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Infrared and Computational Studies of Spontaneously Adsorbed Amine Reagents on $YBa_2Cu_3O_7$: Structural Characterization of Monolayers atop Anisotropic Superconductor Surfaces

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Supplementary Figure S1: Schematic illustration showing the relative crystallographic ordering characteristics for the various types of samples of $YBa_2Cu_3O_7$. Shown in (A) is a polycrystalline ceramic sample; in (B) ordering characteristics fostered by the matching of substrate / film lattice dimensions (arrow represents the a-axis direction of the cuprate sample); in (C) a (001) oriented sample; in (D) a (100) oriented sample; and in (E) a twinned single crystal.

Supplementary Figure S2: Shown are the IR transition dipoles for a linear alkylamine adsorbed to $YBa_2Cu_3O_7$. It is hypothesized that the high value for the tilt angle anticipated for the adsorbate monolayer leads to a decrease in the coupling of the methyl stretching dipole with the incident IR radiation. The shown orientation of the monolayer reagents should lead to a decrease in the GRIFTS signal observed for the methyl vibrations (see Figure 2A in the main section of the paper).

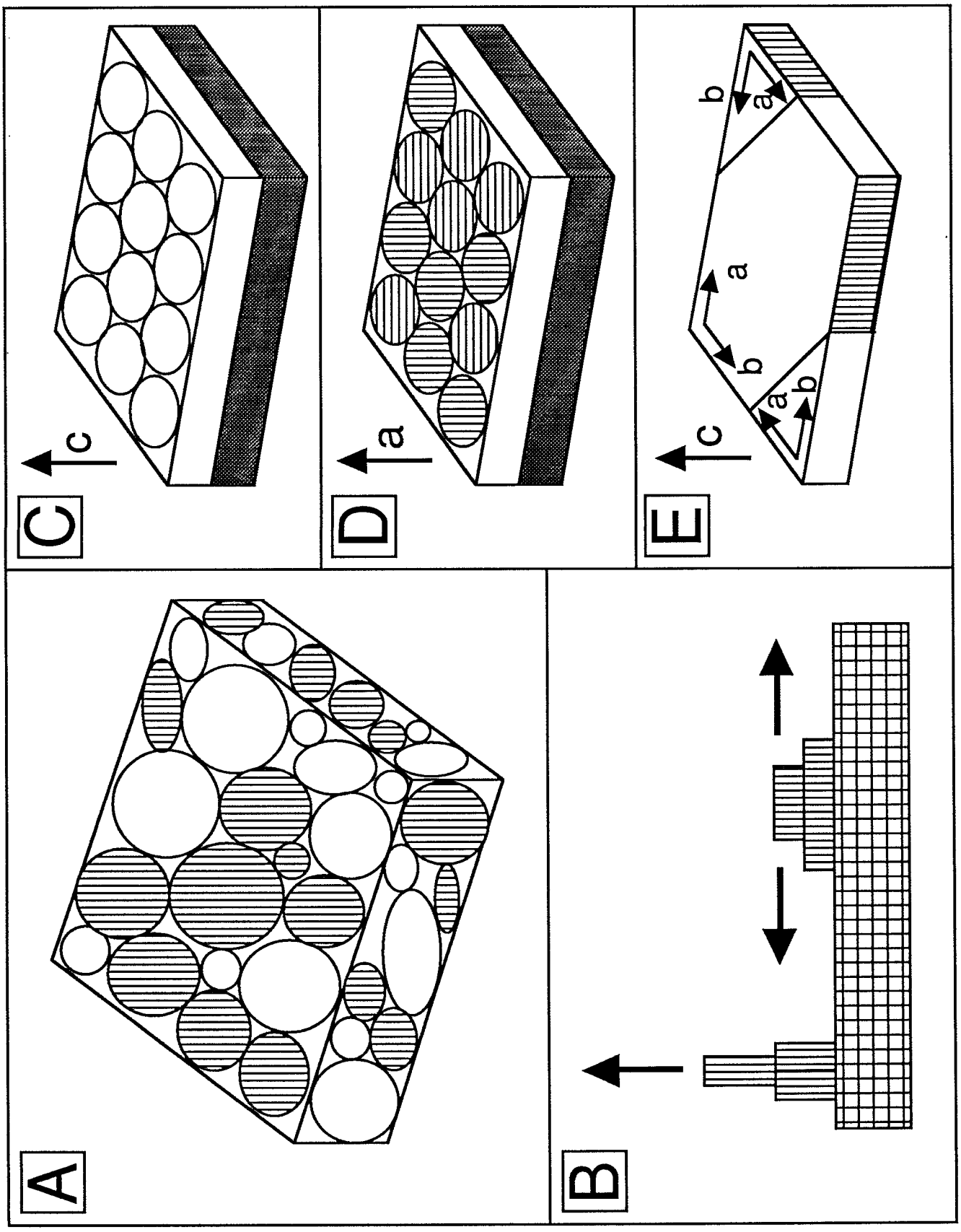
Supplementary Figure S3: Illustrations are included which are relevant to the spontaneous adsorption of alkylamines to $YBa_2Cu_3O_7$ (001) surfaces. Schematic perspectives of the alkylamine adsorption are provided from top and side views. This schematic clearly shows the footprint of the alkylamine on the $YBa_2Cu_3O_7$ (001) surface. From an analysis of the space filling model, it was determined that the most efficient packing of the monolayer reagents yields a molecular tilt angle (θ_m) of 35±5°. Note that this tilting is restricted to the nearest neighbor direction (i.e. within the (110) plane of $YBa_2Cu_3O_7$). If the tilting occurs along the direction of next nearest neighbors (i.e. along (100) or (010) planes), a significantly larger tilt angle of ≈50° ± 5° can be accommodated.

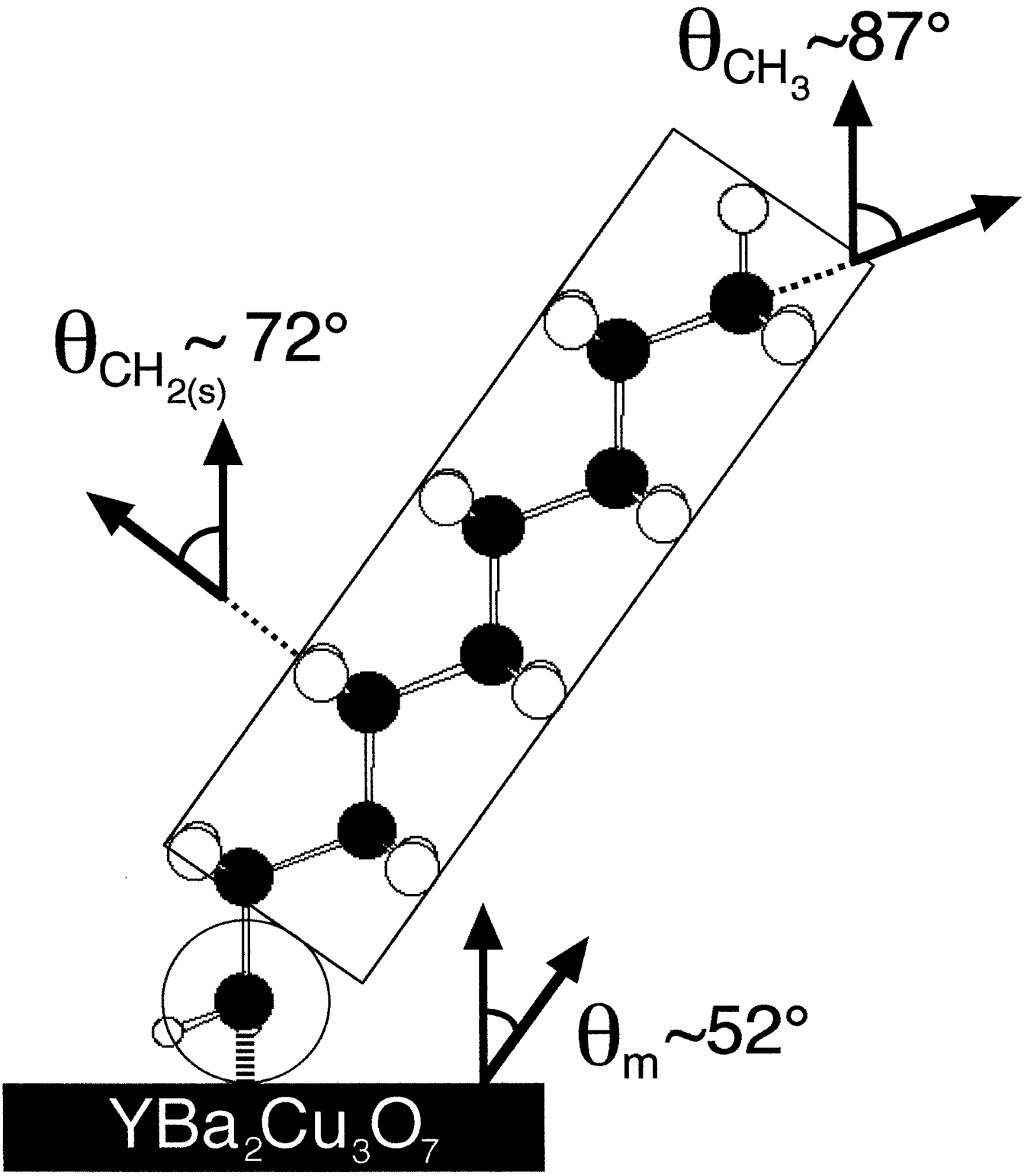
Supplementary Figure S4: Illustrations are included, for comparison purposes, which are relevant to the spontaneous adsorption of alkylthiols to Au (111) surfaces. Schematic perspectives of the alkylthiol adsorption are provided from the top and side views. This schematic clearly shows the footprint of the alkylthiol on the Au (111) surface. From an analysis of the space filling model showing the side

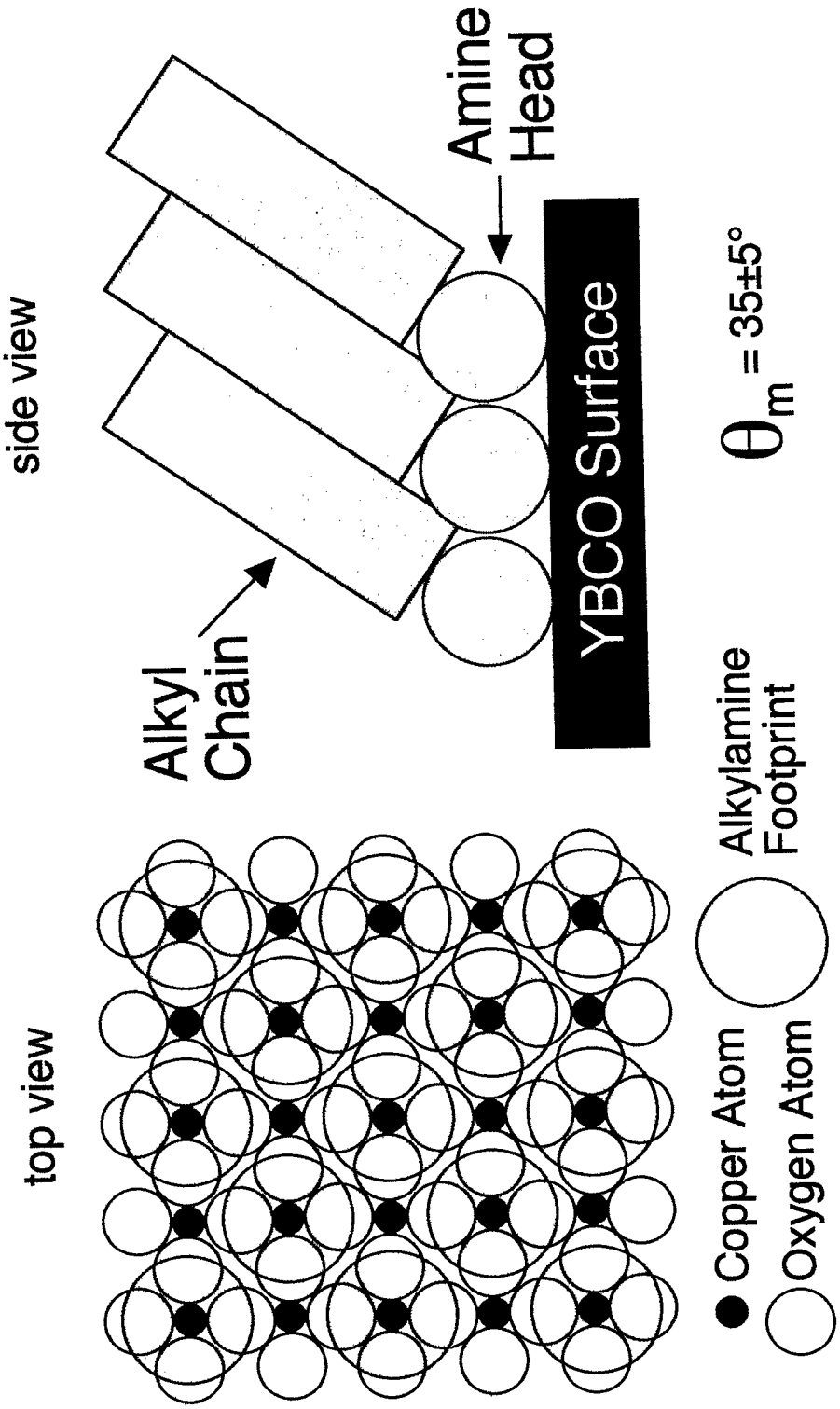
perspective of alkylthiols adsorbed to Au (111), it was determined that the most efficient packing of the monolayer reagents yields a molecular tilt angle (θ_m) of 27±5°.

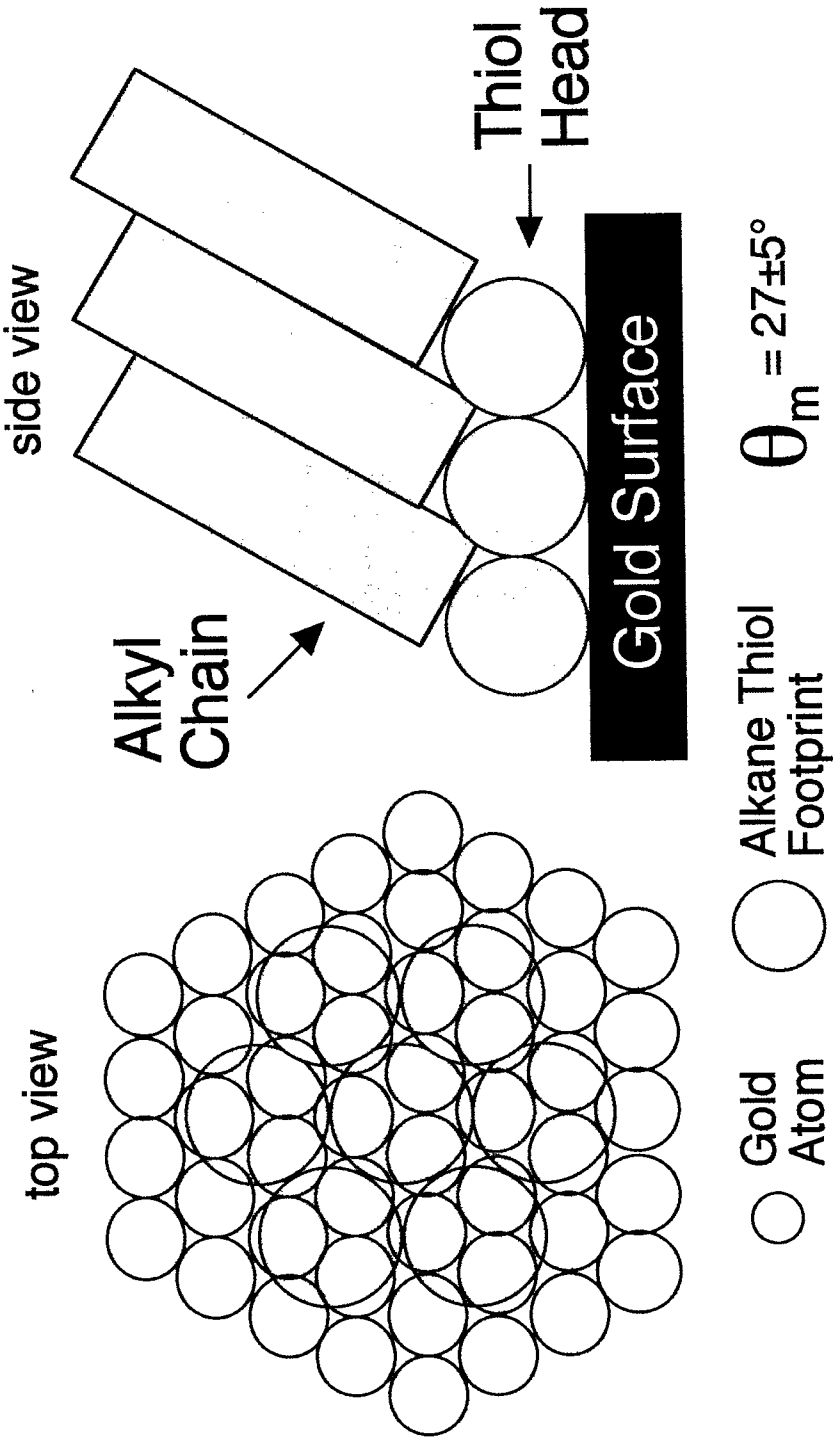
Supplementary Figure S5: Molecular modeling results of the alkylthiol / gold(111) case are provided. Illustrated here are two space filling molecular models, and a surface energy vs. in-plane tilt angle plot. Shown in (A) is a side view of the adsorption of alkylthiols to gold (111). Shown in (B) is a view down the molecular axis of the adsorbate molecules. Shown in (C) is a plot of the surface energy versus the in-plane tilt angle of the alkylthiol adsorbate molecules.

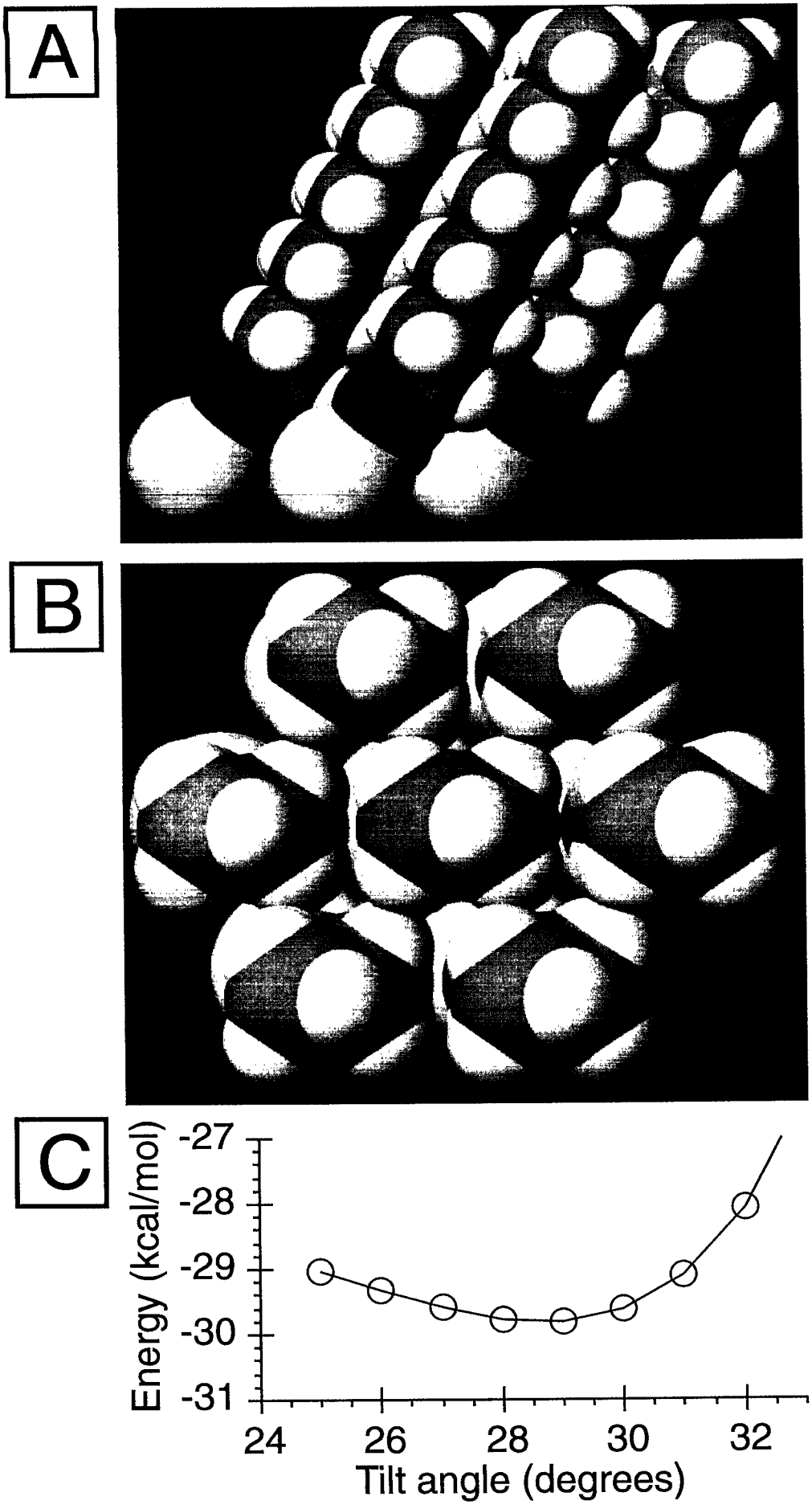
Supplementary Figure S6: Information analogous to that provided in Figure 11 is included here for an alternative energy minimized structure having θ_{ip}=32°, θ_{op}=14°, and α=120°. For this system, the following three curves are shown: (A) energy vs. θ_{ip} where θ_{op}=14° and α=120° are fixed, (B) energy vs. θ_{op} where θ_{ip}=32° and α=120°, and (C) energy vs. α where θ_{ip}=32° and θ_{op}=14°.




θCH3~87°
θCH2(s)~ 72°
θm~52°
YBa2Cu3O7


side view
Amine Head
Alkyl Chain
YBCO Surface
$\theta_m = 35\pm5°$
top view
Alkylamine Footprint
Copper Atom
Oxygen Atom


side view
Thiol Head
Alkyl Chain
Gold Surface
$\theta_m = 27 \pm 5°$
top view
Alkane Thiol Footprint
Gold Atom


A
B
C
Energy (kcal/mol)
-27
-28
-29
-30
-31
24
26
28
30
32
Tilt angle (degrees)