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Modeling IR spectra of CO_2 isotopologues and CH_4 trapped In type I clathrate

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Abstract. To test the hypothesis of atmospheric carbon dioxide or methane storage in metastable clathrate, a theoretical formalism is developed to model and simulate the spectra of the CO_2 or CH_4 molecule trapped in clathrates. 12-6 Lennard-Jones atom-atom potentials are used to account for short and long range interactions between the atoms of the trapped molecules and atoms of H_2O molecules of the cage. Effective electric charges are used for electrostatic interactions with H_2O molecules. The calculations were performed on clathrates of type I, with a small and a large cage to determine equilibrium configurations for both CO_2 and CH_4 and vibrational shifts were determined for CO_2 in an undistorted trapping nano-cage.

1 The interaction potential energy

The interaction potential energy V_{MC} between the trapped CO_2 or CH_4 molecule and the rigid clathrate cage is expressed as:

$$V_{MC} = \sum_{k=1}^{N_W} \sum_{j=1}^{3} \sum_{i=1}^{3} 4\varepsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij_k}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij_k}} \right)^{6} \right\} - \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij_k}}$$

where i and j denote the i^{th} atom of the trapped CO_2 or CH_4 molecule and the j^{th} atom of the k^{th} water molecule of the clathrate matrix, separated by the distance vector r_{ijk} ; and ε_{ij} and σ_{ij} are the mixed LJ potential parameters, obtained from the usual Lorentz-Berthelot combination rules $\varepsilon_{ij} = \sqrt{(\varepsilon_{ii}\ \varepsilon_{jj})}$ and $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$. In the second term of the above equation q_i and q_j are the electric charges of the i^{th} atom of the trapped molecule and the j^{th} atom of the water molecules.

2 Results of equilibrium configuration

Calculations were performed on clathrates of type I, with unit cell consisting of 2 dodecahedral cages (5^{12}) and 6 tetrakaidecahedral cages ($5^{12}6^2$), termed small and large cage respectively and results are given in Figures 1a) and 1b). The minimum configuration energy for the small cage corresponds to an interaction energy of - 378 meV (- 3050 cm^{-1}). The molecule is at the center of the cage opposite to the centers of 2 pentagonal faces and with an allowed translation motion around the center of the cage. For the large cage, energy minimum is calculated to be - 418 meV (- 3375 cm^{-1}). The molecule is parallel to the two hexagonal faces of the cage with a translational motion of large amplitude (0.07 nm) around the center of the cage in the direction parallel to the hexagons. Only librations are expected from calculations [1,2].

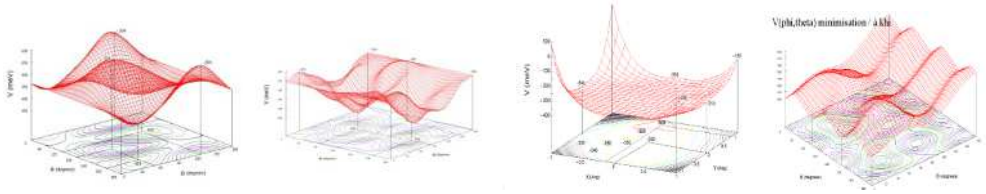

Figure 1 a) CO_2 in large cage b) CO2 in small cage c) CH_4 in large cage d) CH_4 in small cage.

For CH_4, results are given in Figures 1c) and 1d). Calculations give in the small cage a minimum potential energy of - 405 meV (- 3270 cm^{-1}). CH_4 is at the center of the cage, with H atoms more or less facing pentagonal faces. In the large cage : the minimum potential energy is determined to be - 338 meV (- 2730 cm^{-1}). CH_4 is not at the center of the cage and H atoms point more or less to pentagonal faces. For both cages, translational motions of large amplitudes and hindered orientational motions are expected from calculations [3].

Results in the undistorted cages show that the CO_2 vibrational fundamental modes are blue shifted in the small cage and red shifted in the large one. A larger effect is shown for levels coupled by Fermi Resonance and a splitting of the degenerate vibrational mode ν_2 is expected. Preliminary results in distorted cages show only red shifts are to be expected.

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