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Soft-Landing Isolation of Multidecker V_2(benzene)$_3$ Complexes in an Organic Monolayer Matrix: An Infrared Spectroscopy and Thermal Desorption Study

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Gas-phase synthesized metal−benzene sandwich complexes have generated a great deal of attention because of their unique metal- and size-dependent characteristics, originating from their one-dimensional (1-D) anisotropic structures.[1−14] In particular, the complexes consisting of vanadium (V) and benzene, V_n(benzene)$_{n+1}$, efficiently form multidecker sandwich structures. To this point, a number of experimental and theoretical studies have been devoted to the characterization of their geometric,[1−5,8] electronic,[1,4−6,8,13] and magnetic properties.[3,6,7] Their 1-D sandwich structure, for instance, ensures that such V_n(benzene)$_{n+1}$ clusters possess a quasi-band electronic structure,[1,4] and their magnetic moments increase monotonically with the cluster size.[3,8] Thus, this type of cluster is one of the most attractive candidates for molecular-scale building blocks in future spin-electronic devices.

Nondissociative deposition of these gas-phase clusters through size-selection onto an appropriate substrate, a so-called "soft-landing", is one of the newest approaches for building up cluster-based materials. Recently, we have achieved a room-temperature isolation of the gas-phase synthesized V(benzene)$_2$ complex via their soft-landing onto a self-assembled monolayer (SAM) of *n*-alkanethiols.[15,16] The sandwich structure and orientation preference of the V(benzene)$_2$ complex supported by the SAM matrix has been confirmed by infrared reflection absorption spectroscopy (IRAS), and the thermal stability and desorption kinetics have been evaluated with a temperature-programmed desorption (TPD) study. In this work, we discuss the first examination of the soft-landing of a multidecker V_2(benzene)$_3$ complex onto an *n*-octadecanethiol SAM (C_{18}-SAM) substrate. In this endeavor, we performed an infrared spectroscopy of the multidecker sandwich cluster and also evaluated their thermal stability on the SAM substrate.

Vanadium-benzene sandwich complexes were produced in a molecular beam by laser vaporization.[16,17] Cationic complexes were extracted by a quadrupole deflector, and the V_2(benzene)$_3$ cations only were size-selected by a quadrupole mass spectrometer (QMS). The cations were subsequently deposited onto a C_{18}-SAM substrate (10×10 mm^2), cooled to 200 K, with an incident energy of $\sim$20 eV. The deposited cations were neutralized on the SAM substrate,[16] most likely by electron transfer from the SAM-modified gold surface.[18] The IRAS spectra for the deposited complexes were obtained with an IR incident angle of $\sim$80° with respect to the surface normal.[16] The TPD measurements were carried out with a heating rate of 1 K/s after the deposition, and the desorbed species were detected by another QMS via electron impact ionization ($\sim$70 eV).[16] A harmonic frequency analysis of the ideally D_{6h}-symmetric V_2(benzene)$_3$ in the singlet and triplet electronic states was performed by a Gaussian 03 calculation[19] using density functional theory (DFT) with the BLYP functional. The 6-311++G(d,p) basis set was employed for benzene, while the V atoms were represented by a TZVP set. The selection of the BLYP functional had already provided excellent results for the V−benzene complex.[2,3]

Figure 1a shows the IR absorption spectrum in the 800−1500 cm^{-1} region obtained after the soft-landing of 2.0×10^{14} cations ($\sim$1 monolayer) of V_2(benzene)$_3$ complexes onto the C_{18}-SAM substrate at 200 K, together with the calculated IR spectra of the two different electronic spin states. The close similarity in the IR absorption feature between the experimental and calculated results unequivocally indicates that the soft-landed V_2(benzene)$_3$ complexes on the substrate have a multidecker sandwich structure. Although the IR spectrum seems similar to the calculation in the triplet state rather than to that in the singlet state, the electronic spin state of the supported V_2(benzene)$_3$ complexes is not conclusively determined at present; the calculated spectra for species free from the SAM environment are too similar to distinguish the spin states for the species on the SAM. Furthermore, we did not observe any IR peaks assignable to the smaller V(benzene)$_2$ complex, which might be produced by fragmentation collisions with the surface. For example, no peak at 988 cm^{-1} for V(benzene)$_2$ on the C_{18}-SAM[16] could be observed.

Based on the harmonic frequency analysis, we can assign the three IR absorption bands of V_2(benzene)$_3$ as follows: the first at 957 cm^{-1} to the symmetric ring-breathing mode [ν_s(CC)] of the two terminal benzene rings, the second at 979 cm^{-1} to the C−H in-plane bending mode [ν_{i-p}(CH)] of the terminal rings, and the third at 1379 cm^{-1} to the asymmetric C−C stretching mode [ν_a(CC)] of the middle ring. The vibrational frequency of ν_s(CC) for V_2(benzene)$_3$ is the same as that for V(benzene)$_2$ at 956 cm^{-1}, while the frequencies of the ν_{i-p}(CH) and ν_a(CC) modes are red-shifted from those for V(benzene)$_2$ at 988 and 1418 cm^{-1}, respectively.[12,15,16] The measured red-shift of these modes with the complex size is consistent with the computed results.[11]

Displayed in Figure 1b is the temperature dependence of the IRAS spectra for V_2(benzene)$_3$/C_{18}-SAM, revealing the thermal stability of the soft-landed complexes on the substrate. While we observe no spectral change up to a surface temperature of 300 K, the peak intensity of the ν_s(CC) mode (A_{2u} symmetry) at 957 cm^{-1} starts to decrease at 310 K. Subsequent to the partial intensity reduction, the IR spectrum remains unchanged from around 320 to 340 K. However, when the surface temperature is increased to 350 K, the intensity of all the peaks begins to decrease, and the bands completely disappear at 360 K. The results show that the thermal desorption of V_2(benzene)$_3$ supported on the C_{18}-SAM substrate is suppressed in the high-temperature region of $\sim$350 K. The decrease in the A_{2u} mode intensity only at 310 K may indicate an orientational change of the V_2(benzene)$_3$ complex on the SAM substrate, because the relative IR intensities of the A_{2u} and E_{1u} modes reflect the orientational preference of the D_{6h}-symmetric clusters

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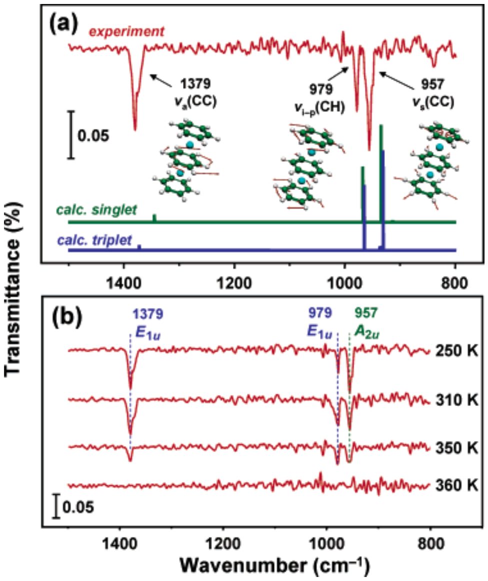

Figure 1. (a) IRAS spectrum of the V_2(benzene)$_3$ complex on C_{18}-SAM, with calculated IR absorption spectra for singlet and triplet states. (b) IRAS spectra showing the temperature-dependent variation of the V_2(benzene)$_3$ complex on C_{18}-SAM.

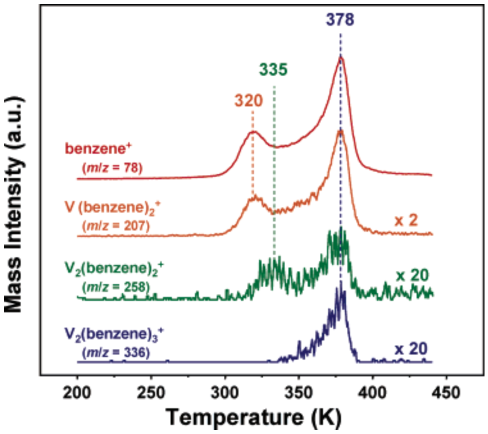

Figure 2. Multiplex thermal desorption data for V_2(benzene)$_3$ complex soft-landed on C_{18}-SAM.

on the surface in the IRAS measurement. On the basis of the surface selection rule, the intensity reduction of the A_{2u} mode means that V_2(benzene)$_3$ tilts its molecular axis (i.e., along the metal−ring direction) toward the surface plane.[15,16]

Figure 2 provides the TPD spectra taken after the deposition of 3×10^{13} V_2(benzene)$_3$ cations onto the C_{18}-SAM at 200 K. We recorded the desorption species for the parent ion, V_2(benzene)$_3^+$, and for its fragment ions: V_2(benzene)$_2^+$, V(benzene)$_2^+$, and benzene$^+$. Only one peak was observed in the desorption spectrum of the V_2(benzene)$_3^+$ at 378 K; however, the other fragment species display two peaks in the spectra. The peak at 378 K, which is observed in all the fragment spectra, is attributed to the desorption of the V_2(benzene)$_3$ complex, and the fragment signals are caused by the electron impact ionization of the desorbed parent clusters in the mass spectrometer. The peak at 320 K seen in the spectra for benzene$^+$ and V(benzene)$_2^+$ is due to the desorption of the V(benzene)$_2$ complex,[16] produced by the deposition impact of V_2(benzene)$_3$ with the surface. In this study, the kinetic energy distribution of the cluster beam is estimated to be ∼20 eV at full-width half-maximum, so that a small amount of the clusters were inevitably deposited with a high collision energy (>40 eV). Such an energy would induce the dissociation of the projectile V_2(benzene)$_3$ complex in the landing process. Furthermore, the peak at 335 K, clearly observed in the signal for V_2(benzene)$_2^+$, should be assigned to the desorption of the V_2(benzene)$_2$, which is also produced on the surface in the landing process. The TPD results indicate that some of the deposited V_2(benzene)$_3$ complexes dissociate to V(benzene)$_2$ and V_2(benzene)$_2$ in the landing process, and these fragments are coadsorbed on the C_{18}-SAM substrate, together with the nondissociatively deposited V_2(benzene)$_3$.

As noted above, however, we observed no IR absorption peak originating from these coadsorbed fragments in the IRAS measurement, an absence indicating that the quantity of the fragments is under the detection limit of the IRAS measurement. The IR absorption intensity for the fragments, furthermore, should be much weaker than that for V_2(benzene)$_3$. Indeed, the DFT calculation suggests that the magnitudes of IR absorption for V(benzene)$_2$ and V_2(benzene)$_2$ are about one-third or one-half, respectively, compared to those for V_2(benzene)$_3$. Ultimately, it should be emphasized that every peak on the IRAS spectra taken above the desorption temperature of the fragments (∼310 K), displayed in Figure 1b, arises completely from the V_2(benzene)$_3$ complexes supported on the C_{18}-SAM matrix. In conclusion, matrix-isolation of gas-phase synthesized, thermally stable multidecker V_2(benzene)$_3$ sandwich complexes on the SAM substrate is anticipated to open up new possibilities for exploiting these complexes as molecular-scale, photomagnetic building blocks in future cluster-based materials.

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Supporting Information Available: Complete ref 19. This material is available free of charge via the Internet at http://pubs.acs.org.

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