COMMENTS

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

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In a recent publication in this journal Street et al.[1] reported electron-energy-loss (EEL) spectra of benzene adsorbed to thin MgO and Al₂O₃ films on top of Mo in the range of the vibrational and low-lying electronic excitations. The lowest electronic transitions were obtained with vibronic resolution, which is important for the discussion of the excited state lifetimes and the interaction between adsorbed molecules and surface material. Relating to this problem, the shifts of the electronic bands of benzene with respect to gas phase values were investigated. Since more data on benzene have been published recently, the assignment of the spectral features given in ref 1 should be considered on the background of these results.

High-resolution EEL data for both gaseous and solid benzene are compiled in Table 1 together with the generally accepted assignment and the values from the vibronically resolved spectra of ref 1. The single vibronic bands, which reflect a progression of the excited state ring breathing mode, represent a more reliable database for discussing spectral shifts of the low-lying transitions than values for band maxima because the latter can shift considerably with the attained instrumental resolution.[4] It must be pointed out that gas phase EEL studies capable of distinguishing between spin-allowed and spin-forbidden transitions by variation of incident energy and scattering angle[2,3] have clearly shown that the transitions $^1A_{1g} \rightarrow {}^1B_{2u}$ (S₁) and $^1A_{1g} \rightarrow {}^3E_{1u}$ (T₂,₃) strongly overlap. Nevertheless, T₂,₃ dominates over S₁ in spectra where the transition $^1A_{1g} \rightarrow {}^3B_{1u}$ (T₁) is intense.[2–4] Therefore, the second band observed in ref 1 must be assigned to T₂,₃. With this assignment the data for benzene adsorbed on MgO/Mo(100) compare closely to the values obtained for solid benzene.[4] Compared to the gas phase,[2] the band position of T₁ is nearly unchanged whereas T₂,₃ and T₄ are lower by about 0.02 and 0.09 eV, respectively. For benzene adsorbed on Al₂O₃/Mo(110) the situation is different. Here all triplet transitions are shifted by 0.05−0.06 eV toward higher energies relative to solid benzene,[4] and the two lowest triplet states are even higher in energy than found for the gas phase.[2] Assuming that the data are not subject to energy calibration errors of about 0.05 eV mentioned in ref 1, the triplet state excitation energies are less influenced by MgO than by Al₂O₃, which is contrary to the original conclusion concerning the $^1E_{1u}$ state. This indicates that the influence of the surface material is not uniform for the different electronic states, and a higher desorption temperature does not necessarily correlate with a larger shift of the excitation band. A more thorough study of these effects would be of

TABLE 1: Comparison of Excitation Energies (eV) in Benzene under Different Conditions as Measured by EELS[a]

state	gas phase[2]	solid[4]	adsorbate MgO/Mo(100)[1]	Al₂O₃/Mo(110)[1]
$^3B_{1u}$	3.665	3.666	3.67	3.73
	3.780	3.780	3.78	3.84
	3.880	3.894	3.89	3.94
	3.990	4.008	4.00	4.06
$^3E_{1u}$	4.610	4.587	4.59	4.64
	4.715	4.701	4.70	4.75
	4.830	4.815	4.81	4.87
	4.940	4.929	4.92	4.98
	5.050	5.043	5.03	5.09
$^3B_{2u}$	5.560	5.470	5.47	5.53
	5.680	5.585	5.60	5.64

[a] The assignment of the adsorbate vibronic structure was modified with respect to ref 1.

interest. In this respect it is unfortunate that ref 1 is ambiguous about the question whether the vibronically resolved data stem from spectra recorded at monolayer or multilayer coverages.

Another point that needs to be adressed is the ground-state vibrational level with a frequency of 989 cm⁻¹ reported for multilayer coverage in ref 1. In the text this vibrational level was assigned to a dipole active in-plane bending mode. This infers an interestingly large frequency drop because the dipole-active e₁u mode, which corresponds to this assignment, was found at 1038 cm⁻¹ in the gas phase[5] and at 1036 cm⁻¹ in a benzene crystal,[6] whereas it is at 1040 cm⁻¹ in benzene adsorbed to Ru(001) at multilayer coverage[7] and is thought to drop only to 1010 cm⁻¹ in the first layer on Ru(001).[8] Following, on the other hand, the assignment as out-of-plane mode given in Table 1 of ref 1, the 989 cm⁻¹ vibration is definitely not dipole active. It should then not be discussed in connection with selection rules concerning the orientation of the molecules with respect to the surface.[9] A clarification concerning the assignment is therefore desirable.

References and Notes

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