Kunzmann et al., 2001; Signorell, 2003a; Firanescu et al., 2006a). Briefly, the cell was cooled to 78 K with liquid nitrogen and then filled with helium bath gas. Before use, the helium bath gas (Praxair, 99.999%) was further purified by flowing through a liquid nitrogen trap to remove trace amounts of water. Injection of dilute, room temperature gases into the cold cell leads to supersaturation and aerosol particle formation. Particles, in the aerosol phase, were analyzed *in situ* with a Bruker IFS66v/S rapid-scan FTIR spectrometer (∼380 ms per scan at 0.5 cm$^{-1}$ spectral resolution), typically over a period of about 30 min.

Previous work in our group established the formation of $N_2O$–$CO_2$ core–shell particles in the cooling cell (Signorell et al., 2006). These conditions were applied to the $H_2O$/$CO_2$ system with the goal to clarify whether $H_2O$–$CO_2$ core–shell particles can form at