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Investigating CH_4 Thermal Activation in Clathrate Nano-cages

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Abstract. The energy levels of methane molecule trapped, at low temperature, in small (*s*) and large (*l*) nano-cages of cubic sI clathrates are calculated in the Born-Oppenheimer approximation using the Extended Lakhlifi-Dahoo model based on pairwise atom-atom effective interaction potentials. In the *s* cage, the center of mass of CH_4 exhibits a slightly asymmetrical 3D oscillation motion with small amplitude around the cage center. Two methods were used to calculate the frequencies of such a motion: a 3D harmonic treatment and a 1D Discrete Variable Representation (DVR) treatment in the *X*, *Y* and *Z* directions. They give approximately the same values of, respectively, 133 cm^{-1}, 108 cm^{-1} and 120 cm^{-1}. In the *l* cage, the oscillations are anharmonic and characterized by large amplitude motions with frequencies of 63 cm^{-1}, 52 cm^{-1} and 47 cm^{-1}. In the *s* and *l* nano-cages, the molecule exhibits strongly perturbed rotational motion. The rotational level schemes are quite different from that of the molecular free rotational motion, and for each nano-cage, the obtained levels are described as combination of the free rotation levels.

1. Introduction

A great number of research activities in the field of astrophysics are devoted to clathrates, crystalline solids formed by a compact assembly of nano-cages. Clathrates exist as three different kinds of Archimedes polyhedra characterized by two types of cubic structures termed sI and sII with a cage-like structure of water molecules surrounding atoms or small molecules and a hexagonal structure-H (sH) [1], which forms in the presence of large guest molecules. The unit cell of sI consists of 46 water molecules with two types of cages; 2 small 5^{12} cages (*s*), and 6 large $5^{12}6^{2}$ cages (*l*) [4]. In the sII structure unit cell there are 136 water molecules which form 16 small 5^{12} and 8 large $5^{12}6^{4}$ cages. In this work, we investigate the effect on the thermal properties of clathrates when they trap methane (CH_4) molecules. This effect is studied through the relaxation channels through which an IR excited CH_4 redistributes its energy. These channels are connected to the structure of the energy levels related to its low frequency motions and which are determined by solving the Schrodinger's eigen-value equation based on the

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Hamiltonian of the encaged molecule. In the following, the Extended Lakhlifi-Dahoo model [2][3] based on pairwise atom-atom effective interaction potentials is applied to CH_4 in sI and sII types clathrate and the results discussed by comparison to previous results obtained on CO_2.

2. The Site inclusion model and interaction potential energy

To simulate the spectra of the CH_4 molecule trapped in clathrate nano-cages, the theoretical model is built as an extension of the site inclusion one applied to study C_3, CO_2 and N_2O molecules [4-6] trapped in rare gas matrices. Electrostatic interactions between atoms of CH_4 and H_2O, are modelled by the usual 12-6 Lennard-Jones (LJ) interatomic potentials at short range and mid-range distances and by effective charges placed on the atoms of the molecules at long range distances. The validity of the Born-Oppenheimer approximation is assumed to separate the vibrational degrees of freedom (high frequency motions) from the orientational and translational degrees of freedom (low frequency motions) of the system formed by the molecule and the nano-cage. Then the total potential energy of the trapped molecule inside the nano-cage is written as:

$$V = \sum_{j} V_{Mj}\left(\mathbf{r}_{0j}\right) + \sum_{jj',j\neq j'} V_{jj'}\left(\mathbf{r}_{jj'}\right) \tag{1}$$

where the term V_{Mj} is the molecule-cage interaction and $\mathbf{r}_{0j}$ is the distance vector between the centre of mass (c.m.) of CH_4 and the jth atom of the cage (*s* or *l*). The second term $V_{jj'}$ represents the interaction potential between two atoms of the cage: *i*) a jth atom, of one H_2O molecule, located at position $\mathbf{r}_j$ and *ii*) a j'^{th} atom, of another H_2O molecule of the cage, located at position $\mathbf{r}_{j'}$ with respect to an absolute frame (O, **X**, **Y**, **Z**) tied to the cage.

The interaction potential energy V_{Mj} between the CH_4 molecule and an atom of the cage is the sum of 12-6 LJ potentials representing the repulsion-dispersion contributions and the electrostatic interaction from effective charges q_i (i=1,…, 5 for CH_4) and q_j on the atoms of the H_2O molecules of the *s* or *l* cage, such that :

$$V_{Mj}\left(\mathbf{r}_{0j}\right) = \sum_{i=1}^{5}\left[4\varepsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right\} + \frac{1}{4\pi\varepsilon_0}\frac{q_i q_j e^2}{r_{ij}}\right] \tag{2}$$

where ε_{ij} and σ_{ij} are the mixed LJ potential parameters from the Lorentz-Berthelot combination rules $\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$ and $\sigma_{ij} = \dfrac{\sigma_{ii}+\sigma_{jj}}{2}$. The distance vector $\mathbf{r}_{ij}$ between *i* and *j* atoms can be expressed in the molecular frame (G, **x**, **y**, **z**) or the crystal frame (O, **X**, **Y**, **Z**) as given in reference [2]. The orientational degrees of freedom, $\mathbf{\Omega} = (\varphi, \theta, \chi)$, of the molecule and the position vector of any atom, *j*, are defined in the absolute crystal frame (O, **X**, **Y**, **Z**).

In the rigid crystal approximation, the potential energy hypersurface of the molecule in its cage, *n* (*n* = *s* or *l*), can then be written as :

$$V_M^{(n)}\left(\boldsymbol{\xi}^e, \mathbf{u_0}, \mathbf{\Omega}, \{Q\}\right) = V_M^{(n)e}\left(\boldsymbol{\xi}^e\right) + V_M^{(n)}\left(\boldsymbol{\xi}^e, \mathbf{u_0}\right) + V_M^{(n)}\left(\boldsymbol{\xi}^e, \{Q\}\right) + V_M^{(n)}\left(\boldsymbol{\xi}^e, \mathbf{\Omega}\right) + \Delta V_M^{(n)}\left(\boldsymbol{\xi}^e, \mathbf{u_0}, \mathbf{\Omega}, \{Q\}\right) \tag{3}$$

where $V_M^{(n)e}\left(\boldsymbol{\xi}^e\right)$ is the minimum of the potential energy corresponding to the equilibrium configuration; $V_M^{(n)}\left(\boldsymbol{\xi}^e, \mathbf{u_0}\right)$ is the c.m. translation dependence in terms of the dynamical coordinate vector; $V_M^{(n)}\left(\boldsymbol{\xi}^e, \{Q\}\right)$ is the vibrational dependence in terms of normal coordinates $\{Q\}$; $V_M^{(n)}\left(\boldsymbol{\xi}^e, \boldsymbol{\Omega}\right)$ is the orientational dependence in terms of Euler angles $\boldsymbol{\Omega} = (\varphi, \theta, \chi)$; $\Delta V_M^{(n)}\left(\boldsymbol{\xi}^e, \mathbf{u_0}, \boldsymbol{\Omega}, \{Q\}\right)$ characterizes the translation-orientation-vibration dynamic coupling term, which can induce the relaxation of vibrational modes onto the translational and orientational modes; and $\boldsymbol{\xi}^e$ represents the equilibrium configuration displacement vector of the c.m. of H_2O molecules of the cage and of the trapped CH_4, determined on the basis of the Green's functions of the perfect crystal.
From the potential energies calculated for the low frequency motions, the Hamiltonian can be solved for the eigen-values of the allowed translation and orientation in each cage (*s* or *l*);

$$H_M^{(n)} = H_{vib}^{(n)} + T_{rot}^{(n)} + T_{trans}^{(n)} + V_M^{(n)}\left(\boldsymbol{\xi}^e, \mathbf{u_0}, \boldsymbol{\Omega}, \{Q\}\right) \tag{4}$$

where the sum of the first three terms, $H_{vib}^{(n)} + T_{rot}^{(n)} + T_{trans}^{(n)}$, corresponds to the free CH_4 molecular Hamiltonian.

3. Results and discussion

Calculations were performed for the CH_4 molecule trapped in clathrate matrices: sI containing 4x4x4 unit cells (up to 2,944 water molecules) and sII with 3x3x3 unit cells (up to 3,672 water molecules). In the *s* cage of sI, the equilibrium configuration corresponds to a minimum energy value of -266 meV (-2,145 cm^{-1}), the molecular c.m. being located nearly at the cage center and oscillating with small amplitude. In the *l* cage, the minimum energy value is of -263 meV (-2,123 cm^{-1}), and the molecule is displaced from the cage center by about 0.3 Å in a direction parallel to the two hexagonal faces and exhibiting a translational motion of large amplitude. In the sII structure, the minimum energy values are of -238 meV and of -229 meV, respectively, for the *s* and *l* cages. These results show that trapping of CH_4 in sI is more favourable than in sII. As a result, we focus our quantum mechanical (molecular internal vibrational and orientational modes) computations on the CH_4-clathrate sI system, only.
Using the Born-Oppenheimer approximation, the c.m. of the rigid molecule is fixed at its equilibrium position in the cages, the orientational part $V_M^{(n)}(\varphi, \theta)$ of the interaction potential energy minimized with respect to the χ proper rotation (spinning) angle, is analysed. Figure 1 gives the 2D contour plot of the energy calculated for CH_4 trapped in the small (a) and large (b) cages.

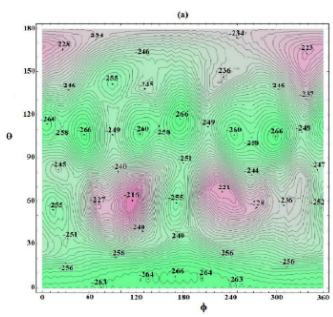

Figure 1 a). Potential energy of CH_4 as a function of orientation in cage *s*.

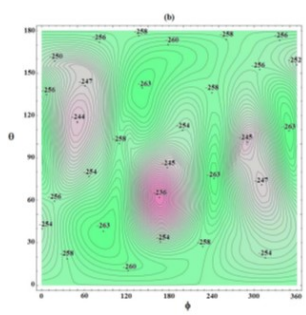

Figure 1 b). Potential energy of CH_4 as a function of orientation in cage *l*.

The Figures show that the molecule exhibits a rather perturbed rotational motion such that the calculated rotational eigen-vectors are linear combinations of eigen states linked to the free rotation of the molecule. It is then necessary to define new quantum numbers to label the resulting eigen-states as given by:

$$\left| j\gamma \right\rangle^{(n)} = \sum_{JMK} \Lambda_{JMK}^{j\gamma} \left| JMK \right\rangle \tag{5}$$

where j is an integer number ($j = 0, 1, 2, \ldots$) and γ takes values: *i*) $\gamma = 0$, for simply degenerate states, for the values $K = 0, \pm 3, \pm 6, \ldots$ of the spinning number and *ii*) $\gamma = \pm$, doubly degenerate states, for the other K values. This is due to the symmetry C_{3v} of the CH_4 molecule. Finally, when the transition elements of the IR rovibrational active modes ν_3 and ν_4 of CH_4 are calculated, the IR spectra are comprised of an intense Q line associated with vibrational transition surrounded by many R branch (blue shift) and P branch (red shift).
The level schemes in the small (Figure 2a) and in the large (Figure 2b) cages are quite different from that of the CH_4 free rotation motion as shown in Figure 2c.

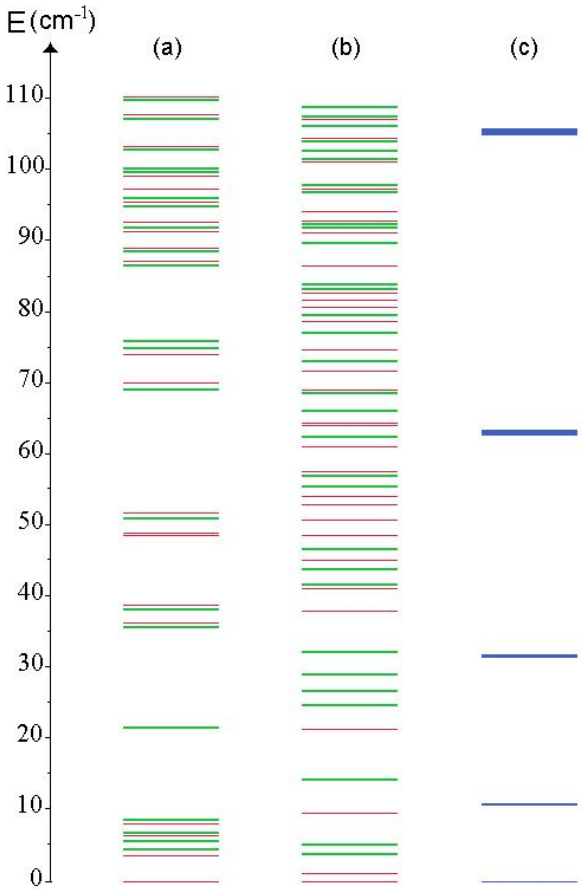

Figure 2. Calculated rotational level schemes of CH_4 in the small (a) and large (b) cages of sI structure. Level scheme (c) corresponds to that of the free molecule. Green levels are doubly degenerate and red ones are simply degenerate.

In the small cage, the orientational levels are roughly grouped in packets of levels in the range of 2 to 4 cm^{-1}, separated by energy gaps of 12 to 18 cm^{-1} in an interval of 110 cm^{-1}. In the large cage, the maximum energy gap between the levels is about 7 cm^{-1}, and in the same interval of 110 cm^{-1}, the levels appear as almost continuous compared to the small cage case. In comparison, calculations performed on CO_2 [2] led to fewer levels within the same range, with 3 levels separated by a first energy gap of 55 cm^{-1} and the next one of about 40 cm^{-1} in the small cage and only 8 levels separated by 30 cm^{-1} for the first two levels and less than 20 cm^{-1} for the other levels. To analyze these structures in terms of thermal properties of the clathrate trapping CH_4 or CO_2, it is necessary to link the redistribution of energy from the excited states of these structures to the solid environment.

Thermal effects are due to the excitation of the phonons that constitutes the quantized thermal bath which absorbs the energy dissipated in the condensed phase matter during a non-radiative transition of an excited molecule. The vibrational or orientational energy of the molecule is thus transferred to this reservoir in the form of kinetic energy to the solid environment thus increasing the temperature of the surroundings. The number of phonons involved in this process is proportional to the energy difference between the levels involved in the transition. This phenomenon has been modelled from two different approaches: one that is based on the short range repulsive forces between the molecule and its environment and assumed to be responsible for the transfer to phonons [7-13] possibly assisted by the rotational motion [14] and one based on the binary collision model [15] initially developed to interpret vibration-translation (V-T) transfers in liquids [16-17] and gases [18].

In the case of CO_2, observations from energy transfer experimental studies carried on low temperature CO_2-rare gas solid systems by laser induced fluorescence and double resonance techniques have shown that radiative relaxation was the main relaxation channel by which the energy from excited vibration-orientational levels was redistributed. Calculations performed on such systems led to energy gaps between the orientational levels corresponding to more than 5 phonons of the different rare gas matrices. Non-radiative relaxation were therefore less probable than radiative relaxation from upper excited levels. Based on these results, it was postulated that since the calculated orientational levels of CO_2 in clathrates had structures similar to those determined in rare gas matrices, then radiative relaxation were the main pathways for redistribution of the energy of excited levels of CO_2 and that the thermal properties of clathrates containing trapped CO_2 were not significantly changed [2].

In the case of CH_4, the situation is quite different because the energy level structures of CH_4 and CO_2 are very different in clathrates. Then, the energy gaps determined for CH_4 should involve 3 or less phonons, which is in favor of non-radiative relaxation in contrast to the CO_2 case which involves more than 5 phonons. The thermal properties of CH_4-clathrate systems should therefore be significantly modified and the nano-cages may free the CH_4 molecules if the temperature rise is significant.

4. Conclusions

In this work, the low frequency energy states of CH_4 trapped in the *s* and *l* nano-cages of cubic sI type clathrate are numerically calculated from a theoretical model and analysed by comparison to former studies on CO_2 trapped in clathrates. The results show that although the molecule is rather isolated in its cage, non-radiative relaxation processes are expected to be more important than radiative ones, in contrast to results obtained for CO_2-clathrate systems.

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