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Confining CO₂ inside the nanocavities of the sI clathrate: a quantum dynamics study

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Synopsis Clathrate hydrates have been found to occur naturally, and have been extensively studied due to their important industrial applications, such as the storage of the CO₂ from the atmosphere and control climate change. Thus, quantitative understanding of physical and chemical properties, as well as the factors that control the formation of CO₂ hydrates, on both macroscopic and microscopic levels is essential in several areas of physical science.

Carbon dioxide clathrate hydrates of sI type are essentially pure, and have been studied experimentally by X-ray, powder X-ray and neutron diffraction methods [1] while their spectroscopic characterization has been reported via Raman, solid-state NMR, and the infrared (IR) [2] spectroscopy. These experimental studies motivated us to perform [3] quantum calculations of the T-R-V dynamics of the CO₂ molecule in both 5¹² and 5¹²6² cages of the sI clathrate hydrate, within the MCTDH framework. The present study had two objectives. The first was to investigate the quantum T-R dynamics of the enclathrated CO₂ molecule on a semiempirical PES checking its quality by direct comparison with experimental X-ray results. The second, and indeed the computationally most challenging objective, was to compute specific vibrational states of the CO₂ in both small and large cages of the sI clathrate structure, in order to compare with recent FTIR measurements on fundamental and combination stretching modes. We found that in the small cage the CO₂ molecule is located almost at its center, while in the large one its center of mass is displaced by at least 0.2 Å out off the center of the equatorial plane of the cage (see Fig. 1). This finding is consistent with data available from X-ray diffraction measurements. Also, we show that the quantum dynamics of the rotational and translational excited states of the CO₂ in small and large cages is remarkably different, with the density of states to be higher and the T-R levels to be highly coupled in the large cage, even at low-energies, than in small one. The specific T-R-V levels, corresponding to ν_1 and ν_3 excitations, were calculated for the three different ¹²CO₂, ¹³CO₂, and ¹⁸OCO isotopes. We observe that the fundamental ν_1 and ν_3 frequencies of the CO₂ in the small and large cage are shifted by about 16 cm⁻¹, as well as their overtones and

$\nu_1 + \nu_3$ combination modes. This is in close agreement with the characteristic double-peak profiles observed in the IR spectra of the CO₂ clathrate hydrate at 5.6 K (see Fig. 1), supporting the CO₂ single occupation of small and large cavities of the sI clathrate. Such good agreement, with the data from recent spectroscopic studies of carbon dioxide clathrate hydrate at low temperatures, indicates a single occupancy of the sI structure cages, allowing an assessment of the theoretical approaches employed.

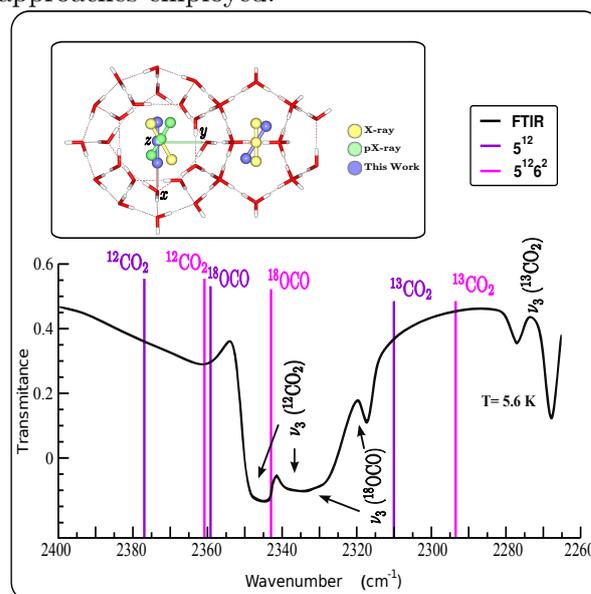


Figure 1. Comparison of the FTIR spectra with the 7D MCTDH vibrational energy levels for the indicated isotopes, and orientation of the CO₂ (see inset plot) in the small and large cages of the sI structure.

References

- [1] S. Takeya *et al* 2010 *J. Am. Chem. Soc.* **132** 524
- [2] E. Dartois *et al* 2009 *A&A* **504** 869
- [3] Á. Valdés *et al* 2015 *J. Phys. Chem. C* **119** 3945

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