

Response to Comment on "Adsorption and Electronic States of Benzene on Ordered MgO and Al₂O₃ Thin Films"

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We were obliged to P. Swiderek for the comments regarding our paper on the electronic states of benzene adsorbed on two metal oxides,¹ particularly for pointing out a reference to recent work on the vibronic spectra of solid benzene,² the dearth of which we lamented in the Introduction of our paper.

The alternate assignment of the transitions ~ 4.8 eV to $^3E_{1u}$ as opposed to $^1B_{2u}$ was pointed out as note *a* in both Table 2 and Table 3; the singlet–triplet excitation may well dominate given the experimental conditions ($E_p < 50$ eV, nongrazing "scattering" angle,^{2,3} but the resulting feature could be the superposition of both.⁴ In any event, precise symmetry arguments do not come into play for the conclusions reached in the paper. The shifts in the energies of the transitions as a function of the surface do, however, and leave us with (at least) two possibilities, assuming the Comment's Table 1 to be correct:

(1) The data set for the adsorbed benzene on the two oxide surfaces are not internally consistent; the differences between then are due only to energy calibration errors, and it is simply fortuitous that the energy for the transitions on MgO(100) match those for the solid benzene in every case. In this view the transitions for benzene adsorbed on Al₂O₃ are off by 0.05–0.06 eV due to experimental error and are in fact indistinguishable from those of benzene adsorbed on MgO. Thus, the spectra are simply in agreement with the solid benzene data and indicate there is *no* influence of the substrate (either MgO or Al₂O₃) on

the electronic transition energies. The conclusions regarding the difference between adsorption on oxides and metals, including lifetimes of the excited states, are unchanged.

(2) The data are internally consistent, and the differences in the transition energies between benzene adsorbed on MgO and Al₂O₃ are real. Then there is an interesting shift in the energies measured for benzene adsorbed on Al₂O₃, which is not as great as that found for adsorption on a metal⁴ but in the same direction (higher energy). As the commentator notes, this is not reflective of the degree of adsorbate–surface interaction as determined by TPD and the nature of the effect is unclear. We would welcome further study to elucidate the mechanism.

It should be noted that it is not a trivial matter to determine whether the vibronic transitions arise solely from molecules in the first chemisorbed layer (monolayer only). As we stated in our Discussion, at the coverage where the vibronic transition become clearly resolved (~ 1 ML) it is not possible to discount the influence of a growing physisorbed layer (or three-dimensional island growth) on the spectra.

It should be noted that the mode at 989 cm^{-1} was incorrectly referred to in the text of ref 1. It is an out-of-plane mode as identified in that reference's Table 1. It is not used to make any orientation determination for the adsorbed monolayer.

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References and Notes

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- (4) Avouris, P.; Demuth, J. E. *J. Chem. Phys.* **1981**, *75*, 4783.