Structure and Energetics of Helium Adsorption on Nanosurfaces

Patrick Huang, Heather D. Whitley, and K. Birgitta Whaley

Department of Chemistry and Kenneth S. Pitzer Center for Theoretical Chemistry, University of California, Berkeley, CA 94720, USA

The ground and excited state properties of small helium clusters, $^4\text{He}_N$, containing nanoscale ($\sim 3–10$ Å) planar aromatic molecules have been studied with quantum Monte Carlo methods. Ground state structures and energies are obtained from importance-sampled, rigid-body diffusion Monte Carlo. Excited state energies due to helium vibrational motion are evaluated using the projection operator, imaginary time spectral evolution technique. We examine the adsorption of $N$ helium atoms ($N \leq 24$) on a series of planar aromatic molecules (benzene, naphthalene, anthracene, tetracene, phthalocyanine). The first layer of helium atoms is well-localized on the molecule surface, and we find well-defined localized excitations due to in-plane vibrational motion of helium on the molecule surface. We discuss the implications of these confined excitations for the molecule spectroscopy.

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1. INTRODUCTION

The utility of He II as a gentle, quantum matrix for the high-resolution spectroscopic study of impurity molecules is now well-established. Accompanying these recent developments in experimental methodology is an interest in examining the spectroscopy of large, planar aromatic molecules (PAM) in helium. These PAMs can be viewed as nanoscale precursors to bulk graphite surfaces, whose size and geometry can be systematically tuned. The experiments have examined the electronic spectra of the molecules, and can be divided into two general classes: a) those involving small numbers of helium atoms ($N \leq 17$) around the impurity molecule, and b) those where the PAM is embedded in a large helium droplet ($N \sim 10000$).
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The electronic spectra of PAMs in helium exhibit features not found for the corresponding bare molecules. These new features are presumably due to the presence of helium on the molecule surface, but a more specific understanding of their origins does not yet exist. In the absorption experiments, sharp excitations have been observed at \( \sim 3 - 30 \) K above the electronic origin, which have been qualitatively attributed to the localized vibrations of helium atoms adsorbed on the molecule surface.\(^2\)\(^3\)\(^4\) This energy range also encompasses the band of states (phonon wings) associated with collective compressional excitations of the cluster interior,\(^5\) and in the large cluster experiments these localized excitations appear as additional structure superimposed on the phonon wing sidebands.

For the electronic spectra of a number of different PAMs (tetracene, Mg-phthalocyanine, and various indole derivatives) in large He droplets, the peak associated with the electronic origin (zero-phonon line) also exhibits additional structure, with splittings on the order of \( \sim 1.5 \) K.\(^6\)\(^7\) These splittings are not observed in the small cluster experiments,\(^3\) and their physical origins are not completely understood at this point. One possibility is that they are due to the excitation of low-energy modes involving the collective motion of helium atoms on the molecule surface. Theoretical calculations for the He\(_{24}\)-benzene cluster suggest that individual helium atoms are strongly localized on the molecule surface.\(^8\)\(^9\) As we discuss further below, this is a general feature which we find for a number of other PAMs, so another possible explanation is that these splittings do not arise from elastic transitions at all, but are instead due to inhomogeneities in the local helium environment around the molecule. Recent emission experiments have also revealed additional features not previously seen in absorption. For a number of other PAMs (phthalocyanine, Mg-phthalocyanine, pentacene), when an electronic and vibrational mode in the impurity molecule are simultaneously excited, the resulting emission spectrum as the molecule relaxes to the ground state is similar to that for absorption, except each line is split into two peaks that are separated by \( \sim 14.8 \) K.\(^10\) This suggests that the helium dynamics after electronic excitation are more complicated than previously thought.

In this work, we present the results of quantum Monte Carlo calculations for small numbers of helium atoms \((N \leq 24)\) around various PAMs. The strength and anisotropy of the molecule-helium interaction gives rise to a strongly localized layer of helium atoms on the molecule surface in the cluster ground states. This localization has important consequences for the excited states,\(^2\) and we report some preliminary results for excitations due to the vibrational motion of helium atoms in this first monolayer. We propose that the strong ground state localization implies similar confinement of the excited state, which may consequently affect the dynamics of energy transfer.
2. THEORY AND METHODS

The Hamiltonian for the $^4\text{He}_N$-PAM cluster consists of the rigid-body kinetic energy for the PAM, the translational kinetic energy for the $N$ $^4\text{He}$ atoms, and the total potential energy $\hat{V}$. This $\hat{V}$ is taken as a sum over two-body helium-helium and helium-PAM interactions, where the helium-PAM interaction $V_I$ is a sum of atom-atom Lennard-Jones pair potentials in the principal axis frame of the molecule:

$$V_I(r) = \sum_{\alpha} 4\epsilon_\alpha \left[ \left( \frac{\sigma_\alpha}{|r - r_\alpha|} \right)^{12} - \left( \frac{\sigma_\alpha}{|r - r_\alpha|} \right)^6 \right].$$ (1)

The sum over $\alpha = \text{C}, \text{H}, \text{N}$ runs over the individual atoms of the molecule situated at the position $r_\alpha$, and Lennard-Jones parameters $\epsilon_\alpha, \sigma_\alpha$ were taken from Vidali et al. The potentials evaluated in this manner are qualitatively similar. Each of the potentials for the linear PAMs exhibits minima near the center of the aromatic rings. The global minima in the potential of each molecule occur at $\sim 2.7 \ \text{Å}$ above and below the molecule surface. The potential for tetracene at this distance from the molecule surface is shown in Figure 1c.

Ground state properties are obtained using diffusion Monte Carlo (DMC) methods, in particular the importance-sampled rigid body diffusion Monte Carlo algorithm. The trial functions used here are products of two-body factors,

$$\Psi_T = \prod_{j=1}^N e^{-t_I(r_j)} \prod_{i<j} e^{-t_{\text{He}}(|r_j - r_i|)}$$ (2)

where $t_I$ and $t_{\text{He}}$ describe helium-PAM and helium-helium correlations, respectively:

$$t_I(r) = \sum_{\alpha} \left( \frac{c_{\alpha}}{|r - r_\alpha|} \right)^5 + ax^2 + by^2 + cz^2, \quad t_{\text{He}}(r) = \left( \frac{c_{\text{He}}}{r} \right)^5.$$ (3)

The trial function parameters $c_\alpha, c_{\text{He}}, a, b, c$ are obtained by minimizing the variational energy of $\hat{H}$ with respect to $\Psi_T$. Excited state energies are obtained using the projection operator, imaginary time spectral evolution (POITSE) method. This yields the spectral density function

$$\kappa(E) \propto \sum_n |\langle \phi_n | \hat{A}^\dagger | \Psi_T \rangle|^2 \delta(E - E_n + E_0), \quad \hat{A}^\dagger = \sum_{j=1}^N \hat{a}^\dagger_j,$$ (4)

where $\{\phi_n\}$ and $\{E_n\}$ are the set of eigenfunctions and associated eigenvalues of the Hamiltonian $\hat{H}$, respectively. The many-body operator $\hat{A}^\dagger$ is a
Fig. 1. Helium density distributions at a distance of $z = 2.9$ Å above the molecule plane for (a) $^4$He$_4$-naphtalene, (b) $^4$He$_6$-anthracene, and (d) $^4$He$_8$-tetracene. A cut of the tetracene potential at $z = 2.7$ Å is also shown in (c), where contour lines run from $-160$ K to 0 K, in increments in 15 K. The tetracene molecule on the $z = 0$ plane is drawn in bold lines.

Bose-symmetrized sum of one-body excitation operators $\hat{a}^\dagger$, and is chosen to connect the ground state $\Psi_T$ to the excited state(s) of interest.

3. RESULTS AND DISCUSSION

Ground state helium density distributions for $^4$He$_4$-naphthalene, $^4$He$_6$-anthracene, $^4$He$_8$-tetracene, and $^4$He$_{24}$-phthalocyanine were obtained using the quantum Monte Carlo methods described above. The number of $^4$He atoms around each of the PAMs studied here corresponds to full coverage of both sides of the nanosubstrate surface. In all cases, the global density maxima occur at a distance of $z \sim 2.9 - 3.2$ Å above and below the molecule plane. Figures 1a, 1b, 1d, and 2a show cuts of the local helium density at this distance, along a plane parallel to the molecule surface. It is apparent that the local helium densities consist of well-separated peaks, each corresponding to a single $^4$He atom. For the linear PAMs, each individual $^4$He atom is approximately situated above a six-membered carbon ring. For ph-
Fig. 2. Left: Helium density distribution at a distance of \( z = 3.2 \) Å above the molecule plane for \( ^4\text{He}_{24}\)-phthalocyanine. The phthalocyanine molecule on the \( z = 0 \) plane is drawn in bold lines. Right: Spectral density function for \( ^4\text{He}_8\)-tetracene.

Thalocyanine, we find that this surface can support up to 12 \( ^4\text{He} \) atoms on each side. At full coverage, this 2D layer of \( ^4\text{He} \) on phthalocyanine consists of four \( ^4\text{He} \) atoms grouped near the center of the molecule, surrounded by an outer ring of eight \( ^4\text{He} \) atoms.

Previous work with the \( ^4\text{He}_N\)-benzene system \((N = 1, 2, 3, 14)\) has revealed similar ground state features. The benzene system can be viewed as the simplest \( ^4\text{He}_N\)-PAM system, serving as a building block for models of more complicated one- and two-dimensional nanosubstrates. In that study, not only were the ground states observed to be strongly localized, but the excited states also exhibited localized character. That is, excitations due to the localized vibrational motion of \( ^4\text{He} \) on the benzene surface were found, with energies of up to \( \sim 23 \) K above the ground state. We propose here that these excited state features exist generally for larger \( ^4\text{He}_N\)-PAM systems, and that they are a result of the strong localization of the helium ground state density distribution. Figure 2 shows the spectral density function [Eq. (4)] for \( ^4\text{He}_8\)-tetracene, evaluated using the POITSE methodology discussed above.

For a choice of \( \hat{a}^\dagger = x \) and \( x^2 \), where the \( x \)-direction is taken to be along the long axis of the molecule, we find excitations at 6.3, 9.9, 20.8 K above the ground state. These states correspond to the collective vibrational motion of the \( ^4\text{He} \) atoms moving on the molecule surface along the \( x \)-direction. Work is currently in progress to extend these calculations to larger \( N \), in order to ascertain whether the collective character of these excitations persists as
additional atoms are added around the molecule.

A helium excitation confined on the molecule surface would have important consequences for spectroscopy, particularly for the dynamics of energy dissipation. Typically, the molecule is excited from the electronic ground state $S_0$ to an electronic excited state $S_1$. For a weakly interacting small molecule in a vibrationally excited state of $S_1$, this excess vibrational energy is transferred to the local helium environment. It is generally assumed that this energy is rapidly carried away from the molecule due to the large thermal conductivity of He II.\textsuperscript{14} In a helium droplet, this energy is dissipated as helium atoms boil off the surface of the droplet, and so the relaxation back to $S_0$ derives primarily from the ground vibrational state of $S_1$. On the other hand, if the excess vibrational energy of the molecule is transferred to the helium and trapped near the surface of the molecule, the resulting local helium environment could be very different from that of the ground vibrational state and would then correspond to a metastable state. These two situations could give rise to two distinct $S_1$ surfaces, resulting in a split emission spectrum similar to that observed by Lehnig and Slenczka.\textsuperscript{10} Calculation of the local helium density for the $S_1$ state, which requires a currently unknown interaction potential, would facilitate a more detailed analysis.

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