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Physisorption of Positronium on Quartz Surfaces

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Whether positronium (Ps) can be physisorbed on a material surface is of great fundamental interest, since it can lead to new insight regarding quantum sticking and is a necessary first step to try to obtain a Ps_2 molecule on a material host. Experiments in the past have produced evidence for physisorbed Ps on a quartz surface, but firm theoretical support for such a conclusion was lacking. We present a first-principles density-functional calculation of the key parameters determining the interaction potential between Ps and an α-quartz surface. We show that there is indeed a bound state with an energy of 0.14 eV, a value which agrees very well with the experimental estimate of $\sim$0.15 eV. Further, a brief energy analysis invoking the Langmuir-Hinshelwood mechanism for the reaction of physisorbed atoms shows that the formation and desorption of a Ps_2 molecule in that picture is consistent with the above results.

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Since positronium was first observed in 1951 [1], positronium physics has evolved into a vigorous and fascinating field, at the intersection of nuclear, atomic, and condensed matter physics [2]. The positronium (Ps) atom, i.e., an electron-positron bound state, is rather unique in that it is one of the very few examples of exotic particle-antiparticle atoms that have been observed, and it is the only one in the lepton family (the other examples, such as charmonium, being in the hadron family). Ps is produced by irradiating matter with positrons, and its formation and stability have been studied in a variety of solid hosts [3]. In the case of metals, the injected positrons thermalize and can reach the surface, where they can bind with an electron to form Ps. Thus, Ps desorbed from Cu and Al surfaces has been well measured and characterized [4,5]. In the case of insulators, in which Ps can also be formed in the bulk, Ps emission from Al_2O_3, SiO_2, and MgO powders was reported even earlier [6,7].

A question of great interest in these systems is whether Ps can be bound to the surface of the host. Indeed, this is related to fundamental questions such as the nature of quantum sticking [5] and the potential of a Ps trap to lead to dipositronium (Ps_2) formation and its connection to the realization of a Ps Bose-Einstein condensate [2,8]. In 1976, intriguingly low decay rates in precision Ps lifetime measurements in SiO_2 powders were reported [9]. These findings were analyzed theoretically considering the possibility of Ps physisorption on the surface of the grains [10], but the conclusion was that no surface bound state was possible. Later, however, temperature-dependent Ps emission measurements produced experimental evidence suggesting Ps physisorption on an α-quartz single-crystal surface [11], with an estimated binding energy of $\sim$0.15 eV. Very recently, moreover, Ps lifetime measurements of high-density Ps gas in nanoporous silica suggest the formation of Ps_2 molecules, a conclusion assuming that Ps atoms are previously physisorbed on the surface of the nanopores [12].

Consequently, we think that it is important to reconsider the possibility of Ps physisorption on quartz surfaces. In the case of Al surfaces, for instance, the longer than expected (again) positron lifetimes observed in experiment [13] can be understood in terms of a model calculation [14] of weakly physisorbed Ps on the metal surface. Although an alternative explanation invoking trapped positrons in a slowly varying inhomogeneous electron gas was proposed by other authors [15], the former possibility still exists [16]. Moreover, it is important to recognize that the previous theoretical estimate mentioned was only approximate [10]. It is clear that a more accurate calculation of the Ps-quartz surface interaction potential is essential in order to discard or support the Ps physisorption interpretation of the above experiments and to find reference values for the physical parameters characterizing the Ps-surface interaction. Atomic physisorption on single-crystal surfaces has been extensively studied in the past. Typical experimental values for several characteristic parameters can be found in Ref. [17]. From the theoretical point of view, following the pioneering work of Zaremba and Kohn [18], a good calculational scheme emerged thanks to the contribution of several authors [19], which we essentially follow here. In this respect, of foremost importance are accurate calculations of the dielectric function of the crystal and of the electronic charge density profile at its surface. In this work, we present a density-functional calculation of these two quantities. Our results for the Ps–α-quartz surface interaction potential show that indeed Ps has surface bound states. As will be seen below, we find that the ground state binding energy is very close to the experimentally suggested value, which is also consistent with the possibility of Ps_2 formation via the Langmuir-Hinshelwood reaction mechanism for physisorbed atoms [20].

It is well established that the interaction potential between a physisorbed atom and a solid crystal surface is determined by two main contributions. At large distances the interaction is dominated by the attractive van der Waals polarization interaction, and close to the surface the interaction is repulsive, due in essence to the overlap of the electron wave functions of the two subsystems [17]. At a distance z from a solid surface (the crystal occupying the lower half-space), a physisorbed atom is subject to a potential

$$v(z) = v_R(z) + v_{\mathrm{VW}}(z). \tag{1}$$

The van der Waals interaction is written as

$$v_{\mathrm{VW}}(z) = -\frac{C}{(z - z_{\mathrm{vw}})^3} f(k_c(z - z_{\mathrm{vw}})), \tag{2}$$

with the coefficient C given by [18,21]

$$C = \frac{\hbar}{4\pi}\int_0^\infty d\xi\,\alpha(i\xi)\left(\frac{\epsilon(i\xi) - 1}{\epsilon(i\xi) + 1}\right), \tag{3}$$

where α is the polarizability of the atom and ϵ is the bulk dielectric function of the solid. The function f describes the fact that the van der Waals interaction saturates as z draws closer to the reference plane [22]. The vanishing of the response at short wavelengths introduces the cutoff wave vector k_c [23], for which we take the inverse of the Ps hard-core radius, $r_c = 1.9\ a_0$ [24]. We discuss z_{VW}, the so-called reference plane position, further on, when addressing the repulsive interaction.

To obtain the dielectric function we require first to calculate the electronic structure of the crystal. We considered α-quartz (i.e., $\mathrm{SiO_2}$ with trigonal structure, space group $P3_221$), which is the most common and the one used in Ref. [11], and have employed experimental structural parameters [25]. We used the highly precise all-electron full-potential linearized augmented plane wave (FLAPW) implementation of density-functional theory [26]. The band contribution to the imaginary part of the dielectric function is calculated according to [27]

$$\varepsilon_2(\omega) = \frac{8\pi^2 e^2}{\Omega}\lim_{\mathbf{q}\to 0}\sum_{c,v}\sum_{\mathbf{k}}\frac{1}{q^2}|\langle\mathbf{k}+\mathbf{q}, c|e^{i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}, v\rangle|^2 \times \delta(\epsilon_{\mathbf{k}+\mathbf{q},c} - \epsilon_{\mathbf{k},v} - \hbar\omega). \tag{4}$$

Here Ω is the crystal volume, and c and v denote the conduction and valence bands, respectively. It is important to note that we use the screened-exchange local density approximation (SX-LDA) to the exchange-correlation potential. This approximation is known to give excellent results regarding the band gaps and optical properties of sp semiconductors [27]. This is because of its superior description of the exchange-correlation hole—whose long range behavior is critical in semiconductors—compared to the well-known local density approximation (LDA) [28]. Indeed, the SX-LDA band gap in $\mathrm{SiO_2}$, $E_g = 8.8$ eV agrees very well with the measured value of 8.9 eV [29], while the LDA band gap is only of 6.1 eV.

Now, a recent *ab initio* study of excitonic effects in α-quartz has shown that these are crucial to understand the structure of its optical spectrum [30], most notably the strong peaks observed near the absorption edge [31]. We parametrize these contributions with a Hopfield term of the form $\sum_j \beta_j/(\omega_j^2 - \omega^2 - i\gamma\omega)$. In Fig. 1 we show both the band contribution and the total $\varepsilon_2(\omega)$ for light polarized perpendicular to the c axis of the crystal (α-quartz is optically uniaxial). Our result compares well with the aforementioned works [32]. The real part of the dielectric function, obtained by the Kramers-Kronig relation, yields a calculated macroscopic dielectric constant $\varepsilon_\infty = 2.38$, which is in fact the experimental value [31]. The dielectric function for imaginary argument is obtained by analytic continuation [21]. Our result for the van der Waals coefficient is finally $C = 13.87$ eV a_0^3.

The polarizability of Ps is readily obtained by (reduced) mass rescaling that of hydrogen. For the latter, we take the parametrization of Dalgarno and Victor [33] $\alpha(\omega) = \sum_n f_n/(\omega_n^2 - \omega^2)$, with the oscillator strengths and frequencies they give.

The repulsive part of the interaction is essentially proportional to the valence electron density profile near the surface of the crystal [34]. We write analytically the repulsive potential as [10]

$$v_R(z) = V_0 e^{-(z-z_0)/l}, \tag{5}$$

where V_0 is the intensity of the Ps work function, l is the electron density decay length, and z_0 is the so-called background edge position. For V_0 we take the experimental value, which is 1 eV [35]. To determine the two other quantities we calculate first the electronic density at the surface of the crystal. For this, we considered a single $\mathrm{SiO_2}$ slab in which the crystal exposes the (011) face to the Ps atom, for direct comparison with experiment [11]. The slab

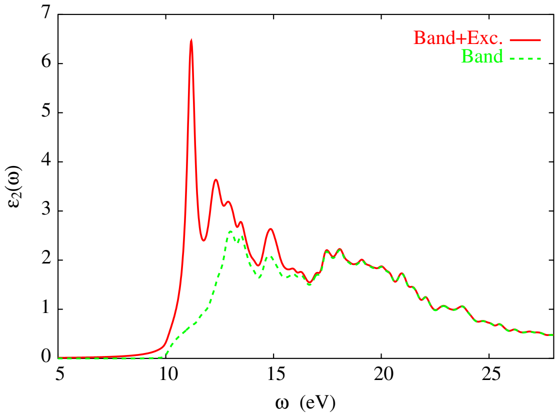

FIG. 1 (color online). Imaginary part of the dielectric function of α-quartz for a polarization vector perpendicular to the c axis. The continuous line shows the total function, arising from interband and exciton excitations. To illustrate the excitonic effects, the dotted line shows the interband contribution only.

thickness was ~24 a_0, and the unit cell contained 6 formula units. Here, two technical points are worth mentioning. To eliminate spurious states and to avoid any possible dipole field effects on the top surface due to the finite thickness of the slab, the dangling bonds at the bottom surface of the slab were passivated with hydrogen at optimized positions. Further, the atoms near a surface generally reconstruct, changing their relative positions with respect to the infinite crystal and possibly affecting the electron density profile. Thus, the atom positions of the upper half of the slab were also relaxed and optimized.

For given z, we define $\bar{n}_z$ as the average of the valence electron density over a section of the unit cell parallel to the xOy plane. In Fig. 2 we show a plot of $\ln\bar{n}_z$, together with a linear fit. The origin of coordinates corresponds to the position of the uppermost layer of atoms (oxygen). The behavior becomes clearly linear at a certain point from the origin, defining both the electron density decay length, l, and the background edge position, z_0 [36]. The slope of the linear fit yields $l^{-1} = 2.06$ a.u., and we find $z_0 = 0.95$ a.u. In our case, furthermore, z_0 also indicates the value of the reference plane position, z_{VW}, for the van der Waals term. Indeed, in their work Zaremba and Kohn [18] found that in the case of insulators z_{VW} is located to a good approximation at the background edge.

Note that the total potential $v(z)$ saturates when reaching the work function value as z draws closer to the crystal. Thus, from this point on, we take a constant potential. Once the interaction potential is determined, we need to solve the Schrödinger equation $[-(\hbar^2/2m)\nabla^2 + v(z)]\psi(z) = E\psi(z)$ and see if it admits any bound state solution. We solve this equation semianalytically, exploiting an analytic expansion for $z \rightarrow +\infty$ of the form $\exp(-|E|z)\sum_{n\geq 0} a_n z^{-n}$, $a_n = -[Ca_{n-2} + n(n-1)a_{n-1}]/2|E|n$. We find two bound states: a ground state ψ_0 with energy $E_0 = -0.14$ eV and a single excited state ψ_1 with energy $E_1 = -5$ meV. In Fig. 3, we show a plot of the probability density for both states, as well as of the potential $v(z)$ in the inset. Thus, the E_0 value we find is remarkably close to the -0.15 eV experimental estimate [11,37].

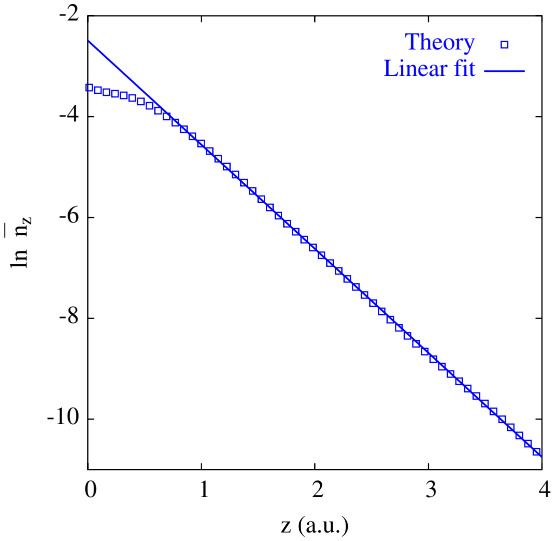

FIG. 2 (color online). Behavior of the electron density at the surface of a α-quartz slab exposing a (011) surface, illustrated by a logarithmic plot of the electron density averaged over the section of the unit cell, as a function of the coordinate z perpendicular to the slab.

Given that there is no previous theoretical study along the above lines of the problem we are considering, and that there is little experimental information to date, it is useful to compare our results with some known facts regarding physisorption. First, we point out that there is an empirical, universal relationship between the van der Waals constant C, the macroscopic dielectric constant of the crystal, and the static atomic polarizability, put forward by Hoinkes [17], which is expected to hold within a spread of roughly 30%. The relation is $C = K\alpha(\varepsilon - 1)/(\varepsilon + 1)$, where $K = 1.41$ eV. With $\alpha = 4.5$ a.u. (static Ps polarizability) and $\varepsilon = 2.38$ one finds $C = 20.7$ eV a_0^3, so that our value is 33% below. It is notable that the Hoinkes law still applies relatively well to such a light atom as Ps. Second, it is of interest to compare the energies we find with those of other systems. If we take H, which is the lightest normal atom, we find that its binding energy on graphite, for example, is 32 meV (for other systems it is even lower) [17]. Thus, at first sight the ground state energy we find for Ps appears to be rather large. One can understand this, however, noting that the well depth in our case is ~1.7 eV, while in the case of H/graphite it is 43 meV. The fact that our value of E_0 is such a small fraction of the well depth is of course due to the lightness of Ps. Also, the potential well in our case is so deep because of the strong polarizability of Ps (8 times that of H) and its relatively small work function. Thus, the values we find, although unusual, are overall well understood in the framework of physisorption. They appear to be robust also in the following sense. For comparison, we have considered the case of a crystal exposing the (001) surface to the Ps atom. The results are very close to those

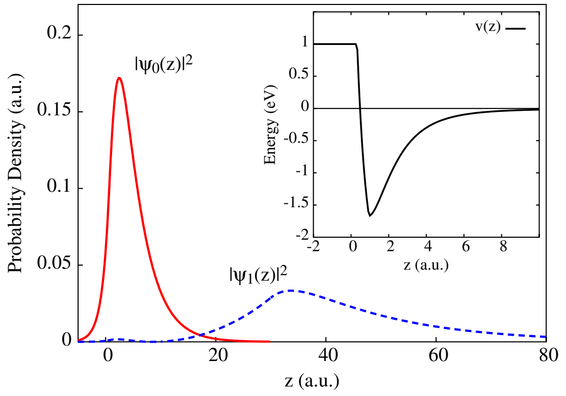

FIG. 3 (color online). Plot of the Ps ground state probability density (solid curve) and of its sole excited state (dotted curve). The inset shows the interaction potential. The potential saturates once it reaches the Ps work function value (1 eV).

above, with a less than 1% difference in the binding energies. Furthermore, the change in energies arising from surface reconstruction is of the same order of magnitude [38].

We now briefly discuss the possibility of Ps_2 formation, for which we invoke the Langmuir-Hinshelwood mechanism [20]. Consider two Ps atoms initially physisorbed on the surface of a crystal. Since the Ps atoms attract each other with an effective Lennard-Jones potential [24], they can eventually collide, recombine, and desorb. First, the fact that the atoms are trapped at the surface increases the chance that they do not simply rebound [20], and second, the Ps_2 binding energy is $E_B = 0.44$ eV. Thus, upon recombination the Ps_2 molecule releases internal energy, which is transferred to its z degree of freedom and causes the molecule to be desorbed with an energy of ~ 0.16 eV (the initial total energy of the two trapped Ps atoms is 0.28 eV).

In summary, we used a first-principles approach to calculate the key parameters describing the Ps–α-quartz interaction potential at physisorption distances and showed that it indeed has a bound ground state, with an energy very close to that estimated in experiment. This result, furthermore, is consistent with the possibility of Ps_2 formation at the quartz surface via the Langmuir-Hinshelwood mechanism.

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