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# Simulating Relaxation Channels of CO<sub>2</sub> in Clathrate Nano-cages

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**Abstract.** The energy levels of CO<sub>2</sub> in the small (*s*) and large (*l*) nano-cages of cubic sI clathrates are calculated in the Born-Oppenheimer approximation using pairwise atom-atom interaction potentials. In the *s* cage, the centre of mass of CO<sub>2</sub> oscillates with small amplitudes, asymmetrically about the cage center with harmonic frequencies around 100 cm<sup>-1</sup>. In the *l* cage, oscillations are anharmonic with large amplitude motions in a plane parallel to the hexagonal faces of the cage and the corresponding frequencies are calculated to be 55 cm<sup>-1</sup> and 30 cm<sup>-1</sup>. Librational harmonic frequencies are calculated at 101.7 cm<sup>-1</sup> and 56.0 cm<sup>-1</sup> in the *s* cage and at 27.9 cm<sup>-1</sup> and 46.4 cm<sup>-1</sup> in the *l* cage. Results show that the coupling between the CO<sub>2</sub> molecule and the nano-cage is quite different for the low frequency translational, rotational or librational modes and the high frequency vibrational modes, which consequently leads to different relaxation channels.

## 1. Introduction

A clathrate is a crystalline solid with a cage-like structure of water molecules surrounding atoms or small molecules. As a compact assembly of nano-cages, clathrates are found as three different kinds of Archimedes polyhedra characterized by a cubic structure-I (sI), a cubic structure-II (sII) or a hexagonal structure-H (sH) [1]. The unit cell of sI consists of 46 water molecules with two types of cages; a small cage (*s*) that is a polyhedron composed of 12 pentagonal faces, and a large cage (*l*) that is a polyhedron consisting of 12 pentagonal faces and two opposite hexagonal faces [2]. Clathrate hydrates are the focus of many astrophysical investigations, as well as a wide range of applications. These materials are considered to be responsible for the anomalous desorption behaviour of gaseous parent molecules in comets [3] by providing a dissociation pressure curve intermediate between the pure compound sublimation equilibrium and the water ice phase. This curve can be calculated by the application of the van der Waals-Platteeuw model, leading to a simple van't Hoff's law [4-5]. Application of this model allows the prediction of the N<sub>2</sub>/CO and Ar/CO ratios of trapped N<sub>2</sub> and Ar in

clathrates that match those measured in the coma of the Jupiter family Comet 67P/Churyumov Gerasimenko [6]. Because of the consequences for global warming and climate change if clathrates release trapped carbon dioxide or methane, research work in this field is of particular importance, including the study of the interactions between the trapped molecule and the host water framework. One aim of such research is to determine how effective the absorption of infrared radiation by trapped CO<sub>2</sub> can be in the warming of clathrates and the subsequent release of CO<sub>2</sub>. Depending on the competition between radiative and non-radiative relaxation, only a limited temperature rise of the clathrate may result because of stimulated emission (S.E.) of radiation, as observed for CO<sub>2</sub> trapped in low temperature rare gas matrices [7] and which should not lead to the break down of the nano-cages. The time and temperature dependence of the S.E. therefore gives some insight into the vibrational dynamics of clathrate-trapped CO<sub>2</sub>.

## 2. The Site inclusion model and interaction potential energy

A theoretical model based on an extension of the site inclusion model used to study C<sub>3</sub>, CO<sub>2</sub> and N<sub>2</sub>O molecules [8-10] trapped in rare gas matrices is used to simulate the spectra of the linear CO<sub>2</sub> molecule trapped in clathrate sI matrix using 12-6 Lennard-Jones (LJ) interatomic potentials and effective charges that are included in order to account for the electrostatic interactions between atoms of CO<sub>2</sub> and H<sub>2</sub>O. The model assumes the validity of the Born-Oppenheimer approximation, 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. The total potential energy of the trapped molecule inside the nano-cage is written as:

$$V = \sum_j V_{Mj}(\mathbf{r}_{0j}) + \sum_{j,j'} V_{jj'}(\mathbf{r}_{jj'}) \quad (1)$$

where the term  $V_{Mj}$  is the molecule-cage interaction and  $\mathbf{r}_{0j}$  is the distance vector between the center of mass (c.m.) of CO<sub>2</sub> and the  $j^{\text{th}}$  atom of the cage ( $s$  or  $l$ ). The second term  $V_{jj'}$  represents the interaction potential between two atoms of the cage:  $i$  a  $j^{\text{th}}$  atom of one H<sub>2</sub>O molecule located at position  $\mathbf{r}_j$  and  $i'$  a  $j'^{\text{th}}$  atom of another H<sub>2</sub>O molecule of the cage located at position  $\mathbf{r}_{j'}$  with respect to an absolute frame tied to the cage.

The interaction potential energy  $V_{Mj}$  between the CO<sub>2</sub> 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  $q_i$  ( $i=1,2,3$  for CO<sub>2</sub>) and  $q_j$  on the atoms of the H<sub>2</sub>O molecules of the  $s$  or  $l$  cage, such that:

$$V_{Mj}(\mathbf{r}_{0j}) = \sum_{i=1}^3 \left[ 4\varepsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} + \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j e^2}{r_{ij}} \right] \quad (2)$$

where  $\varepsilon_{ij}$  and  $\sigma_{ij}$  are the mixed LJ potential parameters from the Lorentz-Berthelot combination rules

$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$  and  $\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}$ . The distance vector,  $\mathbf{r}_{ij}$  between  $i$  and  $j$  atoms can be expressed in the molecular frame ( $G, \mathbf{x}, \mathbf{y}, \mathbf{z}$ ) or the crystal frame ( $O, \mathbf{X}, \mathbf{Y}, \mathbf{Z}$ ) as given in reference [5]. The orientational degrees of freedom,  $\Omega = (\theta, \varphi)$ , of the molecule and the position vector of any atom,  $j$ , are defined in the absolute crystal frame ( $O, \mathbf{X}, \mathbf{Y}, \mathbf{Z}$ ).

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:

$$V_M^{(n)}(\xi^0, \Omega, \{Q\}) = V_M^{(n)e}(\xi^0) + V_M^{(n)}(\xi^0, \{Q\}) + V_M^{(n)}(\xi^0, \Omega) + \Delta V_M^{(n)}(\xi^0, \Omega, \{Q\}) \quad (3)$$

where  $V_M^{(n)e}(\xi^0)$  is the minimum of the potential energy corresponding to the equilibrium configuration;  $V_M^{(n)}(\xi^0, \{Q\})$  is the vibrational dependence in terms of normal coordinates

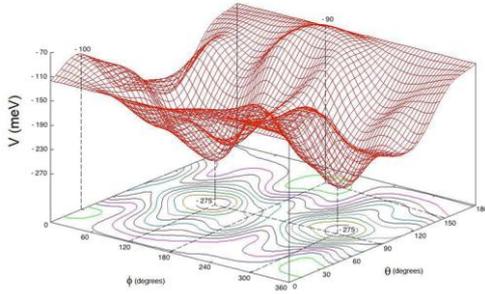
$\{Q\}$ ;  $V_M^{(n)}((\xi^0), \Omega)$  is the orientational dependence in terms of Euler angles ( $\Omega = (\theta, \varphi, \chi)$ ,  $\chi=0$  for a linear molecule);  $\Delta V_M^{(n)}((\xi^0), \Omega, \{Q\})$  characterizes the translation-orientation-vibration dynamic coupling term, which can induce the relaxation of vibrational modes onto the translational and orientational modes; and  $(\xi^0)$  represents the displacement vectors of the c.m. of H<sub>2</sub>O molecules of the cage and of the trapped CO<sub>2</sub>, determined by 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  $l$ );

$$H_M^{(n)} = H_{vib}^{(n)} + T_{rot}^{(n)} + T_{trans}^{(n)} + V_M^{(n)}(\xi^0, \Omega, \{Q\}) \quad (4)$$

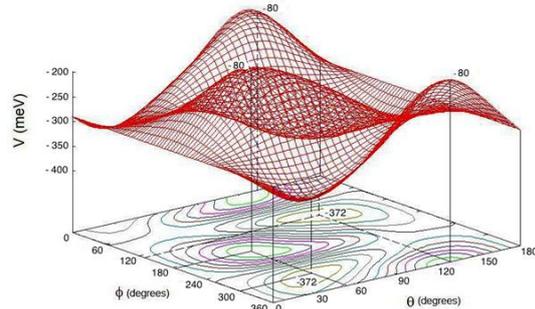
where the first three terms  $H_{vib}^{(n)} + T_{rot}^{(n)} + T_{trans}^{(n)}$  correspond to the free CO<sub>2</sub> molecular Hamiltonian.

### 3. Results and discussion

Calculations were performed for the CO<sub>2</sub> molecule trapped in a clathrate matrix containing 4x4x4 unit cells (up to 2,944 molecules of H<sub>2</sub>O). The calculated potential energy hypersurfaces are plotted in Figure 1 for CO<sub>2</sub> a) in cage  $s$  and b) in cage  $l$  as a function of its orientation. The equilibrium configuration for cage  $s$  corresponds to minimum energy value -275 meV (-2,200 cm<sup>-1</sup>). The molecule is at the cage centre, perpendicular to two pentagonal faces and with an allowed translation motion around the centre of the cage. For the cage  $l$ , the minimum energy value is -372 meV (-2,976 cm<sup>-1</sup>). The molecule is displaced from the cage centre by about 0.5 Å and can have a translational motion of large amplitude in a direction parallel to the two hexagonal faces.



**Figure 1 a).** Potential energy of CO<sub>2</sub> as a function of orientation in cage  $s$ .



**Figure 1 b).** Potential energy of CO<sub>2</sub> as a function of orientation in cage  $l$ .

The contour plots of the orientational potential energy surfaces for CO<sub>2</sub> trapped in the clathrate  $sl$  structure type are calculated at its c.m. equilibrium translational positions in cages  $s$  and  $l$ . The two contour plots show a certain symmetry. In the small cage, the rotational symmetry of 180 deg about the direction defined by  $\theta = 90$  deg and  $\varphi = 180$  deg corresponds to the symmetry of the molecule i.e.:  $V_M(\varphi, \theta) = V_M(\varphi + \pi, \pi - \theta)$ . Analysis of these contour plots shows that the orientational motions of the molecule are strongly hindered in the two cavities. They correspond to two-dimensional librational motions around  $\theta^e = 90$  deg and  $\varphi^e = 115$  deg in cage  $s$ , and around  $\theta^e = 130$  deg and  $\varphi^e = 110$  deg in cage  $l$ .

In each cage, the rotational kinetic Hamiltonian,  $T_{rot}$ , and the orientational potential energy,  $V_M(\varphi, \theta)$ , of the molecule are expanded as a power series with respect to new variables ( $u_\theta = \cos(\theta)$  and  $u_\varphi = \varphi - \varphi^e$  for cage  $s$  and  $u_\theta = \sin(\theta - \theta^e)$  and  $u_\varphi = \varphi - \varphi^e$  for cage  $l$ ), which allows the labeling of the energy states with appropriate librational quantum numbers ( $j, m$ ). As the harmonic terms are much greater than the anharmonic ones, the energy levels can first be determined in the harmonic approximation and then their calculation refined by applying standard perturbation techniques. The eigen-solutions of the orientational Hamiltonian are expressed as:

$$\begin{aligned}
 E_{jm} &= \hbar\omega_\theta(j + 1/2) + \hbar\omega_\phi(m + 1/2) \\
 |jm\rangle &= N_j N_m \exp(-(u_\theta^2 + u_\phi^2)/2) H_j(u_\theta) H_m(u_\phi)
 \end{aligned}
 \tag{5}$$

where  $\omega$ ,  $N$  and  $H$  are the librational harmonic frequencies, the normalization factors and the Hermite polynomials, connected to the two librational motions. The quantum numbers  $j$  and  $m$  are independent integers. The calculated harmonic frequencies are *i*)  $\omega_\theta = 101.7 \text{ cm}^{-1}$  and  $\omega_\phi = 56.9 \text{ cm}^{-1}$  in cage *s* and *ii*)  $\omega_\theta = 27.9 \text{ cm}^{-1}$  and  $\omega_\phi = 46.4 \text{ cm}^{-1}$  in cage *l*. The calculated orientational levels up to  $200 \text{ cm}^{-1}$  show that there are only few well separated levels in cage *s*, while in cage *l* several intermixed levels are present. This can be explained by less hindered librational motions in the cage *l* when compared to motions in the cage *s*.

For high vibrational frequency modes, calculations show that the direct electrostatic interaction between the charges does not reproduce the shifts determined from observed transitions but that the coupling is much weaker in contrast to the coupling with low frequency modes. Decreasing the value of the effective charges leads to calculated vibrational shifts that compare better with available experimental shifts which are less than a few percent of the vibrational transition frequencies.

These results can be compared to the calculations performed on  $\text{CO}_2$  trapped in low temperature rare gas matrix. The librational energies compare with those calculated for  $\text{CO}_2$  in Ar [9] and in which laser induced fluorescence techniques [7] lead to the observation of amplified vibrational stimulated emission rather than a thermal effect resulting from energy transfer through non-radiative processes. In matrices,  $\text{O}_3$  relaxes through binary collisions rather than by a multiphonon process [11] because the coupling of the vibrational degrees of freedom and the matrix is negligible. In comparison with the results reported in this work, the coupling scheme is consistent with a relaxation process by binary collisions. The high frequency vibrational degrees of freedom are almost isolated in the nano-cages because of a very weak coupling scheme which is unfavourable for relaxation by a multiphonon process through an energy gap law [11]. Then vibrationally excited  $\text{CO}_2$  is expected to relax radiatively rather than by non-radiative processes. This analysis is also consistent with the results reported in reference [6] regarding molecules trapped in clathrates of Comet 67P/Churyumov Gerasimenko, which remain isolated in the nano-cages until the comet passes by a radiative source like the sun. The various trapped species are then freed allowing for possible chemical reactions to occur as speculated from a recent laboratory experimental work [12].

#### 4. Conclusions

In this work, the low frequency energy states of  $\text{CO}_2$  trapped in the *s* and *l* nano-cages of cubic type I clathrate are numerically calculated and analyzed from a theoretical model. The results show that the molecule is rather isolated in its cage and that non-radiative relaxation processes are expected to be slower than radiative ones just as for  $\text{CO}_2$  isolated in rare gas argon matrix.

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