

### Comment on “Role of Electron-Hole Pair Excitations in the Dissociative Adsorption of Diatomic Molecules on Metal Surfaces”

In their recent Letter [1], Juaristi *et al.* claimed that they determined quantitatively the role of electronic nonadiabaticity in the dissociative dynamics of H<sub>2</sub> on Cu(110) and N<sub>2</sub> on W(110) and that electron-hole pair excitations are a marginal correction to adiabatic dynamics. These results were based on a local density approximation for the electronic friction (LDAF) using electronic friction coefficients calculated within density functional theory (DFT) for single H and N atoms embedded in a homogeneous electron gas. While we cannot comment on the specific systems discussed by them, the methodology behind the conclusions is challenged by DFT calculations of the electronic friction coefficient for hydrogen and nitrogen molecules on other metal surfaces, which show that LDAF is in general *not* reliable for estimating the electronic friction for molecules on metal surfaces.

Our conclusion is based on DFT calculations of the electronic friction coefficients for H<sub>2</sub> on Cu(111) and N<sub>2</sub> on Ru(0001) along a reaction path [2] that captures the characteristic changes in the electronic structure upon dissociative adsorption. In contrast to the calculations of the friction coefficients of atoms embedded in a homogeneous electron gas, these calculations use the ground state electronic structure of the molecule *interacting* with the metal surface. The employed DFT approach for electronic friction gives results in good agreement with observed vibrational damping rates for a diatomic molecule adsorbed on a metal surface [3]. The reaction path represents the minimum energy path for dissociation in which the molecule is oriented parallel to the surface at a distance  $z$  from the surface with an interatomic distance  $d$ . In Fig. 1, we reproduce the calculated diagonal components of the friction tensor,  $\eta_{zz}$  and  $\eta_{dd}$ , with respect to these coordinates for a few points along the reaction path. The results for  $\eta_{dd}$  have been scaled by a factor of 4 in Fig. 1 to facilitate a direct comparison with the results for the corresponding components of the friction tensor in the LDAF given by

$$\eta_{zz}^{(\text{LDAF})} = 4\eta_{dd}^{(\text{LDAF})} = \eta_1^{\text{hom}} + \eta_2^{\text{hom}}. \quad (1)$$

Here  $\eta_i^{\text{hom}}$  is the friction coefficient of atom  $i$  of the molecule in a homogeneous electron gas with a density given by the local electron density of the bare surface at the position of the atom  $i$ . The results for  $\eta^{(\text{LDAF})}$  ( $\equiv \eta_{zz}^{(\text{LDAF})}$ ) presented in Fig. 1 were obtained using the calculated values of  $\eta^{\text{hom}}$  as a function of the electron density, as used in Ref. [1].

Figure 1 clearly shows that the LDAF does *not* give reliable values for the friction coefficient of a molecule interacting with a metal surface. In the entrance channel of N<sub>2</sub> on Ru(0001), the LDAF underestimates  $\eta_{dd}$  by a factor of  $\sim 30$  and  $\eta_{zz}$  by a factor of  $\sim 6$ . For the case of H<sub>2</sub> on Cu

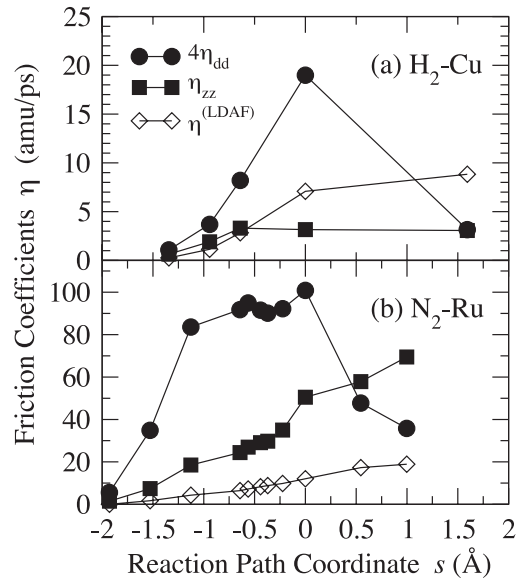


FIG. 1. Comparison of calculated electronic friction coefficients,  $\eta_{zz}$  and  $\eta_{dd}$ , with  $\eta^{(\text{LDAF})}$  for (a) H<sub>2</sub>/Cu(111) and (b) N<sub>2</sub>/Ru(0001) along the reaction path parametrized by the distance  $s$  from the transition state. The entrance and exit channels correspond to  $s < 0$  and  $s > 0$ , respectively.

(111), the discrepancy is less severe but the large enhancement of  $\eta_{dd}$  at the transition state is simply missed by the LDAF. These calculations quite clearly demonstrate that it will generally be necessary to go beyond embedding atoms in a homogenous electron gas to evaluate quantitatively nonadiabatic parameters describing molecules interacting with metal surfaces.

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