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Review

Potential infrared relaxation channels calculated for CO_2 clathrate hydrates

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ABSTRACT

The infrared bar-spectrum of a single carbon dioxide molecule encapsulated in nano-cage clathrate hydrate is determined using the LD (Lakhlifi–Dahoo) extended site inclusion model successfully applied to analyze the spectra of CO_2 isotopologues isolated in rare gas matrices. Trapping is energetically more favorable in clathrate structure of type sI than sII. CO_2 exhibits hindered orientational motions (librational motions) around its equilibrium configurations in the small and large nano-cages. The orientation transitions are weak, and the spectra are purely vibrational. In the static field inside the cage, the doubly degenerate bending mode ν_2 is blue shifted and split. From the scheme of the calculated energy levels for the different degrees of freedom, which is comparable to that of CO_2 in rare gas matrices, it is conjectured that infrared excited CO_2 will rather relax radiatively. Non-radiative channels can be analyzed by binary collision model.

Contents

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1. Introduction

Clathrate hydrates are characterized by a compact assembly of nano-cages that naturally contain some atoms and/or molecules that stabilize their formation. They are thought to be present in numerous bodies of the Solar System. Several gas species observed in the Martian atmosphere (CO_2, CH_4, noble gases,…) could have been stored in subsurface clathrate reservoirs in the past [11,44,31], and/or be possibly involved in the present seasonal cycle of volatiles resulting from the alternate condensation of CO_2 and H_2O on seasonal hemispheric polar caps [22]. Clathrate hydrates are thought to be present on other bodies of the Solar System like comets, giants planets, the satellite Titan of Saturn, in ice mantles of dust in the interstellar medium (ISM) and to have been a major component of outer solar nebula planetesimals ([18], and references therein).

One major challenge of today's planetary sciences is to observe clathrate hydrates on other bodies of the Solar System. High resolution solar reflectance near infrared spectroscopy is a powerful way to detect clathrate hydrates at the surface of planets. CO_2 is the major constituent of Mars atmosphere. Thermodynamic conditions in polar regions theoretically allow the formation of CO_2 clathrates, possibly containing traces of other gases. The lowest temperature reached on the south polar cap of Mars in winter is in the range from 140 to 160 K. At such temperatures, some spectral features of CO_2 encaged in clathrates, quite pronounced at lower temperatures relevant to molecular clouds, are still detectable provided the spectral resolution is high enough, typically $1\ cm^{-1}$, at $2330–2350\ cm^{-1}$ [21]. Such a high spectral resolution is provided by the ACS spectrometer on the Exomars Trace Gas Orbiter mission presently underway to Mars [46]. A detection of CO_2 clathrates at the surface of Mars is therefore theoretically possible in a near future.

Another interesting output of this paper is to understand the detailed radiative behavior of molecules of exobiological interest within clathrates, which drives the evolution of the temperature of clathrates in presence of an ambient infrared radiation. It is of particular interest to understand the physics and chemistry of the processes of formation of complex molecules on icy grains in the interstellar medium, knowing that molecules trapped in clathrates cannot react together to form more complex matter. Observations in the cold regions of the interstellar medium have revealed the presence of icy grains which contain atoms, radicals and simple molecules such as H_2O (the most abundant molecule), H_2, CO, CO_2, HCN, NH_3, H_2CO, CH_4, CH_3OH, as well as larger molecules such as polycyclic aromatic hydrocarbons (PAH) [20,29]. It is nowadays thought that the dominant mechanism for the formation of molecules is provided by surface-catalyzed chemical reactions on low temperatures interstellar dust grains. For instance, Watanabe and Kouchi [49] have experimentally produced the formaldehyde H_2CO and methanol CH_3OH molecules by successive hydrogenation of CO on the surface of icy grains at 10 K. Laboratory experiments reported that organic molecules such as glycine and other amino acids can be formed from ultraviolet photo-irradiation of cold interstellar ice analogs containing mixtures of H_2O, CO, CO_2, NH_3, CH_4, and CH_3OH species [6,33,36] and, more recently, nucleobases such as uracil, cytosine and thymine compounds were produced by photo-irradiating pyrimidine-H_2O–CH_3OH–NH_3 and pyrimidine-H_2O–CH_3OH–NH_3–CH_4 ice mixtures [37]. Moreover, very recently, Meinert et al. [30] observed the formation of ribose and diverse related sugar molecules by irradiating an interstellar ice analogs containing H_2O, CH_3OH, and NH_3 molecules at a temperature of 78 K. Theoretically, *ab initio* quantum chemical computations have been performed in order to understand the mechanisms for the formation of uracil and thymine from pyrimidine-pure H_2O, pyrimidine-H_2O–CH_3OH and pyrimidine-H_2O–CH_4 ice mixtures at low temperatures (15–20 K) [4,5].

In low temperature clathrates, vibrational frequencies of triatomic carbon dioxide CO_2 trapped in nano-cages occur at infrared frequencies shifted from those observed in gas phase. The spectra are generally simpler as the rotational and translational degrees of freedom of the trapped molecule are hindered inside the cage. The vibrational shifts are relatively small, typically less than 0.5% of the observed gas phase frequencies. The shifts can thus be determined by considering that the intramolecular electronic potential that drives the vibrations of the CO_2 trapped molecule is slightly perturbed.

The aim of this paper is to calculate, within the frame of the Born–Oppenheimer approximation, the energy levels of the different degrees of freedom of CO_2 clathrate hydrates and thus determine the different channels through which energy can spread inside the clathrate after CO_2 absorbs infrared radiation. The results of these calculations are connected to the effects of global warming on the stability of clathrates. This work is an attempt to simulate the relaxation of absorbed infrared energy in a clathrate. There may be different channels that does not lead directly to the release of the trapped CO_2 through a warming effect because the energy may be released radiatively with limited temperature rise of the clathrate. This depends on how isolated CO_2 is inside the nano-cages of a clathrate. Another field in which these results may be useful is in the indirect determination of isotopic ratios