The second class of compounds to which we have applied the ^{31}P NMR method are the edge-sharing bioctahedral complexes of molybdenum(III) and tungsten(III) of structure type II. In this case, the M–M interactions consist of fully formed σ and π bonds plus a weak antibonding interaction between δ orbitals.[13] Table I gives values of the energy transition from $^1A_{1g}$ to $^3B_{1u}$ for edge-sharing bioctahedral complexes with metal cores of Mo_2, W_2, and Mo–W and the bidentate phosphines dppm (bridging) and dppe (chelating).

The values of the singlet–triplet separations for edge-sharing bioctahedral complexes obtained using the ^{31}P NMR technique are in reasonable agreement with values previously obtained by solid-state magnetic susceptibility measurements on bulk samples requiring corrections for paramagnetic impurities. In addition to the data presented here for $Mo_2Cl_4(L\text{-}L)_2$ and edge-sharing bioctahedral complexes, studies of other quadruply bonded transition metal complexes as well as additional edge-sharing complexes are in progress.

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Quantized Adhesion Detected with the Atomic Force Microscope

Jan H. Hoh, Jason P. Cleveland, Craig B. Prater,
Jean-Paul Revel,† and Paul K. Hansma*

Department of Physics, University of California
Santa Barbara, California 93106
Division of Biology, California Institute of
Technology, Pasadena, California 91125

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The atomic force microscope (AFM)[1] is rapidly becoming a powerful tool for investigating surface chemistry and adhesion.[2-7] Current efforts with this new instrument are guided by the pioneering research of Israelachvili and his colleagues, whose work with the surface force apparatus has laid the foundation for investigating interactions near and between surfaces.[8-13] The AFM is capable of measuring forces of less than 10^{-11} N with high spatial resolution, thus making possible the study of very weak interactions and local surface chemistry. Here we report the first (to our knowledge) observation of discrete adhesive interactions with measured forces of 1×10^{-11} N. Two mechanisms for this effect are proposed: individual hydrogen bonds between the tip and surface are resolved or ordered water layers create different force minima near the surface.

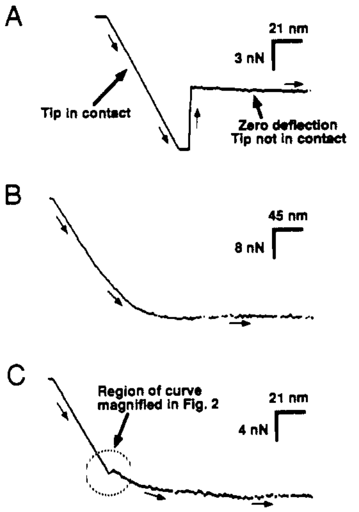

Figure 1. Cantilever deflection versus sample position curves (often called force curves) of a silicon nitride tip breaking contact with a glass surface in water, acquired with digital control. The full scan range is shown. A: At pH 5 a large adhesive interaction of 9×10^{-9} N is evident (the bottom of the trace, with the jump-off point, is off the scale). B: At pH > 9 the interaction became strongly repulsive. C: At pH's between 8 and 9, a small adhesive interaction is present. High-resolution measurements with analog electronics were made when this interaction was near 1×10^{-9} N. The region circled is that examined closely in Figure 2.

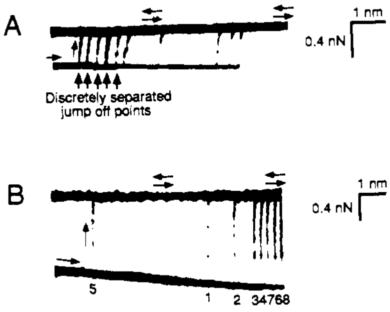

Figure 2. Multiple oscilloscope traces showing discrete jump-off forces of the silicon nitride tip from glass surface at pH 8.5–9. Note that, as in Figure 1, the *x* axis does not represent the separation distance between tip and sample as is the case for many force versus distance plots; instead, the *x* axis is the movement of the glass surface mounted to the piezo and the *y* axis reflects the position of the tip. While the tip is in contact with the surface, the movement of the tip and glass are coupled. This allows us to resolve differences in cantilever deflection *at jump-offs* of less than 10^{-10} m (about 10^{-12} N). A: Traces are from about 12 sequential scans. The left-to-right traces clearly show the discrete cantilever deflections at jump-off. Several events retraced the exact same lines. The top horizontal line is broader because it also contains the approaching trace (right-to-left). The *z* piezo cycled a total of 180 nm at 0.5 Hz. B: An identical experiment to A in which the relative order of jump-off events was recorded (numbered 1–8). The adhesion increases and decreases randomly, demonstrating that directional drift is not a factor.

We have examined the interaction between a standard silicon nitride microfabricated AFM stylus[14] and a glass surface[15] in water. A NanoScope II scanning probe microscope (Digital Instruments, Santa Barbara, CA) equipped with an AFM stage, D type scanner, and fluid cell was operated in the force mode.[6,7] For the high-resolution measurements, control and output from the AFM stage was switched to an analog wave generator for *z* input voltage and a storage oscilloscope for the output. The pH of the water (>10 MΩ) was adjusted with NaOH. Fluid in the cell was changed every 10–20 min to compensate for what ap-

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† California Institute of Technology.

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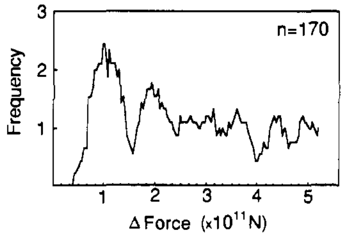

Figure 3. Distribution of differences between 170 pairs of adhesion measurements from one experiment. The measurements were divided into 4×10^{-13} N bins, and data was smoothed by a five-point averaging. There is a well-defined peak at 1.2×10^{-11} N. The next multiple can also be seen, but higher multiples are lost because of peak broadening.

peared to be a CO_2-driven pH decrease. The cantilevers were 120 or 200 μm, V-shaped, with spring constants of roughly 0.2 or 0.04 N/m, respectively.[14,16]

At pH 5 the adhesive force between silicon nitride AFM tips and glass in water is generally 5×10^{-9} to 4×10^{-8} N,[17] while at pH > 9.3 the adhesion is reduced below the limits of detection and the interaction is strongly repulsive (Figure 1). In the high-resolution experiments the adhesion is measured at pH 8.5–9, where the adhesive force is about 0.5×10^{-9} to 1.5×10^{-9} N. As this curve (Figure 1C, but with analog control) was examined closely over time, it became evident that the adhesive interaction fluctuated in discrete steps (Figure 2). A large number of these events ($n > 4000$) were examined, and the difference in adhesive force between pairs of scans was tabulated. The criteria for counting an interaction were that the two measurements were immediately sequential (i.e., within 2 s, to minimize drift), that the path of the trace was identical before and after the jump off, and that the difference between two jumps was less than 1.8 nm. The latter was an arbitrary number selected to limit the size of the data set, while including several multiples of the discrete interaction. The smoothed distribution of all events that satisfied these criteria from one experiment is shown in Figure 3. A similar distribution was seen for several experiments; however, variability prevented pooling of data from separate experiments. The oscilloscope traces and the distribution plot clearly show the discrete nature of the adhesive interaction between silicon nitride and glass of roughly 1×10^{-11} N.

The high density of silanol groups on both surfaces leads us to suggest that these discrete interactions may be due to variations in the number of hydrogen bonds formed between the surfaces at subsequent contacts.[18,19] Indeed the strength of the interaction is of the order of magnitude expected for a single hydrogen bond. Since there is also a repulsive double layer present, the force of adhesion measured from cantilever deflection should be an underestimate of the actual bond force. Another possible explanation of the data stems from the breakdown of the continuum properties of water near surfaces.[20] Israelachvili and Pashley[10] have shown that ordered water layers near a mica surface caused oscillations in the measured force as two surfaces were brought together. It is possible that the quantized adhesion described here results from the tip pulling away from different force minima generated by the ordered water layers. In fact, the depth of the corresponding energy wells may be sufficiently near kT (at jump-off) to allow the tip to jump between the different wells, effectively resulting in a Boltzman sampling. Several other explanations for the data such as digital signal noise, drift, double layer repulsion, and other adhesive forces have been considered, but do not provide adequate explanations for the data.

The observation of a quantized adhesive interaction between silicon nitride and glass presents a potentially important phenomenon. The most likely explanations for the effect are individual hydrogen bonds being resolved or force minima from ordered hydration layers. While the exact mechanism remains to be determined, the results demonstrate that the AFM has the sensitivity for studying subtle details of intermolecular forces.

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(16) Preliminary results from direct measurements suggest that spring constants can vary by a factor of 2 for the same type of cantilever within a wafer (Cleveland *et al.*, unpublished observation). The average value for the V-shaped 200 μm long with 36 μm wide legs cantilever measured to date is 0.04 N/m, though no calibrated cantilevers were available for this study.

(17) Most low-resolution measurements were made with 120-μm V-shaped cantilevers with spring constants of 0.2 N/m. Since the total adhesive force is load dependent, these values are lower for the 200-μm cantilevers.

(18) The density of silanol groups on silicon nitride and typical glass surfaces is about 5 hydroxyl groups per nm^2. Iler, R. K. *The Chemistry of Silica*; Wiley and Sons: New York, 1979. Bousse, L.; Mostarshed, S. *J. Electroanal. Chem.* **1991**, *302*, 269–274. Amino groups on the surface of silicon nitride are only about 1% as frequent as hydroxyl groups, and their contribution is here considered negligible. Bousse, L.; Mostarshed, S. *J. Electroanal. Chem.* **1991**, *302*, 269–274.

(19) The pK_a of surface silanol groups is usually 6–7; however, as these two surfaces are brought into contact, the pK_a will shift up substantially (often 1–3 units in other systems). The silanols will therefore be partially protonated, though the exact protonation state is not known.

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A New Type of Bridging Carbonyl Ligand: μ_3-η^2, and not One but Two

Richard D. Adams,* Zhaoyang Li, Jau-Ching Lii, and Wengan Wu

Department of Chemistry and Biochemistry
University of South Carolina
Columbia, South Carolina 29208

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Bridging coordination is a principal mode for the activation of CO by metal cluster complexes.[1] It is believed to play a key role in the transformations of CO on metal surfaces.[2] A variety of bridging coordination modes for CO have been characterized. These range from the simple two-center carbon bridge A to the complex μ_4-η^2 B.[1] Triply bridging carbonyl ligands that have been characterized include μ_3-η^1 C and μ_3-η^2 D.[3] There are also a number of variations of these forms in which Lewis acid centers are strongly associated to the oxygen atom.[1a] We now wish to report what appears to be a new triple bridge, E, in which the carbon atom bridges two of the metals of an *open* triangle and the oxygen atom alone is coordinated to the third one.

The compound $Ru_8Pt_2(CO)_{23}(\mu_3\text{-}H)_2$[4] (**1**) was isolated in 22% yield from the reaction of $Ru_4Pt_2(CO)_{18}$[5] with $Ru_4(CO)_{13}(\mu\text{-}H)_2$

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(4) $Ru_4Pt_2(CO)_{18}$[5] (30.0 mg, 0.0231 mmol) and 18.0 mg (0.0233 mmol) of $Ru_4(CO)_{13}(\mu\text{-}H)_2$ were dissolved in 30 mL of heptane and heated to reflux for 45 min. The products were separated by TLC on silica gel with a hexane/CH_2Cl_2 (2/1) solvent mixture. This yielded the following, in order: 2.1 mg of a mixture of $Ru_4(CO)_{12}(\mu\text{-}H)_4$ and $Ru_3(CO)_{12}$, 12.0 mg of unreacted $Ru_4(CO)_{13}(\mu\text{-}H)_2$, 2.1 mg of unreacted $Ru_4Pt_2(CO)_{18}$, and 8.9 mg of dark green $Ru_8Pt_2(CO)_{23}(\mu_3\text{-}H)_2$ (**1**) (22%). For **1**: IR (ν_{CO} in CH_2Cl_2) 2074 (vs), 2046 (w), 2033 (w); ^{1}H NMR (δ in CD_2Cl_2) −15.79 (2 H, J_{Pt-H} = 22.2 Hz). Satisfactory elemental analyses have been obtained.

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