Behler, Reuter, and Scheffler Reply: In our recent work [1] we showed that the experimentally established low sticking probability of thermal oxygen molecules at Al(111) [2] cannot be reproduced by adiabatic state-of-the-art density functional theory (DFT) calculations. Concluding that nonadiabatic effects must play a significant role, we developed a locally constrained formulation of DFT, which enables us to compute well-defined diabatic potential-energy surfaces (PESs) representing different charge and spin states of the incoming molecule. A full account of this approach is given in Ref. [3]. The PES corresponding to the spin-triplet state of free gas-phase O_2 molecules exhibits dissociation barriers already at distances from the surface, where hybridization with metal states is only starting to set in. A low spin-flip probability hindering electronic relaxation of the impinging spin-triplet molecules leads therefore to a reduced sticking coefficient in agreement with experiment.

The preceding Comment [4] by Fan, Lau, and Liu discusses the well-known harpooning mechanisms, where an electron from the metal hops to the incoming molecule. In full agreement with our results and conclusion, and with those of other authors, they then dismiss this mechanism. Fan *et al.* furthermore argue that a barrierless adiabatic description is in conflict with the near zero sticking coefficient at thermal energies. Obviously, this statement is correct as well, and it was in fact the starting point of our advanced treatment.

The conflict is that the authors of the Comment dismiss the existence of nonadiabatic effects in this system and argue that “the spin-selection rule represents an unreasonable constraint.”

These statements are supposedly justified by the following reasoning: Fan *et al.* claim that the $2\pi^*$ level of a gas-phase O_2 molecule is above the Fermi level of Al(111), so that an adiabatic picture would properly describe the system at large molecule-surface distances. This is a significant misinterpretation of the data they quote. Our work, in full agreement with that of others, yield the $2\pi^*$ LUMO of free gas-phase O_2 molecules slightly below the Al(111) Fermi level. Therefore, in an adiabatic DFT study of the combined system (metal plus molecule) a small amount of

charge is transferred from the metal to the molecule already at macroscopic distances. This unphysical effect increases the energetic position of the $2\pi^*$ level and is the reason why the majority of the $2\pi^*$ peak in the local density of states is above the Fermi level in Fig. 14 of Ref. [5].

Even at macroscopic molecule-surface distances an adiabatic description is therefore inadequate, and will remain to be so until significant molecule-surface hybridization sets in at shorter distances. The absence of noticeable broadening in the computed $2\pi^*$ Kohn-Sham resonance [shown in Fig. 3 of our work [1]] shows that this has not happened at distances of about 3 Å, disproving Fan *et al.*'s conjecture of a then significant overlap between O and Al orbitals. At these distances, the molecule continues therefore to travel on its initial diabatic triplet PES, and this is what we computed with our locally constrained DFT approach.

The authors' reasoning is thus incorrect, and their Comment contains not a single computed number that would challenge the previous theoretical results of Refs. [1,5] and others. We see no necessity to alter any of our conclusions.

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