

characteristic of the pure  $\text{Rh}^0_x$  surface<sup>48</sup> are obtained by using our method of K modification of the  $\text{Al}_2\text{O}_3$ .

**C. Behavior of Rh/K- $\text{Al}_2\text{O}_3$  under Extreme Hydrolysis Conditions.** A series of experiments shown in Figure 5A,B were designed to determine whether Rh/K- $\text{Al}_2\text{O}_3$  catalysts, subjected to extreme hydrolysis treatment, might re-form  $\text{Rh}^1(\text{CO})_2$  if Al-OH groups are re-formed on the support. This experiment involved monitoring the CO and OH IR spectra following treatment of the CO-covered catalyst for 30 min with 2 Torr of water vapor pressure in the temperature range 300-770 K. In Figure 5, the IR spectra for the various hydrolysis treatments are shown as a function of the treatment temperature. It is observed that the  $\text{Rh}^1(\text{CO})_2$  species are actually destroyed during these hydrolysis experiments.

Spectrum A.a of Figure 5 represents the starting point for these measurements. Both  $\text{Rh}^0_x$  and  $\text{Rh}^1$  sites are present. Upon heating to 470 K under  $\text{H}_2\text{O}(\text{g})$  (spectrum b),  $\text{Rh}^1(\text{CO})_2$  has started to disappear and both bridged- and terminal-CO species undergo enhancement of their absorbance. Continued  $\text{H}_2\text{O}(\text{g})$  treatment to 570 K resulted in complete loss of CO absorbance (not shown; due to expected thermal desorption of CO); the spectra shown in Figure 5A.c,d were obtained by additional CO adsorption at 2 Torr (following heating under  $\text{H}_2\text{O}(\text{g})$  and evacuation at 300 K). It is noted that a partial recovery of  $\text{Rh}^1(\text{CO})_2$  absorbance is obtained at 570 K, but this trend is reversed again upon heating to 770 K.

The hydroxyl spectra (Figure 5B) indicate that hydrolysis causes a significant enhancement of the associated-OH absorbance but only a *small* enhancement of the isolated-OH absorbances above  $3680\text{ cm}^{-1}$ . Thus, Al-OK groups are stable under extreme hydrolysis conditions.

Mass spectroscopic studies of the gas-phase composition during hydrolysis indicate that  $\text{CO}_2$  is a major product, along with  $\text{H}_2$ . The  $\text{H}_2$  produced above the catalyst (water gas shift reaction:  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ) may participate in reduction of  $\text{Rh}^1$  to  $\text{Rh}^0$ , causing  $\text{Rh}^1(\text{CO})_2$  to be consumed as has been observed previously for pure  $\text{H}_2$  treatment.<sup>6,7</sup>

(47) Kesraoui, S.; Oukaci, R.; Blackmond, D. G. *J. Catal.* **1987**, *105*, 432.

(48) Dubois, L. H.; Somorjai, G. A. *Surf. Sci.* **1980**, *91*, 514.

#### IV. Summary of Results

The results of this study are summarized below:

1.  $\text{K}_2\text{CO}_3$  may be used to convert isolated Al-OH groups to Al-OK groups on  $\gamma\text{-Al}_2\text{O}_3$  catalyst support material.
2. High-temperature treatment of  $\text{K}_2\text{CO}_3$ -treated catalysts in the range 570-870 K leads to  $\text{CO}_3^{2-}$  decomposition at temperatures below the decomposition temperature for bulk  $\text{K}_2\text{CO}_3$ .
3. The K- $\text{Al}_2\text{O}_3$  catalyst support material does not exhibit new bulk phases observable by XRD analysis, following calcination at 973 K, suggesting that Al-OK groups are produced on the surface of the  $\text{Al}_2\text{O}_3$ .
4. Rh/K- $\text{Al}_2\text{O}_3$  catalysts exhibit a limited tendency to produce  $\text{Rh}^1(\text{CO})_2$  species in the presence of  $\text{CO}(\text{g})$ . However, IR results indicate that  $\text{Rh}^0_x$  sites remain abundant. This is due to the replacement of isolated Al-OH groups by Al-OK groups, removing the Al-OH as an agent for  $(1/x)\text{Rh}^0_x \rightarrow \text{Rh}^1(\text{CO})_2$  formation.
5. Rh/K- $\text{Al}_2\text{O}_3$  catalysts are stabilized against hydrolysis processes to produce  $\text{Rh}^1(\text{CO})_2$  at temperatures up to 770 K in  $\text{H}_2\text{O}(\text{g})$  at 2 Torr pressure. Only a small regeneration of isolated Al-OH groups is observed under these extreme hydrolysis conditions.
6. The results, when compared to other studies involving the removal of Al-OH groups by heat treatment, or by functionalization to produce Al-O-SiR<sub>3</sub> species, strongly support the concept that isolated Al-OH groups are necessary for the degradation of  $\text{Rh}^0_x$  species in the presence of  $\text{CO}(\text{g})$ , producing  $\text{Rh}^1(\text{CO})_2$ .
7. These experiments suggest that oxidative degradation of supported  $\text{Rh}_x$  automotive exhaust catalysts, to produce the catalytically inactive  $\text{Rh}^1$  site, may be extensively diminished alkali-metal functionalization of isolated Al-OH species on the  $\text{Al}_2\text{O}_3$  support, producing Al-OK surface species adjacent to  $\text{Rh}^0_x$  metal particles.

*Acknowledgment.* We thank the Department of Energy, Office of Basic Energy Sciences, for support of this work. M.I.Z. acknowledges support of a sabbatical visit by the Fulbright Foundation.

**Registry No.**  $\text{Al}_2\text{O}_3$ , 1344-28-1;  $\text{K}_2\text{CO}_3$ , 584-08-7; Rh, 7440-16-6; CO, 630-08-0.

## Surface Assisted Xe-Xe Bonding?

Roald Hoffmann,\* Meinolf Kersting, and Zafiria Nomikou

Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853

(Received: July 17, 1990)

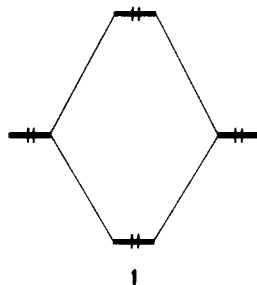
An idea for forming noble gas atom-noble gas atom bonds on a surface is explored theoretically, for Xe on Pd. The notion is that interaction with the surface should withdraw electrons from the top of the forming Xe 5p band, thus allowing Xe-Xe bonding, truly compressed structures. Molecular orbital studies of Xe overlays and  $\text{Xe}_2$  pairs on Pd(100) and Pd(111) are not encouraging; the Xe-Pd interaction appears insufficient to produce the desired effect.

Surfaces often bind molecules. And the involvement of a surface may lower barriers to chemical reactions. From a chemical point of view, the most interesting surface phenomena occur when a molecule is formed on the surface that has little kinetic or thermodynamic stability in the gas phase (e.g. CCH,  $\text{CCH}_3$ ), or when the catalyzed reaction is one that is difficult normally, therefore a desired transformation.

It is interesting then to think of molecular species that could exist on surfaces, perhaps *only* on surfaces. This contribution, speculative and, as it emerges, not all that encouraging, addresses such a problem.

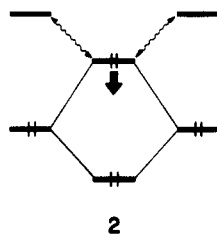
The context is the formation of bonds between inert or noble gas atoms. The potential energy curve between He (or Xe) atoms is, of course, repulsive, except for the van der Waals minimum.<sup>1</sup> The reason for this is obvious; the 1s orbitals interact as shown in 1. The antibonding  $\sigma_1^*$  combination is raised in energy more than the bonding  $\sigma_g$  one is lowered. Filling of both levels results

(1) See, inter alia: (a) Patil, S. H. *J. Phys. B: At. Mol. Phys.* **1987**, *20*, 3075. (b) Krauss, M.; Regan, R. M.; Konowalow, D. D. *J. Phys. Chem.* **1988**, *92*, 4329. (c) Dias da Silva, J.; Brandão, J.; Varandas, A. J. C. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 1851.



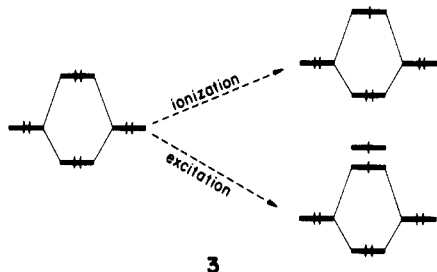
in a net repulsion. This is a typical two-orbital, four-electron interaction, within the framework of the one-electron model that informs this discussion.<sup>2</sup> This interaction is responsible not only for the repulsive part of the He-He potential but also for steric effects in chemistry.

There are some strategies for turning this situation around. First, low-lying empty orbitals on the interacting atoms could mix into the *ns* orbitals and ameliorate the repulsion, essentially by hybridization. This is shown schematically in 2. The *np* orbitals



of the noble gases do not lie sufficiently low to accomplish this. But for the alkaline-earth-metal dimers one begins to get some bonding,<sup>3</sup> the same as for Be<sub>n</sub> clusters.<sup>4</sup> A similar phenomenon, now *s*, *p* mixing into formally filled *d* shells, is responsible for the aggregation of Cu<sup>+</sup>- and Au<sup>+</sup>-containing clusters.<sup>5</sup>

Another workable strategy is excitation or ionization, as diagrammed in 3. While He<sub>2</sub> is not bound, He<sub>2</sub><sup>+</sup> and He<sub>2</sub><sup>\*</sup> are.



The dissociation energy of the <sup>2</sup>Σ<sub>u</sub><sup>+</sup> state of He<sub>2</sub><sup>+</sup> is 2.365 eV, while that of the <sup>3</sup>Σ<sub>u</sub><sup>+</sup> state of He<sub>2</sub> is 1.850 eV and that of the <sup>1</sup>Σ<sub>u</sub><sup>+</sup> state is 2.355 eV.<sup>6</sup> We have just begun to get some information on the binding energies of higher noble gas clusters from gas-phase studies.<sup>7</sup>

(2) Hoffmann, R. *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*; VCH: New York, 1988; pp 65-71.

(3) Jones, R. O. *Ab Initio Methods in Quantum Chemistry—Part I. In Molecular Calculations with the Density Functional Formalism*; Lawley, K. P., Ed.; John Wiley: New York, 1987; Vol. 67, pp 424-427.

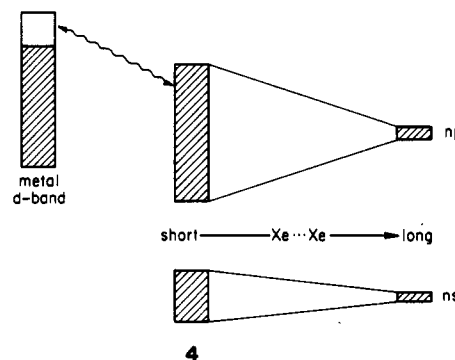
(4) (a) Marino, M. M.; Ermler, W. C. *J. Chem. Phys.* **1987**, *86*, 6283 and references therein. (b) Ermler, W. C.; Ross, R. B.; Kern, C. W.; Pitzer, R. M.; Winter, N. W. *J. Phys. Chem.* **1988**, *92*, 3042.

(5) (a) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187. (b) Jiang, Y.; Alvarez, S.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 749. (c) Merz, K. M., Jr.; Hoffmann, R. *Inorg. Chem.* **1988**, *27*, 2120. (d) Dedieu, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2074. (e) Janiak, C.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 5924.

(6) (a) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand Reinhold: New York, 1979; Vol. 4, pp 298, 292. (b) For a discussion of three-electron-bonded systems see: Clark, T. *J. Am. Chem. Soc.* **1988**, *110*, 1672. Gill, P. M. W.; Radom, L. *J. Am. Chem. Soc.* **1988**, *110*, 4931.

(7) (a) Levinger, N. E.; Douglas, R.; Murray, K. K.; Mullin, A. S.; Schulz, C. P.; Lineberger, W. C. *J. Chem. Phys.* **1988**, *89*, 71. (b) Levinger, N. E.; Ray, D.; Alexander, M. L.; Lineberger, W. C. *J. Chem. Phys.* **1988**, *89*, 5654. (c) Hiraoka, K.; Mori, T. *J. Chem. Phys.* **1990**, *92*, 4408.

The question we posed to ourselves was the following: Could a surface induce bonding between noble gas atoms in an overlayer? If the Xe atoms in a hypothetical Xe overlayer on a metal are forced close together, past their van der Waals minimum, a bandwidth will develop, as shown in 4, and a repulsion. But now



suppose that a metal surface is available in contact with this hypothetical compressed Xe layer. Suppose further that it interacts significantly, depopulating the top of the Xe *np* band. That would allow some Xe-Xe bonding, as well as Xe-metal bonding. The schematic of 4 summarizes the idea. It might operate for a fully two-dimensional Xe overlayer or for Xe<sub>2</sub> pairs.

It is obvious that this is not going to be easy; the ionization potential of the noble gases is high, and the electron affinity of metal surfaces relatively low. To maximize the chances for such a surface-assisted noble gas bond formation process, it seems to us that one needs to move to Xe and a surface that is a good acceptor, i.e. for metals on the right side of the transition series.

At this point, the story connects to the interesting information we have on so-called compressed Xe structures.

The physical adsorption of xenon on Pd(100) surfaces has been investigated extensively. Xenon physisorbs on a Pd(100) surface, forming an ordered hexagonal overlayer with a lateral Xe-Xe contact of 4.48 Å (as compared to 4.37 Å in bulk xenon) and a substrate-adsorbate separation of 3.55 Å. According to LEED studies, the adsorbate xenon overlayer is not in registry with the substrate and both layers form an incommensurate system.<sup>8</sup>

Photoemission spectra of the Xe/Pd system show a splitting of the 5p<sub>3/2</sub> and 5p<sub>1/2</sub> levels, due to spin-orbit coupling, and an additional broadening of the 5p<sub>3/2</sub> peak. This broadening, which is most pronounced at the maximum coverage of 0.44 and even results in a splitting of that peak, has been attributed to lateral interactions (overlap) of Xe atoms.<sup>9,10</sup> Both the 5p<sub>1/2</sub> and 5p<sub>3/2</sub> peaks appear broadened by about 0.5 eV (full width at half-maximum) at maximum coverage. This phenomenon suggests that Xe-Xe interactions do play a role. Adsorbate-substrate interactions cannot be neglected, even if the adsorbate layer is not aligned with the surface of the substrate. In an excellent study combining LEED, UPS, and flash desorption techniques to describe the adsorption of Xe on different Pd faces, Wandelt et al. derived adsorption energies of 9.4 kcal/mol on Pd(100) and 8.3 kcal/mol on Pd(111) surfaces.<sup>11</sup> Earlier studies on the coverage dependence of these adsorption energies were carried out by Palmberg.<sup>8</sup> Theoretical studies of this system and of other discrete noble gas atoms interacting with metal surfaces are also available.<sup>12</sup>

(8) Palmberg, P. W. *Surf. Sci.* **1971**, *25*, 598.

(9) Horn, K.; Scheffler, M.; Bradshaw, A. M. *Phys. Rev. Lett.* **1978**, *41*, 822.

(10) Scheffler, M.; Horn, K.; Bradshaw, A. M.; Kambe, K. *Surf. Sci.* **1979**, *80*, 69.

(11) (a) Wandelt, K.; Hulse, J. E. *J. Chem. Phys.* **1984**, *80*, 1340. (b) Wandelt, K.; Gumhalter, B. *Surf. Sci.* **1984**, *140*, 355. For an intriguing use of adsorbed xenon photoemission see: Wandelt, K. In *Chemistry and Physics of Solid Surfaces VIII*; Vanselow, R., Howe, R., Eds.; Springer: Berlin, 1990; pp 289-334.

(12) (a) Lang, N. D. *Phys. Rev. Lett.* **1981**, *46*, 842. (b) Lang, N. D.; Nørskov, J. K. *Phys. Rev. B* **1983**, *27*, 4612. (c) Udatchin, I. V.; Ivanovsky, A. L.; Gubanov, V. A. *Surf. Sci.* **1990**, *225*, 184. (d) For an important recent study of single and paired Xe atoms on Pt(111) models see: Müller, J. E. *Phys. Rev. Lett.* **1990**, *65*, 3021.

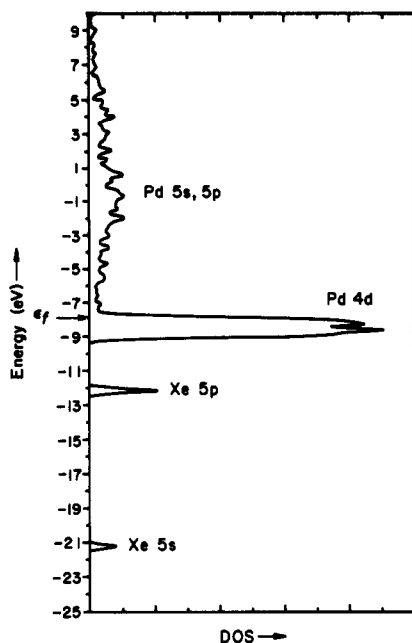


Figure 1. Total DOS of the surface-adsorbate composite system: Pd(111)-( $\sqrt{3}\times\sqrt{3}$ )R30°-Xe.

We also mention here the intriguing recent STM studies of Weiss and co-workers,<sup>13</sup> which demonstrate the existence and coherence of Xe<sub>n</sub> clusters,  $n = 3-13$  and greater, on the Pt(111) surface.

These highly interesting studies thus show some slight Xe-Pd surface bonding and moderate Xe-Xe interaction. But no real Xe-Xe bonding occurs, in the sense that we see no really short Xe-Xe contacts. One of the (very, very few) things theory can do better than experiment is to probe inaccessible regions of a potential surface. So began a study of Xe-Pd surface interaction.

The calculations reported here are extended Hückel band calculations of Xe monolayers covering one side of a three-layer slab modeling a Pd(100) surface and a nine-layer slab modeling a Pd(111) surface. The parameters used are reported in the Appendix.

Since two-dimensional periodicity is essential to our calculations, we could not investigate incommensurate models. So we covered the Pd(100) and Pd(111) surfaces (Pd-Pd nearest-neighbor contact 2.749 Å) with three commensurate "on-top" structures, generating a range of Xe-Xe contacts from 4.761 Å (5,  $p(\sqrt{3}\times\sqrt{3})R30^\circ$ -Xe on Pd(111)) through 3.887 Å (6,  $c(2\times 2)$ -Xe on Pd(100)) to 2.749 Å (7, on-top (1 $\times$ 1)-Xe on Pd(111)). The

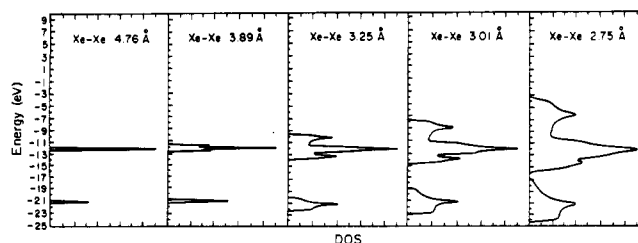
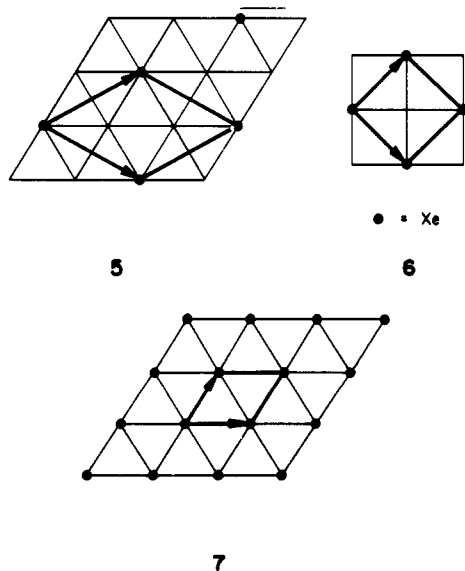


Figure 2. DOS of square xenon overlayers as a function of Xe-Xe separation. Note the spreading of the bands.

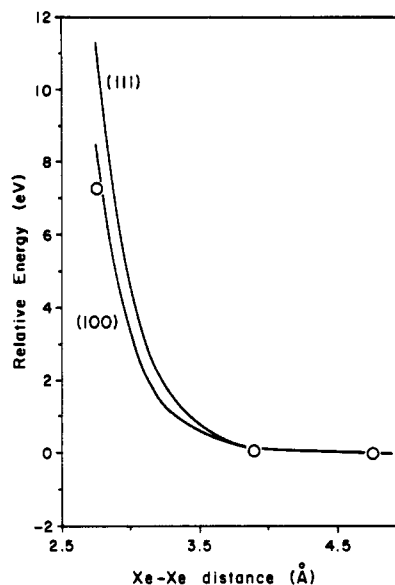


Figure 3. Relative energies per atom of Xe overlayers as a function of Xe-Xe distance. The solid curves are calculated energies for hexagonal (111) and square (100) surfaces; the three data points are the corresponding energies of Xe on Pd for structures 5-7. 5 and 7 should be referred to the (111) curve, and 6 to the (100) curve.

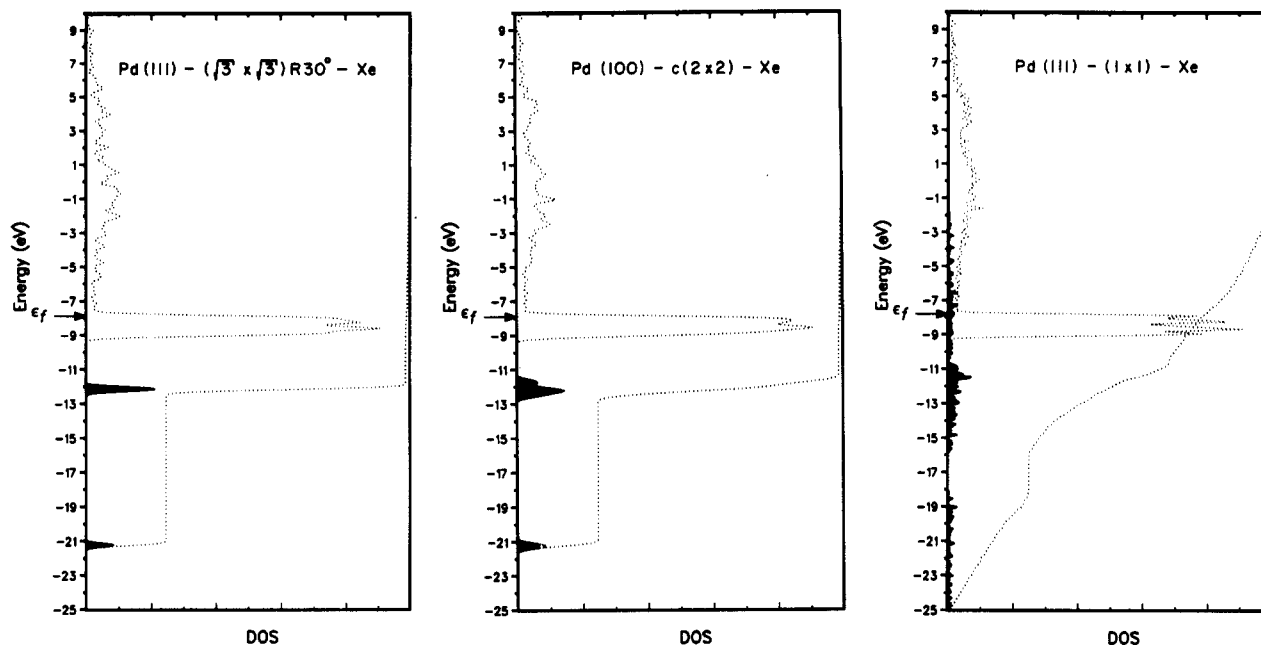
range is not optimal for, as we will see, too much happens between 3.887 and 2.749 Å. But it is the best we could do. We assumed a rather short Xe-Pd separation of 3.00 Å. The idea was to induce as much Xe-Pd bonding as possible; calculations were also done at the longer Xe-Pd separation, with similar results.

Figure 1 shows the total density of states (DOS) of 5, the system with the xenons farthest apart. We see the Xe 5s and 5p bands and the typical Pd 4d, 5s, and 5p bands. There is little interaction, by any criterion.

As the xenons approach each other, their interaction grows. Figure 2 shows schematically the density of states of hypothetical square Xe monolayers (no Pd here!) as a function of Xe-Xe distance. The obvious happens; the bands become wider as one moves below a Xe-Xe contact of 4.5 Å. The price is repulsion; Figure 3 shows the total energy of the Xe monolayers. At Xe-Xe separations of about 3.01 Å, the energy of the top of the Xe 6p band is around our calculated Pd surface Fermi level; the repulsion at this point is a staggering 3.10 eV per Xe.

Figure 4 shows the computed results for our three model systems; in particular, the total DOS and the Xe contribution to that. From 5 to 6, the Xe band spreads little; much more drastic changes occur on moving to the (too compressed) structure 7 (Xe in a coverage of 1 on top of Pd(111)). Here some Xe states are pushed above the Fermi level, which in fact has risen in this finite slab model.

Some of the results of the calculations are summarized in Table I. It is seen that a small Xe-Pd positive overlap population develops whenever one puts the Xe on the surface. On the other hand, no net Xe-Xe bonding shows up, the Xe-Xe overlap population (OP) remaining negative, except for the case (coverage = 1, Xe-Xe distance 2.749 Å) where one squeezes the xenons together too much. Table I shows that in the high-coverage case (7) the repulsive interaction of the xenons is very much reduced,



**Figure 4.** Projected DOS of Xe (shaded) in the adsorbate-surface system Pd-Xe. Dotted lines indicate total DOS and integral of projections of Xe.

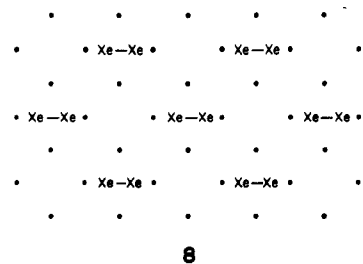
**TABLE I: Results of Computations for Three Model Systems**

	structure		
	5	6	7
Xe-Xe dist, Å	4.761	3.887	2.749
$E(\text{rel to Xe atoms} + \text{Pd surface}), \text{eV}$	-0.057	0.002	7.227
$E(\text{rel to monolayers}), \text{eV}$	-0.059	-0.065	-4.001
charge per Xe	+0.082	+0.081	+1.645
overlap pop.			
Xe-Xe(in monolayer)	0.000	-0.003	-0.348
Xe-Xe(in Xe/Pd system)	-0.002	-0.003	+0.038
Xe-Pd	0.099	0.099	0.122

relative to the isolated overlayer (Xe-Xe OP +0.038 compared to -0.348). The xenons become positively charged, consistent with vacation of part of the Xe 6p band.

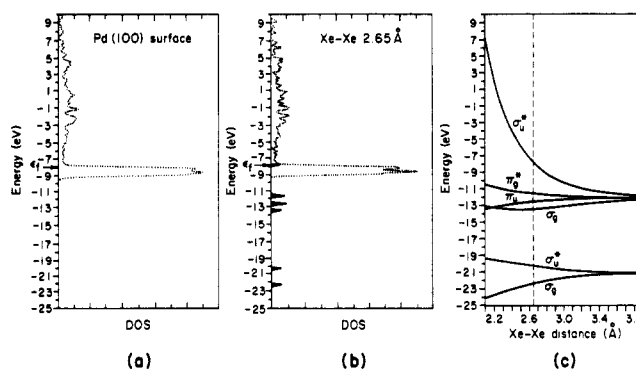
The energy measure supports this. This may be seen in Figure 3 (repulsions of xenons in square and hexagonal isolated layers, compared to three points for the computed composite Xe on Pd) and the entries in Table I. The coverage = 1 compressed structure is stabilized by 4.0 eV per Xe atom relative to a Pd surface plus the corresponding Xe overlayer. But it still emerges 7.23 eV above the same Pd surface and isolated Xe atoms. Obviously, the net price of bringing the Xe atoms close to each other is not overcome by Xe-Pd and fractional Xe-Xe bonding.

Next we tried to explore the possibility of formation of isolated Xe<sub>2</sub> pairs. This was done as follows: On the Pd(100) model we put a 1/4 coverage of Xe<sub>2</sub> pairs, placed along a 2-fold diagonal as shown in 8. We started by putting the Xe atoms in the on-top

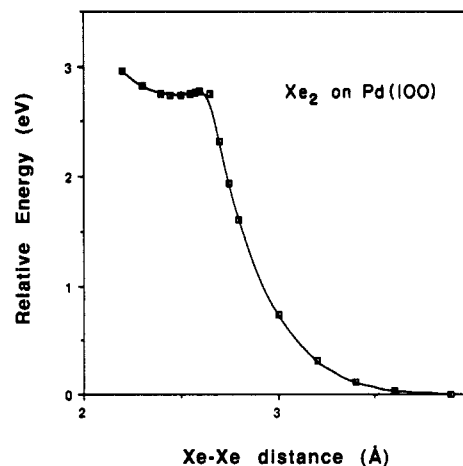


position and then moved them toward each other in pairs, to reach the geometry indicated in 8.

We show a typical DOS curve for this system in Figure 5, with a Xe-Xe pair distance of 2.65 Å. (The reason for this choice of distance will become clear in a moment.) Along with it, we include the density of states of the Pd surface, modeled by a three-layer slab, and the energy levels of an isolated Xe<sub>2</sub> molecule as a function of the Xe-Xe separation. These levels, of course, are



**Figure 5.** (a) DOS of the Pd(100) surface modeled by three layers. (b) Total DOS of the composite system Pd(100)-p(2x2)-Xe<sub>2</sub> at the Xe-Xe distance of 2.65 Å. Shaded are the projections of Xe<sub>2</sub> states. (c) Walsh diagram of a free Xe<sub>2</sub> pair with respect to Xe-Xe distance.



**Figure 6.** Total energy of the system Pd(100)-p(2x2)-Xe<sub>2</sub> as a function of Xe-Xe distance.

typical of a homonuclear diatomic. The critical orbital is the highest one,  $\sigma_u^*$ . If it could be vacated, even partially, Xe-Xe bonding would follow. This  $\sigma_u^*$  comes above the Pd Fermi level at Xe-Xe distances  $\leq 2.65$  Å, therefore the choice of this particular distance for the central graph, Figure 5b.

Note from the darkened areas, which are the contributions of the Xe<sub>2</sub> fragment MO's to the total DOS, that these are narrow bands, even for  $\sigma_u^*$ . Their energies are close to those of the free

TABLE II: Parameters Used in the Extended Hückel Calculations

atom	orbital	$H_{ii}$ , eV	$\zeta_1$	$\zeta_2$	$C_1^a$	$C_2^a$
Pd	4d	-8.43	5.98	2.61	0.55	0.67
	5s	-5.92	2.19			
	5p	-2.35	2.15			
Xe	5s	-21.21	2.84			
	5p	-12.13	2.49			

<sup>a</sup>Coefficients used in the double- $\zeta$  expansion of the d orbitals

Xe<sub>2</sub> orbitals. The Xe<sub>2</sub>-Pd interactions are obviously small.

Figure 6 shows the total energy of the system as a function of Xe-Xe separation. Our reference zero is for Xe-Xe = 3.887 Å, before the pairing begins. Note the steep rise in energy before one enters a shallow minimum at Xe-Xe ~ 2.45 Å. The shallow minimum corresponds to the  $\sigma_u^*$  band being vacated, i.e. essentially a Xe<sub>2</sub><sup>2+</sup> ion on a negatively charged surface.

The depth of this well is not, in our estimate, sufficient to allow observation of such a species, coming, as it does, on the repulsive wall of two Xe atoms interacting.

The results are thus discouraging. It appears that our extended Hückel calculations do not give sufficient Xe-Pd interaction to overcome the strong Xe-Xe repulsion. There is no experimental reason to argue this away as a deficiency of the method, so we have to accept it. What is required is a surface or defect that is electrophilic enough to oxidize two Xe atoms. Perhaps a

metal-exposing surface of a metal oxide or a salt, or even isolated metal ion sites at an oxide surface, could accomplish this.

*Acknowledgment.* We are grateful to the Office of Naval Research for its support of this work. M.K. is grateful to the Deutscher Akademischer Austauschdienst for the award of a NATO postdoctoral fellowship.

#### Appendix

The tight-binding extended Hückel method<sup>14,15</sup> was used for all the calculations. Parameters are listed in Table II.

For model chemisorption system 5, a set of 14k points<sup>16</sup> were used in the calculations; a 15k-point set was used for 6, and 65k points were used for 7. The Xe-Pd distance was kept at 3.00 Å in all cases.

The parameters (orbital exponents) for xenon were taken from Clementi et al.,<sup>17</sup> and the  $H_{ii}$  values from Moore.<sup>18</sup>

- 
- (14) (a) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *37*, 2872. (b) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (c) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. (15) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093. (16) Ramirez, R.; Böhm, M. C. *Int. J. Quantum Chem.* **1986**, *30*, 391. (17) Clementi, E.; Raimondi, D. L.; Reinhardt, W. P. *J. Chem. Phys.* **1967**, *47*, 1300. (18) Moore, C. E. *Analyses of Optical Spectra*; NSRDS-NBS 34; Office of Standard Reference Data, National Bureau of Standards: Washington, DC, 1970; p 4.