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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$_2$O molecules of the cage. Effective electric charges are used for electrostatic interactions with H$_2$O 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:

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

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 $\varepsilon_{ij}$ and $\sigma_{ij}$ 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.

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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](image)

Figure 1 a) CO\(_2\) in large cage b) CO\(_2\) 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 \(v_2\) is expected. Preliminary results in distorted cages show only red shifts are to be expected.

References


