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

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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.

Keywords:

carbon capture and storage, preferential adsorption, Casimir-Polder energy, three-layered systems

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 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.

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

Figure 1: (Color online) Schematic diagram of a three-layered structure with the molecule in the middle layer at a distance z from the first surface.

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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 Sec. 2, we state the established theory of dispersion interaction of a molecule near a surface in the presence of a background medium. In Sec. 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 Secs. 4 and 5 respectively. We present our main results in Sec. 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, 8, 9, 10, 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

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

$$B = \frac{k_B T}{2} \sum_{n=0}^{\infty} \alpha^*(i\xi_n) \frac{\epsilon_{\text{water}} - \epsilon_{\text{surface}}}{\epsilon_{\text{water}} + \epsilon_{\text{surface}}}, \quad (1)$$

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

where $a = 1.57\text{\AA}$ is the Gaussian radius of the CO₂ molecule and $\alpha^*(i\xi_n)$ is the excess polarisability 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 Sec. 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

Figure 2: (Color online) The mean polarizabilities of CO₂ in vacuum and excess polarizabilities of CO₂ in water in units of Å³ on the imaginary frequency axis. The polarizabilities corresponding to $n = 0$ are shown on the y-axis.

CGS units, this expression for the van der Waals potential turns out to be,

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

$$f(q) = f_1^s + f_1^p + f_2^s + f_2^p, \quad (3)$$

$$f_1^s = \frac{\Delta_{21}^s \exp[-2\gamma_2 z]}{1 - \Delta_{21}^s \Delta_{23}^s \exp[-2\gamma_2 d_2]}, \quad (4)$$

$$f_1^p = -(1 + \frac{2q^2 c^2}{\xi_n^2 \epsilon_2}) \frac{\Delta_{21}^p \exp[-2\gamma_2 z]}{1 - \Delta_{21}^p \Delta_{23}^p \exp[-2\gamma_2 d_2]}, \quad (5)$$

$$f_2^s = \frac{\Delta_{23}^s \exp[-2\gamma_2 (d_2 - z)]}{1 - \Delta_{21}^s \Delta_{23}^s \exp[-2\gamma_2 d_2]}, \quad (6)$$

$$f_2^p = -(1 + \frac{2q^2 c^2}{\xi_n^2 \epsilon_2}) \frac{\Delta_{23}^p \exp[-2\gamma_2 (d_2 - z)]}{1 - \Delta_{21}^p \Delta_{23}^p \exp[-2\gamma_2 d_2]}. \quad (7)$$

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

$$\Delta_{ij}^s = \frac{\gamma_i - \gamma_j}{\gamma_i + \gamma_j}; \Delta_{ij}^p = \frac{\epsilon_j \gamma_i - \epsilon_i \gamma_j}{\epsilon_j \gamma_i + \epsilon_i \gamma_j}, \quad (8)$$

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

Figure 3: (Color online) The dielectric functions of cellulose, SiO₂, hexane and water as functions of imaginary Matsubara frequencies. The corresponding values for $n = 0$ are shown on the y-axis.

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 for a dielectric sphere embedded in a dielectric medium [16], $\alpha^*(i\xi_n) = \alpha^3(\epsilon_a - \epsilon_w)/(\epsilon_a + 2\epsilon_w)$, where ϵ_w is the dielectric function of water. ϵ_a is the effective dielectric function of the molecular sphere, determined from the molecular polarizability in vacuum as $\epsilon_a(i\xi_n) = 1 + 4\pi\alpha(i\xi_n)/V$, where V is the volume of the molecular sphere. The polarizabilities of CO₂ in vacuum and excess polarizabilities of CO₂ in water are shown in Fig. 2. The polarizabilities corresponding to $n = 0$ are shown on the y-axis.

5. The dielectric function of hexane, water, SiO₂ and cellulose

The dielectric function of hexane was calculated using a model dielectric function as given by Masuda [17]. The dielectric function of water was based on the extensive experimental data found in the *Handbook of Optical Constants of Solids II* [18]. The dielectric function on the imaginary axis was obtained from the imaginary part of the function using the following version of the Kramers-Kronig dispersion relation

$$\epsilon(i\xi) = 1 + \frac{2}{\pi} \int_0^\infty d\omega \frac{\omega \epsilon_2(\omega)}{\omega^2 + \xi^2}. \quad (9)$$

This relation is the result of the analytical properties of the dielectric function. [13] In the integration we made a cubic spline interpolation of $\ln(\epsilon_2(\omega))$ as a function of $\ln(\omega)$.

For SiO₂ we calculated the dielectric function by means of first-principles atomistic models. Here the electronic structure of SiO₂ was calculated by employing a partial self-consistent GW method where the Green functions were updated iteratively while the screened Coulomb potential W was fixed. [19, 20, 21]

Figure 4: (Color online) Casimir-Polder energy of a CO₂ molecule in units of $k_B T$ near a water-cellulose interface with and without effects of finite size. Including the finite-size effects removes the divergence at zero separation distance.

Figure 5: (Color online) Comparing the Casimir-Polder energy in units of $k_B T$ of a finite-sized CO₂ molecule in water near different surfaces. A CO₂ molecule is attracted towards SiO₂ surface but repulsed from air and hexane surfaces.

The electron-phonon coupling was initially neglected. From the electronic dispersion, the imaginary part of the dielectric functions was calculated from the linear response in the long wave length limit ($\lambda_q = 2\pi/q \rightarrow \infty$) through [22]

$$\epsilon_{2,j}(\omega) = \lim_{q \rightarrow 0} \frac{4\pi^2 e^2}{\Omega q^2} \sum_{c,v,\mathbf{k}} 2w_{\mathbf{k}} \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega) \times \langle u_c(\mathbf{k} + \mathbf{e}_j \mathbf{q}) | u_v(\mathbf{k}) \rangle \langle u_c(\mathbf{k} + \mathbf{e}_j \mathbf{q}) | u_v(\mathbf{k}) \rangle^*. \quad (10)$$

Here, $u_l(\mathbf{k})$ is the cell periodic part of the l :th wave function, $E_l(\mathbf{k})$ are the energies of the corresponding conduction ($l = c$) and valence ($l = v$) band states, and Ω is the volume of the primitive cell. The function $w_{\mathbf{k}}$ is the weight of the $\mathbf{k}$ -points, and $\mathbf{e}_j$ is the unit vector in the Cartesian coordinates. The dielectric function on the imaginary axis was obtained via the Kramers-Kronig dispersion relation, Eq. (9), for each cartesian component.

The dielectric function in polar materials depends on the electron-optical-phonon coupling. We modeled this contribution employing the Lorentz model and the Kramers-Heisenberg formula [23, 24]

$$\varepsilon_{ph}(\omega) = 1 + \sum_{\eta} \frac{(\omega_{LO,\eta}^2 - \omega_{TO,\eta}^2) \varepsilon_{\eta}}{\omega_{TO,\eta}^2 - \omega^2 - i\gamma_{\eta}\omega}, \quad (11)$$

using small phonon damping parameters (*i.e.*, $\gamma_{\eta} \rightarrow 0$). The parameters $\omega_{LO,\eta}$ and $\omega_{TO,\eta}$ are the phonon frequencies of the η :th longitudinal optical (LO) and transverse optical (TO) mode, respectively, and ε_{η} is the high frequency dielectric constant of the TO phonon mode. These optical modes are responsible for the change in the dielectric function for $n = 0$ and 1 (see Fig. 3). The static dielectric constant of SiO_2 is 3.9 which is in agreement with the measured data of 3.9-4.4. [25]

We consider the properties of pure crystalline cellulose [26]. Our atomistic modeling of a (110) cellulose surface is based on density functional theory with dispersion correction (DFT-D2). [27] The surface is constructed by a $\sqrt{2} \times \sqrt{2} \times 1$ supercell slab with a 35 Å vacuum region. An energy cutoff of 500 eV and a special $\mathbf{k}$ -point sampling over a $4 \times 4 \times 1$ Monkhorst-Pack mesh are used for the surface system. The crystal structure of cellulose I_{β} was chosen to be the triclinic P1 structure. Our calculated structure parameters for bulk I_{β} ($a = 7.64$ Å, $b = 8.13$ Å, $c = 10.38$ Å, $\alpha = \beta = 90^\circ$, and $\gamma = 96.69^\circ$) are consistent with the experimental data [28] and other calculated results. [29, 30] The imaginary part of the dielectric function is calculated by an independent-particle approximation, in which the wavefunction is generated by the DFT-D2 method. Thereafter, the spectra on the imaginary frequency axis are again obtained via the Kramers-Kronig relation, Eq. (9). The corrected band gap value E_g is estimated to 8.58 eV by means of the partial self-consistent GW_0 method. [31, 32] The static ion-clamped dielectric matrix is calculated by using the density functional perturbation theory. [22]

The calculated dielectric functions of SiO_2 , cellulose, hexane, and water on the imaginary frequency axis are shown in Fig. 3. The values of dielectric functions for $n = 0$ are shown on the y-axis.

6. Numerical Results and Discussions: Casimir-Polder Energies of a Molecule in Water-filled Slit bounded by Two Surfaces and of a Molecule near Planar Interfaces

Fig. 4 demonstrates the attraction of a CO_2 molecule towards cellulose surface and the convergence of the Casimir-Polder energy at very near separation distances as a result of consideration of the finite-size of the molecule in the formalism. At room temperature, we estimate this van der Waals binding energy of the CO_2 molecule in water to the cellulose surface to be around $-1.10 k_B T$ at $\rho = a$, *i.e.*, at a distance of one molecule (CO_2) radius from the surface. The reason for choosing this distance for an estimation of the binding energy is because the electron clouds of the molecule and the surface start to overlap at a distance closer than one molecule radius rendering the interaction

Figure 6: (Color online) Casimir-Polder energy in units of $k_B T$ of a CO_2 molecule in the water phase in cellulose-water-cellulose system for different widths d_2 of the water layer.

Figure 7: (Color online) Casimir-Polder energy in units of $k_B T$ of a CO_2 molecule in the water phase in cellulose-water-vapor system for different widths d_2 of the water layer.

Figure 8: (Color online) Comparing the Casimir-Polder energy in units of $k_B T$ of a CO_2 molecule in water layer of width 15 Å in cellulose-water-cellulose and cellulose-water-vapor systems.

repulsive and one would need more rigorous quantum chemistry calculations in this regime [5, 33]. In Fig. 5, we show the different curves of interaction versus separation distance of a finite-sized CO_2 molecule in water with different surfaces. We provide estimates of the contribution of the van der Waals energy to the binding energy of CO_2 molecule in water near different surfaces again at $\rho = a$ in Table 1. Here, we point out that comparison with similar studies with the methane molecule [5] reveals that a CO_2 molecule indeed adsorbs to a SiO_2 surface with a greater binding energy than that of a methane molecule. In addition, in the case of interaction near hexane and air surfaces where there is repulsion, a CO_2 molecule desorbs more strongly than a methane molecule does. This property greatly influences the mechanism of preferential adsorption and desorption for capture and storage. In Fig. 6, we present the interaction energy curves for a CO_2 molecule in the three-layered cellulose-water-cellulose system with CO_2 molecule in the middle water layer for different widths of this layer. As we can see from this figure, both the cellulose surfaces attract the CO_2 molecule. The CO_2 molecule will be drawn towards the nearer cellulose surface. We observe similar behavior for different slit widths, i.e., attraction towards both the surfaces and negligible interaction in the middle. This system can be a model for porous cellulose where CO_2 molecules can be transported in the water phase and be adsorbed at the cellulose surfaces. CO_2 molecules may be effectively stored in porous cellulose. In Fig. 7, we show similar curves but with the third cellulose layer substituted by a vapor layer. It is interesting to note that the CO_2 molecule is repulsed from the vapor phase and is attracted towards the cellulose layer through the water. So, if there is an air bubble of micrometer size (so that it can be considered as a planar surface) with CO_2 molecule in the bubble, then the CO_2 molecule escaping from the bubble will experience repulsion away from the water-air interface after it has come into water and be attracted towards the cellulose-water interface. Fig. 8 shows a simple comparison of the attraction and repulsion of

Table 1: The van der Waals binding energy with and without finite-size corrections of a CO_2 molecule in water towards different surfaces. All energies are in units of $k_B T$.

Background	Surface	vdW	vdW for zero-size
Water	SiO_2	-0.94	-1.50
Water	Hexane	0.23	0.36
Water	Air	1.73	2.76
Water	Cellulose	-1.10	-1.75

CO_2 molecule in these two systems for $d_2 = 15$ Å. The presence of different third layers can be seen effective from around the middle of the water slit.

7. Conclusions

We have discussed the van der Waals and Casimir-Polder interactions of a finite-sized molecule near a single interface. Incorporating the effects of finite size facilitates the estimation of the van der Waals contribution to the binding energy of the molecule towards different surfaces. Further, we discuss these dispersion interactions for the case of three-layered geometry when the molecule is in the middle water filled layer bounded by two other surfaces. We predict a potential capture and storage mechanism for CO_2 molecules driven by dispersion interactions inside a system consisting of nanoporous cellulose surfaces with thin water films inside the pores. Using the formalism developed by Parashar et al. [34] we are currently exploring how to determine the interaction energy corresponding to various orientations of the molecule with respect to the dielectric slab; the parallel and the perpendicular configurations being particular cases. One can estimate the difference in adsorption energy for parallel and perpendicular configurations. In a liquid the rapid movement will make the orientation averaged result a reasonable approximation. We will explore this in detail in future work.

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