



Trends of CO₂ adsorption on cellulose due to van der Waals forces



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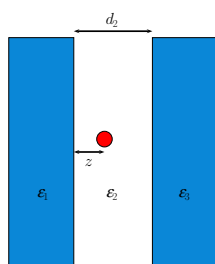
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HIGHLIGHTS

- We explore the Casimir–Polder interactions of a CO₂ molecule near interfaces.
- A potential mechanism of capture and storage of CO₂ molecules in a three-layered cellulose–water–vapor system is proposed.
- The vdW binding energies of CO₂ molecule in water towards different surfaces are provided.
- The attraction or repulsion of the CO₂ molecule depends on the surface material.

GRAPHICAL ABSTRACT



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ABSTRACT

The non-retarded van der Waals and Casimir–Polder forces on a CO₂ molecule in water near a single surface and between surfaces are explored. We observe preferential adsorption and desorption of CO₂ molecules depending on the material of the surfaces. We also find a potential mechanism of capture and storage of CO₂ molecules in a geometry consisting of a cellulose surface coated by a thin film of water and then by air.

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1. Introduction

In view of the current interest in carbon capture and sequestration (CCS) program for the greenhouse gas management and

the simultaneous methane gas recovery, study regarding preferential adsorption of the CO₂ gas molecule onto different surfaces stands highly relevant. Physical adsorption has been speculated as one of the main technologies of pre- and postcombustion CO₂ capture [1], and also as an effective mechanism of the storage of the released methane gas. Polymers, metal membranes and porous inorganic membranes are the main materials considered for CO₂ capture [1]. Among the polymers, cellulose due to its abundance and high mechanical strength remains one of the most keenly

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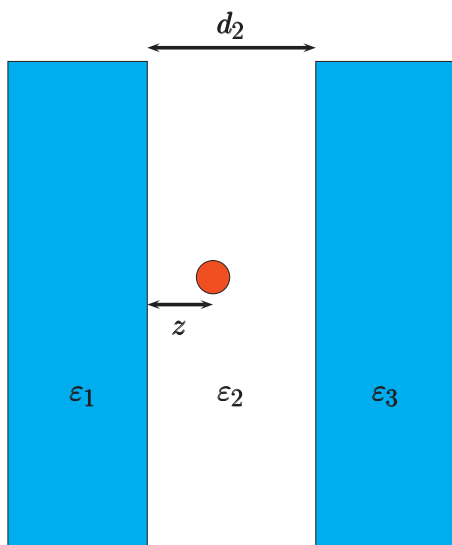


Fig. 1. Schematic diagram of a three-layered structure with the molecule in the middle layer at a distance z from the first surface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

studied materials for the aforementioned purposes. In addition, it may play a significant role in future energy storage applications such as batteries [2,3] as well as for biomedical applications as dispersion agent, etc. [4]. The dispersion interactions such as the van der Waals and the Casimir–Polder energies play an important role in these contexts (Fig. 1).

In the present work, we explore the non-retarded van der Waals and Casimir–Polder interaction energy of a CO₂ molecule in water in the presence of surfaces. We observe that the attraction or repulsion of a CO₂ molecule towards or away from a surface depends on the surface material. We notice that a CO₂ molecule in water is attracted towards cellulose and silica surfaces and repulsed from hexane and air surfaces. Comparing with our previous work on methane molecule interactions [5], we also note that the degree of attraction and repulsion on corresponding surfaces is greater for a CO₂ molecule than for a methane molecule. Following the formalism of Sambale et al. [6], we further investigate the interaction of a CO₂ molecule with surfaces, cellulose in particular, in a three-layered structure. In water-filled nanoslit in cellulose, i.e., in a cellulose–water–cellulose system, CO₂ molecules can diffuse in the water phase and physisorb to the nearest cellulose surface. A CO₂ molecule in the water phase is attracted towards the cellulose surface while if we consider a cellulose–water–vapor geometry, we observe repulsion from the vapor surface. Hence the CO₂ molecules are driven towards the cellulose surface where they can be stored. Such a system may be used as a model for a CO₂ gas bubble in water near a cellulose surface. In Section 2, we state the established theory of dispersion interaction of a molecule near a surface in the presence of a background medium. In Section 3, we briefly describe the retarded van der Waals interactions of a molecule in a three-layered system. We then explain the computation of excess polarizability of a molecule solved in a medium and the dielectric functions of the considered surfaces in Sections 4 and 5, respectively. We present our main results in Section 6 and end with conclusions.

2. Non-retarded van der Waals energy of a molecule in water near a surface

The non-retarded van der Waals energy of a finite-sized molecule in a medium near a surface has been derived by Ninham and co-workers, considering a Gaussian function to represent the

finite spatial spread of the polarization cloud of a real molecule [7–11]. The dispersion interaction free energy of a molecule in water at a distance ρ from an interface between water and a second medium with dielectric function $\epsilon_{\text{surface}}$ is

$$U = \frac{Bf(\rho)}{\rho^3},$$

$$B = \frac{k_B T}{2} \sum_{n=0}^{\infty} i \alpha^*(i\xi_n) \frac{\epsilon_{\text{water}} - \epsilon_{\text{surface}}}{\epsilon_{\text{water}} + \epsilon_{\text{surface}}},$$

$$f(\rho) = 1 + \frac{2\rho}{a\sqrt{\pi}} \left(\frac{2\rho^2}{a^2} - 1 \right) \exp\left(-\frac{\rho^2}{a^2}\right) - \left(1 + \frac{4\rho^4}{a^4}\right) \text{erfc}\left(\frac{\rho}{a}\right),$$

where $a = 1.57 \text{ \AA}$ is the Gaussian radius of the CO₂ molecule and $\alpha^*(i\xi_n)$ is the excess polarizability of the molecule in water at the Matsubara frequencies $\xi_n = 2\pi k_B T n / \hbar$ [7,12,13]. The method of determination of the excess polarizabilities is briefly explained in Section 4. Here, k_B as the Boltzmann constant, T the temperature, and the prime on the summation indicates that the $n=0$ term shall be divided by 2. Including the effects of finite size in the formalism enables us to determine the van der Waals contribution to the binding energy of the molecule to the surface.

3. van der Waals energy of a molecule in a three-layer system

We re-write the expressions given by Sambale et al. [6] to focus on the distance-dependent part of the retarded van der Waals interactions [7,14] of a polarizable point particle in water-filled nanoslit of width d_2 at a distance z from the first interface. In CGS units, this expression for the van der Waals potential turns out to be,

$$U(z) = \frac{k_B T}{c^2} \sum_{n=0}^{\infty} i \xi_n^2 \alpha^*(i\xi_n) \int_0^{\infty} \frac{dq q f(q)}{\gamma_2},$$

$$f(q) = f_1^s + f_1^p + f_2^s + f_2^p,$$

$$f_1^s = \frac{\Delta_{21}^s \exp[-2\gamma_2 z]}{1 - \Delta_{21}^s \Delta_{23}^s \exp[-2\gamma_2 d_2]},$$

$$f_1^p = - \left(1 + \frac{2q^2 c^2}{\xi_n^2 \epsilon_2}\right) \frac{\Delta_{21}^p \exp[-2\gamma_2 z]}{1 - \Delta_{21}^p \Delta_{23}^p \exp[-2\gamma_2 d_2]},$$

$$f_2^s = \frac{\Delta_{23}^s \exp[-2\gamma_2 (d_2 - z)]}{1 - \Delta_{21}^s \Delta_{23}^s \exp[-2\gamma_2 d_2]},$$

$$f_2^p = - \left(1 + \frac{2q^2 c^2}{\xi_n^2 \epsilon_2}\right) \frac{\Delta_{23}^p \exp[-2\gamma_2 (d_2 - z)]}{1 - \Delta_{21}^p \Delta_{23}^p \exp[-2\gamma_2 d_2]}.$$

Here the reflection coefficients at the two interfaces for s and p polarized modes are,

$$\Delta_{ij}^s = \frac{\gamma_i - \gamma_j}{\gamma_i + \gamma_j}; \quad \Delta_{ij}^p = \frac{\epsilon_j \gamma_i - \epsilon_i \gamma_j}{\epsilon_j \gamma_i + \epsilon_i \gamma_j},$$

where $\gamma_i = \sqrt{(\xi_n^2 \epsilon_i / c^2) + q^2}$ and c is the velocity of light in vacuum.

4. Excess polarizability of molecules dissolved in water

The excess polarizabilities at Matsubara frequencies and Gaussian radii for CO₂ solved in water were derived as in, for instance, papers by Parsons and Ninham [10,11]. The polarizability of CO₂ is highly anisotropic. However, due to rapid movements of the molecules in water we can use the orientation averaged excess polarizability for CO₂. Dynamic polarizabilities of the considered molecules in vacuum (see Fig. 2) were calculated using MOLPRO [15] at a coupled cluster singles and double (CCSD) level of theory. The excess polarisabilities, $\alpha^*(i\xi)$, in water were obtained from the polarisabilities, $\alpha(i\xi)$, in vacuum using the relation

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