Vanmaekelbergh *et al.* Reply Our recent work on the storage and long-range transport of electrons in a ZnO quantum-dot assembly [1], and on the optical transitions between the atomlike conduction orbitals [2], is based on the control of the average number of electrons $\langle n \rangle$ per quantum dot by the electrochemical potential of the assembly. Shim and Guyot-Sionnest (SG) [3] claim that the injected electrons occupy not only delocalized conduction levels but also trap states. They are surprised that the bleaching of the band edge absorption tails off at about 0.2 eV above the edge [1]. In [1], we wanted to show that quenching of the HOMO-LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) absorption occurs as soon as electrons are present in the assembly. Therefore, we did not include results at higher electron occupation. In Fig. 1, we give the complete set of data obtained with this assembly. It is clear that at potentials more negative than -1 V, where $\langle n \rangle$ increases up to 7, the absorption quenching spectrum $\Delta A(E)$ develops a shoulder on the high energy side, i.e., at photon energies between 3.75 and 4 eV. This agrees with the expectations of SG that occupation of P and D orbitals should produce bleaching which extends 0.25 and 0.5 eV, respectively, into the UV.

Evidence for the unimportance of electron traps is provided in the inset. If electrons were to occupy traps located between the LUMO and the HOMO, the integrated absorbance difference should be reduced to zero before $\langle n \rangle$ is zero which is not the case. If electrons were to occupy traps located above the LUMO S, the absorption quenching should level off with increasing $\langle n \rangle$; this is not seen in the data.

SG question the interpretation of the IR results, in particular, the occurrence of transitions other then S-P. They state that the IR signal cannot be used to ascertain the number of electrons in the quantum dots. We agree; $\langle n \rangle$ is determined independently from the charging experiments. In addition, we have calculated the electron occupation of all quantum dots in the assembly as a function of their size for a given average electron number $\langle n \rangle$ ([4]). The spectra can then be explained quantitatively by the allowed transitions between the S, P, D, S', and F conduction orbitals. The fact that the experimentally obtained oscillator strengths for the P-D, D-F, and P-S' transitions, referred to that of the S-P transition, agree well with tight-binding theory [2] supports the validity of our analysis, contrary to the argumentation of SG. Furthermore, Germeau has calculated the average cross section for an S-P absorption on the basis of Fermi's golden rule with the S-P oscillator strength from tight-binding theory: $\sigma_{SP} = 0.09\ (\pm 0.03)\ \mathrm{nm}^2$ ([4]). This is in fair agreement with the experimental value obtained from the number of absorbed photons and the number of quantum dots in the light beam giving $0.1\ (\pm 0.05)\ \mathrm{nm}^2$ ([4]).

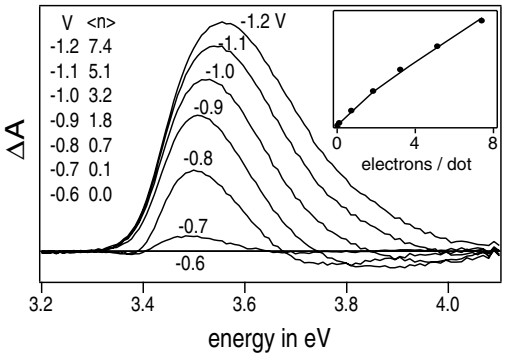

FIG. 1. The absorbance-difference spectra: the electrochemical potentials and the corresponding value for $\langle n \rangle$ are indicated in the figure. The inset shows the integrated ΔA vs $\langle n \rangle$; the line is the result of a tight-binding calculation.

In conclusion, we have shown that there is no basis for the suggestion of SG that the electrons injected in an assembly of ZnO quantum dots occupy trap levels. The results that we have presented in [1,2] are in agreement with a model in which the injected electrons occupy the delocalized S, P, ... conduction orbitals.

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