



Spectral nature of CO₂ adsorption onto meteorites

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ABSTRACT

Previous studies have identified carbon dioxide (CO₂) on the surfaces of jovian and Galilean satellites in regions of non-ice material that are too warm for CO₂ ice to exist. CO₂ ice would quickly sublimate if not retained by a less-volatile material. To ascertain what non-ice species may be responsible for stabilizing this CO₂, we performed CO₂ gas adsorption experiments on thirteen powdered CM, CI, and CV carbonaceous chondrite meteorites. Reflectance spectra of the ν₃ feature associated with adsorbed CO₂ near 4.27 μm were recorded. Results show that many meteorites adsorbed some amount of CO₂, as evidenced by an absorption feature that was stable over several hours at ultra-high vacuum (UHV) and high vacuum, (1.0 × 10⁻⁸ and 1.0 × 10⁻⁷ Torr, respectively). Ivuna, the only CI chondrite studied, adsorbed significantly more CO₂ than the others. We found that CO₂ abundance did not vary with 'water' abundance, organics, or carbonates as inferred from the area of the 3-μm band, the 3.2–3.4 μm C–H feature, and the ~3.8-μm band respectively, but did correlate with hydrous/anhydrous phyllosilicate ratios. Furthermore, we did not observe CO₂ ice because the position of the CO₂ feature was generally shifted 3–10 nm from that of the 4.27 μm absorption characteristic of ice. The strongest compositional relationship observed was a possible affinity of CO₂ for total FeO abundance and complex clay minerals, which make up the bulk of the CI chondrite matrix. This finding implies that the most primitive refractory materials in the Solar System may also act as reservoirs of CO₂, and possibly other volatiles, delivering them to parts of the Solar System where their ices would not be stable.

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1. Introduction

The Solar System can be divided into regions where ices of various volatiles are stable. Jupiter is near the 'frost line' where water ice sublimates over geologic time. Farther away, water ice is stable over the age of the Solar System. Similar lines can be drawn at greater distances from the Sun where CO₂, CO, CH₄ and other ices are stable, and these distances correlate with compositions of icy satellites whose surfaces contain such icy volatiles (e.g., Grundy et al., 2003). However, volatiles are found within the surfaces of objects at distances closer to the Sun where their ices are not stable. For example, CO₂ has been found on the surfaces of the icy satellites of Jupiter and Saturn (Carlson et al., 1996; McCord et al., 1998; Hibbitts et al., 2000, 2002, 2003; Hibbitts, 2006; Brown et al., 2006; Palmer and Brown, 2008, 2011; Buratti et al., 2005; Clark et al., 2005) and water and/or hydroxyl has been detected

on the warm illuminated surface of the Moon (Clark, 2009; Pieters et al., 2009; Sunshine et al., 2009).

The presence of volatiles on surfaces in areas of the Solar System at temperatures where their ices are not stable implies the existence of a physical process that may considerably affect their distribution throughout portions of the Solar System. Our experiments explore the relationship between adsorbed CO₂ abundance, its spectral signatures, and carbonaceous chondrite meteorite composition at a temperature relevant to the non-ice material on the icy jovian satellites, Jupiter Trojan Asteroids, and to some extent asteroids in the outer Main Belt. These results have implications for the presence of CO₂ in the refractory non-ice materials on the icy satellites of Jupiter and Saturn. We also examine how adsorbed CO₂ is spectrally distinct from CO_{2(solid)} and CO_{2(gaseous)}, which provides a spectral tool for the identification of the sub-monolayer adsorbed phase of CO₂, providing insights into a process that can be fundamental within a wide range of environments in the Solar System. Here we quantify the spectral nature of CO₂ adsorbed onto carbonaceous chondrite meteorites, well above the CO₂-ice sublimation temperature and qualitatively investigate its thermal stability.

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2. Background

Examples of CO₂ trapping above its sublimation temperature have been suggested in experiments by others. Collings et al. (2004) demonstrated the co-deposition and retention of gases in H₂O ice. CO₂ gas was largely retained up to right before ~160 K, their observed water sublimation temperature. Gudipati et al. (2013) and Baragiola et al. (2013) report on increased gas adsorption in heavily irradiated water ice, through pore adsorption and subsequent pore collapse and entrapment. CO₂ can also form from irradiation of carbon-containing species and water with the CO₂ remaining trapped inside the resulting solid (see review by Bennett et al., 2013). Poston et al. (2015) demonstrated adsorption of H₂O molecules onto lunar samples above water-ice sublimation temperatures. Hibbitts et al. (2007) reported CO₂ adsorption onto clays such as montmorillonite at temperatures found in the icy satellites of Jupiter and Saturn. Dyar et al. (2010) reported on three main mechanisms for volatile retention on the Moon, such as hydrogen trapped within nominally anhydrous minerals. One process that is potentially relevant to the outer Solar System is the adsorption of CO₂ molecules to silicate materials.

2.1. Adsorption mechanisms

The CO₂ molecule is linear, covalently bonded, and centrosymmetric with characteristic double bonds between C and O. It has no dipole and thus is quite volatile despite its rather large mass, subliming under vacuum in laboratory timescales at ~72 K (Crovisier and Encrenaz, 2000). CO₂ molecules can be weakly adsorbed onto surfaces through a variety of forces ranging from its intrinsically weak quadrupole moment to weak dispersion forces (London forces) and stronger induced dipole interactions. Induced charge asymmetry and changes in bond lengths can result from the presence of localized charge centers in the host material. CO₂ can also more strongly adsorb onto surfaces, even participating in electron exchange that results in chemical reactions. For example, coupling with an oxygen ligand would result in forming a carbonate (CO₃²⁻) radical, a reaction product that can be stable at room temperature or higher. If CO₂ strongly bonds with hydrogen, it can form a carboxyl (COOH) group, which is also stable. Stable is defined as chemical bonds whose total combination energy is lower than the separated atoms. Intermediate bonds where electrons are shared, to a greater or lesser extent, with atoms in the adsorbate, can also occur with varying strengths (Gerakines, 1994; Hansen, 2012). Thus, the characteristics of the host material will affect the strength and nature of CO₂ adsorption due to variations in the presence, strength, and accessibility of adsorption sites.

Spectral characteristics of the CO₂ molecule are determined by its internal bonds and any bonds with other molecules when adsorbed. The double bonds between the carbon and oxygen atoms induce an antisymmetric stretching mode at 4.268 μm and a bending mode at 15.015 μm in its ice (Bernstein et al., 2005). When an otherwise volatile molecule is electronically trapped by adsorption, it interacts with nearby electric fields that induce a change in its charge distribution somewhere between that of a gas and solid (McCord et al., 1998). Because the physical state and the electronic environment around the CO₂ molecule affect its spectral characteristics, the absorption bands for adsorbed CO₂, CO_{2(solid)}, and CO_{2(gaseous)} are generally different. Strong interactions, such as charge transfer associated with chemical bonds, may result in the onset of new adsorption features such as the 3.8–4.0 μm spectral feature in carbonate. Weaker electronic interactions that distort the electric field around the CO₂ molecule can shift, distort, and activate otherwise inactive modes in the CO₂ IR spectrum (e.g., Bernstein et al., 2005). The changes in bond lengths cause a shift

in the ν₃ band either to higher energy wavelengths shortward of 4.268 μm or to lower energy wavelengths longward of 4.268 μm. For example, a change in the C=O bond length was observed as a shift in the position of the ν₃ band in CO₂ adsorbed onto refractory materials (Buckingham and Disch, 1963). Because of the observed spectral dependency on the nature and degree of CO₂ adsorption on a host material, we here explore the possibility that variations in meteorite composition could result in changes in its affinity for adsorbing CO₂ and in the spectral characteristics of the adsorbed CO₂.

The amount of CO₂ that adsorbs onto materials is dependent on several physical characteristics. Some of these factors, such as composition, mineral structure, and microporosity within the grain, are intrinsic characteristics. Other factors such as grain size and temperature are extrinsic factors. Variations in the charge density of the accessible cations due to compositional variations may explain variations in CO₂ adsorption. With increasing size of the replaceable cation, the van der Waals forces become weaker between phyllosilicates sheets allowing for greater CO₂ mobility in and out of phyllosilicate sheets (Thomas and Bohor, 1967). The microscopic surface area, or microporosity, of the adsorbate greatly affects the effective surface area (e.g., Chiou, 2002), and thus the total area onto which CO₂ can adsorb. Clays, for instance, can have surface areas on the order of 100 m²/g due to their complex structures with significant void spaces larger than the size of the CO₂ molecule (Chiou, 2002). This relative large surface area, and the availability of charge compensating cations as adsorption sites, has been claimed as responsible for the large amount of adsorption and apparent stability for CO₂ onto zeolites (Bolis et al., 2004) and onto complex clay minerals at ~150 K (Hibbitts and Szanyi, 2007). Additionally, grain size directly impacts surface area, with smaller grains having a greater surface area per unit volume or mass than do larger grains (e.g., Dyar et al., 2010). Adsorption is also greatly affected by the pressure at which the experiments are conducted. Physisorption CO₂ experiments conducted at pressures of a few torr for application to Mars (e.g., Fanale and Cannon, 1979) demonstrated over 2% of CO₂ will adsorb onto fine-grained complex clay minerals. Under the vacuum conditions of the experiments conducted in this research, ~1.0 × 10⁻⁸ to 1.0 × 10⁻⁷ Torr, there is essentially no overburden pressure and physisorption will not occur.

2.2. Carbonaceous chondrite meteorites: primitive refractory Solar System materials

Carbonaceous chondrites can be subdivided into at least eight groups trending from most aqueously altered to the most thermally metamorphosed. These groups were classified on the basis of bulk composition, hydrogen and oxygen isotopes, chondrule abundances, and refractory elemental abundances (e.g., Clayton and Mayeda 1999; Eiler and Kitchen 2004; Brearly, 1995, 2010; Buseck and Hua, 1993; Botta and Bada, 2001). Our study focuses on the most primitive and aqueously altered groups: CI and CM carbonaceous chondrites. We also explore CV chondrites for comparison against CI and CM chondrites. The studied meteorites are tabulated in Table 1.

CI chondrites contain similar elemental and mineralogical compositions to the primordial Solar System, along with high carbon, volatile, and indigenous water contents (e.g. Cloutis et al., 2011; Wilkening, 1978). The typically fine-grained material exhibits grain sizes down to the sub-micron level and complex, poorly crystallized layer-lattice phyllosilicates hosting hydroxyl and lesser amounts of organics, oxides, Ni-rich sulfides, sulfates, carbonates, pyroxenes, and olivines. The phyllosilicates primarily include serpentine, smectite, and saponite group minerals along with cronstedtite. Sulfides, oxides, and orthosilicates include tochilinite,

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