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Additions and Corrections

# ADDITIONS AND CORRECTIONS

2006 Volume 110B

**Jarl Nissfolk, Kristofer Fredin, Anders Hagfeldt, and Gerrit Boschloo\*:** Recombination and Transport Processes in Dye-Sensitized Solar Cells Investigated under Working Conditions

Page 17715. In our recently published Letter, the effect of RC attenuation was not correctly taken into account. This led to a misinterpretation of the photocurrent response data shown in Figure 3a and further discussion.

Under operating conditions, electrons are accumulated throughout the nanostructured $TiO_2$, rendering the film conducting. The photocurrent response under such conditions is affected or
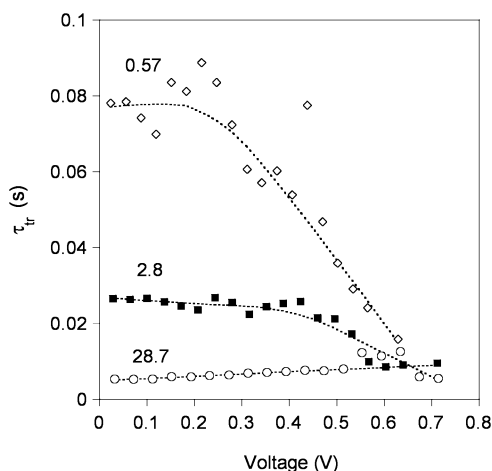


**Figure 3.** (b) Electron transport times as function of voltage. The transport time was calculated as follows: $\tau_{tr} = \tau_{resp} - R_{SnO_2} \times C_{TiO_2}$. The resistance due to the conduction glass ($R_{SnO_2}$) was determined to be 15 Ohm. The capacitance of the $TiO_2$ ($C_{TiO_2}$) was calculated from the experimentally measured relationship between extracted charge and open-circuit potential.

**TABLE 2: Electron Lifetimes and Potentiostatic Response Times at the Maximum Power Point Voltage ($V_{MPP}$) at the Three Light Intensities, and Calculated Values of the Transport Time, the Effective Diffusion Coefficient $D_{eff}$ and the Diffusion Length $L$**

| $I_0$ (mW cm$^{-2}$) | $V_{MPP}$(V) | $\tau_{e,MPP}$ (s) | $\tau_{resp,MPP}$ (ms) | $\tau_{tr,MPP}$ (ms) | $D_{eff,MPP}$ (m$^2$ s$^{-1}$) | $L_{MPP}$ ($\mu$m) |
|---|---|---|---|---|---|---|
| 28.7 | 0.55 | 0.16 | 23 | 12 | $4.3 \times 10^{-9}$ | 26 |
| 2.8 | 0.60 | 1.2 | 23 | 9 | $5.7 \times 10^{-9}$ | 83 |
| 0.57 | 0.57 | 2.6 | 36 | 24 | $2.1 \times 10^{-9}$ | 75 |

dominated by the RC time of the solar cell, where the resistance $R$ is the sum of the resistances of the conducting glass and that of the $TiO_2$ film, and the capacitance $C$ the sum of the capacity of the conducting glass/electrolyte interface and the chemical capacitance of the nanostructured $TiO_2$. Figure 3b (given here) shows the transport time calculated from the data of Figure 3a using appropriate correction for the RC time. At lower light intensities transport time decreased with voltage, whereas little change was observed at the highest light intensity. At voltages higher than 0.65 V transport times were independent of light intensity. Table 2 (given here) shows calculated effective diffusion coefficients and diffusion lengths using the corrected values of $\tau_{tr}$.

We thank Dr. B. C. O'Regan, Imperial College London, for rapidly pointing out our error and we would like to refer to his recent paper[1] that deals with similar issues.

### References and Notes

(1) O'Regan, B. C.; Bakker, K.; Kroeze, J.; Smit, H.; Sommeling, P.; Durrant, J. R. *J. Phys. Chem. B* **2006**, *110*, 17155.

2006 Volume 110B

**Quanqin Dai, Dongmei Li, Haiyong Chen, Shihai Kan\* Hongdong Li, Shiyong Gao, Yuanyuan Hou, Bingbing Liu, and Guangtian Zou:** Colloidal CdSe Nanocrystals Synthesized in Noncoordinating Solvents with the Addition of a Secondary Ligand: Exceptional Growth Kinetics

Page 16508. The original CdSe nanocrystal FTIR spectrum in Figure S2 of Supporting Information published in *J. Phys. Chem. B* **2006**, *110*(33), 16508−16513, is not the one we want to provide. When preparing Figure S2 involving CdSe FTIR spectrum, we confused the right spectrum with another one, and misconsidered the original CdSe spectrum as the one we should provide. We sincerely apologize for this confusion and now provide the corrected Figure S2. A comparison between the corrected Figure S2 and the original one reveals that the corrected CdSe FTIR spectrum is similar to the original one, which implies that this correction will have no effect on the understanding of the original article.
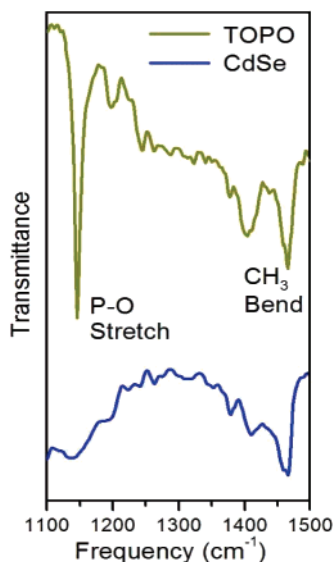


**Figure 1.** Figure S2.

**Mohamed Haouas\* and Francis Taulelle:** Revisiting the Identification of Structural Units in Aqueous Silicate Solutions by Two-Dimensional Silicon-29 INADEQUATE

In the above paper (*J. Phys. Chem. B* **2006**, *110*, 3007) a referencing mistake is left in the text that could generate some confusion concerning the credits given to authors. We referred to the contributions of R. K. Harris and C. T. G. Knight several times in the article. In two occasions in the text we used the expression of Knight's "group", instead of Harris' "group". This was unconsciously done mixing both the existence of R. K. Harris' group and the contributions of C. T. G. Knight. To properly give credit to each author, the text should be corrected as follows. In page 3012 the text should be read as

"Assignments of such species are provided based upon previous published contributions of Martens et al.,[11] Knight,[34,52] Swaddle et al.,[42,60] Harris,[52] and Bell,[60] so species **15−23** presented in Chart 8 can easily be identified and correspond to a structure with only equivalent sites."

In page 3013 the text should be read as

"In summary, the results presented here provide the most complete silicate oligomers speciation and are consistent with previously published contributions of Knight,[34,50,52,53] Engelhardt et al.,[48,51,54,55] Harris,[50,52,53] and Swaddle et al.[56,57]".

**Cristian Predescu\* and William H. Miller:** Optimal Choice of Dividing Surface for the Computation of Quantum Reaction Rates

In ref 1, the present authors have put forward a criterion of optimality for choosing the dividing surface in quantum rate theories. The mathematical justification was based on Hadamard's requirement that numerical outputs of mathematical models for physical phenomena must depend continuously on the input data. In chemists' language, this means that the input data must be highly sensitive to changes in the values of the physical quantity to be evaluated.

In quantum rate theory, the input data are overlap integrals of the form

$$\mu_k = \int_\mathbb{R} \bar{C}_{F,\nu}(\omega)g_k(\omega)\,d\omega \qquad (1)$$

with certain families of functions such as $\{g_k(\omega) = \omega^k; k \geq 0\}$, if moments are computed, $\{g_\tau(\omega) = \exp(\omega\tau); \tau \in (-\eta, \eta)\}$, if imaginary-time correlation functions are computed, or $\{g_t(\omega) = \exp(i\omega t); t \in (-\eta, \eta)\}$, if real-time correlation functions are computed. $\bar{C}_{F,\nu}(\omega)$ is a flux–flux spectral function of a general form given by eq A2 of ref 1. It is a positive distribution that is continuous at the origin. Save for a factor of $\pi$, the value at the origin is the reaction rate. It is independent of the dividing surface (thus, of the flux operator $\hat{F}$) and of the measure $d\nu(\lambda)$. The common value at the origin represents the quantity we want to evaluate given the overlap integrals described by eq 1. The spectral functions are related to the MST spectral function (defined by eq 14 of ref 1) by the identity

$$\bar{C}_{F,\nu}(\omega) = \bar{C}_F^{MST}(\omega) \int_0^\beta \cosh[(\lambda - \beta/2)\omega\hbar]\,d\nu(\lambda) \qquad (2)$$

Owing to the assumed continuity at the origin of $\bar{C}_{F,\nu}(\omega)$, the overlap integrals can be decomposed as

$$\mu_k = \bar{C}_{F,\nu}(0) \int_{-\epsilon}^{\epsilon} g_k(\omega)\,d\omega + \int_{\mathbb{R}/[-\epsilon,\,\epsilon]} \bar{C}_{F,\nu}(\omega)g_k(\omega)\,d\omega \qquad (3)$$

for a sufficiently small $\epsilon > 0$. The sensitivity of the overlap integrals with respect to changes in the relative value of $\bar{C}_{F,\nu}(0)$ increases with the increase of the ratio between the first term and the second in the above decomposition. Because the value of $\bar{C}_{F,\nu}(0)$ and the nature of the functions $g_k(\omega)$ do not change with $\hat{F}$ and $d\nu(\lambda)$, it suffices to minimize the magnitude of the second term, by varying $\hat{F}$ (that is, the dividing surface) or $d\nu(\lambda)$ over the set of admissible values. However, this must be done in a way that does not depend on the functions $g_k(\omega)$.

The strategy adopted in ref 1, consistent with what we assumed that could actually be computed, was to minimize the overlap

$$\int_\mathbb{R} \bar{C}_{F,\nu}(\omega)f(\omega)\,d\omega \qquad (4)$$

with a certain positive function $f(\omega)$. The function $f(\omega)$ must be chosen by compromising on the following rules: (i) in order to selectively decrease the importance of $\bar{C}_{F,\nu}(\omega)$ outside the small interval $[-\epsilon, \epsilon]$, the function $f(\omega)$ must have a fast increase immediately away from the origin, (ii) the overlap integral of $\bar{C}_{F,\nu}(\omega)$ with $f(\omega)$ must be easy to evaluate so that it can be employed for an actual search.

In ref 1, for the MST spectral function, we have made the choice $f(\omega) = 1$, based on what we have perceived to be the optimal balance between the cost of the optimization algorithm and its benefits. However, a better choice can be inferred from eq 2. Clearly, if

$$f(\omega) = \int_0^\beta \cosh[(\lambda - \beta/2)\omega\hbar]d\nu(\lambda) \qquad (5)$$

then the quantity

$$C_{F,\nu}(0) = \int_\mathbb{R} \bar{C}_F^{MST}(\omega)f(\omega)\,d\omega \qquad (6)$$

which is the value at the origin of some flux–flux correlation function, is as easy to evaluate as the value at the origin of the MST correlation function. On the other hand, the function $f(\omega)$ increases to infinity faster than 1. In fact, the fastest increase is obtained for the case when $d\nu(\lambda)$ becomes a $\delta$ function localized near one of the symmetric ends $\lambda = 0$ or $\lambda = \beta$. In the limit $\lambda \rightarrow 0$, the value at the origin of the correlation function

$$C_{F,\lambda}(t) = \text{Tr}[e^{-(\lambda - it/\hbar)H}\hat{F}\,e^{-(\beta - \lambda + it/\hbar)H}\hat{F}] \qquad (7)$$

diverges as fast as $\lambda^{-3/2}$, according to

$$C_{F,\lambda}(0) \approx \frac{1}{\lambda^{3/2}}\frac{1}{4\hbar(2\pi m_0)^{1/2}} \times$$
$$\int_{\mathbb{R}^d}\rho(\mathbf{x}, \mathbf{x}; \beta)\,\delta(s(\mathbf{x}))\,||\nabla s(\mathbf{x})||\,d\mathbf{x} \qquad (8)$$

The divergence constant, which is the surface integral of the diagonal density matrix in mass-weighted coordinates, is the revised optimality criterion. Since this surface integral is easier to evaluate than the value at the origin of the MST correlation function, the revised optimality criterion represents a superior compromise of the two rules for choosing the function $f(\omega)$: rate of increase of $f(\omega)$ versus ease of computation of the ensuing overlap integral.

**References and Notes**

(1) Predescu, C.; Miller, W. H. *J. Phys. Chem. B* **2005**, *109*, 6491.