

PHYSISORPTION: TRAPPING VOLATILES IN THE SURFACES OF ICY SATELLITES. C. A. Hibbitts¹ and J. Szanyi², ¹Johns Hopkins Univ. Applied Physics Laboratory, 11100 Johns Hopkins Rd., Laurel, Md. 20723, email: karl.hibbitts@jhuapl.edu, ²Pacific Northwest National Laboratory, EMSL, Richland, Wa., 99352, email: janos.szanyi@pnl.gov.

Introduction: Frozen water and non-ice materials dominate the surfaces of the icy satellites orbiting Jupiter and Saturn [1,2,3,4]. Observations by spacecraft and earth-based telescopes have also discovered a few additional materials at lower abundances. Of these, carbon dioxide is one of the most prevalent, having been detected over much of Callisto, Ganymede, Iapetus, Phoebe, and to a lesser extent on Europa, Enceladus, Dione, Hyperion, and Saturn's F-ring [5,6,7,8,9,10,11,12,13]. On Ganymede and Callisto the molar CO₂ abundance is estimated to be ~ 0.1 % [14,15,16]. However, its physical state and origin remain only partly understood.

In an attempt to address the question of how it is held in these satellites' surfaces, we have measured the infrared (IR) ν_3 feature of CO₂ adsorbed onto a selection of minerals that are potential compositional and spectral analogs to the nonice materials on these satellites. This is particularly relevant to the Galilean satellites Callisto and Ganymede where the CO₂ detected by infrared spectroscopy is most likely contained within the nonice material [8,15]. Results from these laboratory experiments support the hypothesis that some of this CO₂ may be physisorbed. This mechanism of binding the CO₂ to the surface places few constraints on the origin or host material of the CO₂.

CO₂ in the satellites' surfaces: The shape and position of the infrared reflectance minimum for the CO₂ ν_3 band at ~ 4.26 μm is distinctly different from that of pure CO₂ ice or gas, and is consistent with CO₂ trapped in one or more host materials [e.g. 8]. Spectral mixing models demonstrate that most of the CO₂ on Callisto and Ganymede responsible for the distorted ν_3 band cannot be in the ice, which is large-grained, but is contained within the non-ice material [15,16]. Additionally, the surfaces of the Galilean and at least some of the Saturnian satellites are sufficiently warm that the CO₂ must be stabilized in a host material to prevent its escape into space. The spectral characteristics of the CO₂ absorption band are also similar on several of the Galilean and Saturnian satellites [16,9,10]. This similarity implies similar physical states for the trapped CO₂ and possibly a single trapping mechanism

Physisorption: We propose that this trapping mechanism may be physisorption. Physisorption is caused by weak inter-molecular van der Waals forces between the adsorbate molecules and areas of asymmetric charge distribution within the adsorbing host

material. The van der Waals force can exist between CO₂ and an adsorbent when a charge asymmetry in the adsorbent induces a weak dipole within the otherwise symmetric CO₂ molecule. This partial electronic polarization of the CO₂ is thus a function of the structure of the host molecule and the charge distribution within the host molecule. Complex silicates offer excellent structures for the adsorption of CO₂ because of their significant asymmetric distribution of charges within a unit cell and their large microporosity offering many sites for CO₂ to adhere [17]. This results in considerable absorption. However, at room temperature, the strength of the van der Waals bond is insufficient to keep the CO₂ adsorbed when the host material is exposed to vacuum.

Results and Conclusions: We have found that CO₂ can remain physisorb onto some clays when the CO₂ partial pressure is effectively zero under ultra-high vacuum (UHV) if the adsorbent is cooled to the surface temperatures of the icy satellites of Jupiter and Saturn (Figure 1). CO₂ remains adsorbed onto the clay mineral montmorillonite for > 10s of minutes when exposed to a vacuum of ~1 x10⁻⁸ Torr at ~ 125K. However, CO₂ does not adsorb onto serpentine, goethite, or palagonite under these conditions. A small

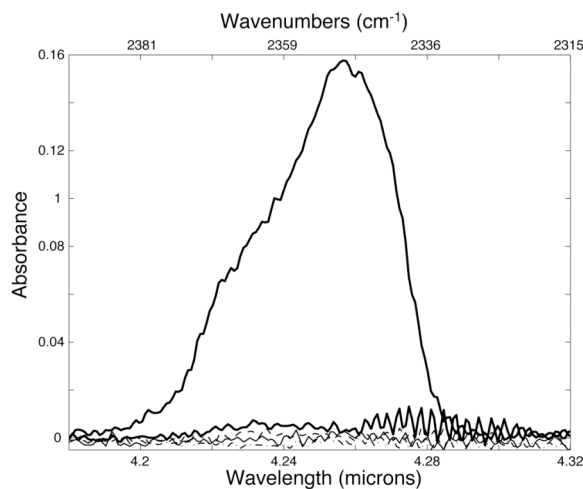


Figure 1. CO₂ adsorption onto nonice materials at ~ 125-142K under ~1x10⁻⁸ Torr. Ca-montmorillonite strongly adsorbs CO₂ (thick black line). Kaolinite may adsorb a small amount (thick black line). Serpentine, goethite, and palagonite (thin lines) do not adsorb detectable quantities.

amount may adsorb onto kaolinite. These are materials that may have similar microporosities, but whose unit cells possess much less charge asymmetry than smectites. When heated above 150K under vacuum, the CO₂ desorbs from the montmorillonite within a few minutes. We infer that the presence of a strong charge asymmetry which can induce a strong dipole in the CO₂ molecule is the most important requirement for physisorption at cryogenic temperatures.

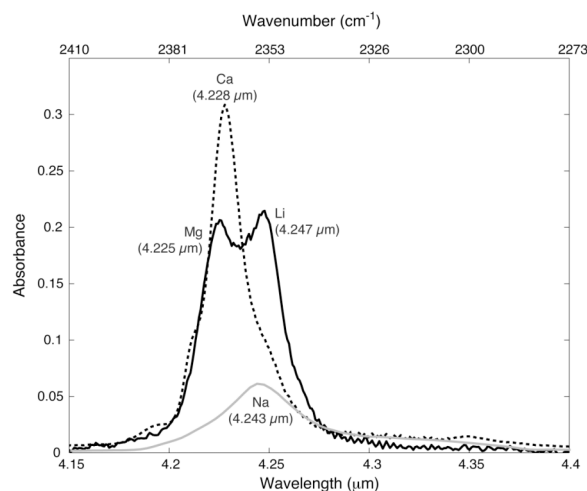


Figure 2. . **Room-temperature** spectra of CO₂ physisorbed onto various montmorillonite minerals. The cation composition of the montmorillonite affects the shape of the absorbance spectrum. Black: Mg,Li. Gray: Na (scaled x8), Dotted: Ca.

The strength of adsorption and the spectral characteristics of the adsorbed CO₂ infrared ν_3 absorption band near 4.25 μm also can depend on the composition of the adsorbent (Figure 2). The ν_3 absorption band of CO₂ adsorbed onto montmorillonite at 125K is similar to that of the CO₂ detected on the Saturnian and Galilean satellites (Figure 3) and is markedly different from CO₂ adsorbed onto the same montmorillonite at room temperature. The temperature-dependency may signify that different sites are accessed by CO₂ at cryogenic and room temperatures. The temperature dependency in the stability of the CO₂ and on its spectral characteristics, and the compositional dependency on the spectral characteristics of the CO₂ are consistent with the adsorption process being physisorption. We postulate that this mechanism may explain the presence and spectral characteristics of the CO₂ detected in the surfaces of the Jovian and Saturnian icy satellites.

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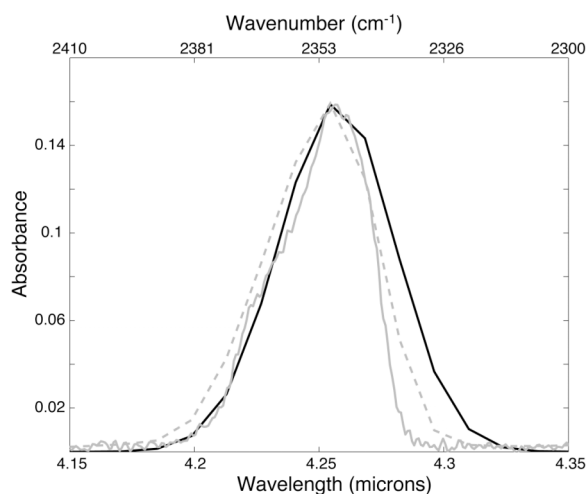


Figure 3. The laboratory spectrum of CO₂ physisorbed onto Ca-montmorillonite at 125K is similar to the Galileo NIMS spectrum of CO₂ in the surfaces of the Galilean satellites. Black line: NIMS spectrum CO₂ in the surface of Callisto (scaled x 0.17). Gray line: Laboratory data at full resolution of ~2nm (solid); and resampled to NIMS channels and spectral resolution (dashed).

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