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# ADDITIONS AND CORRECTIONS

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**Colin L. Weeks, Ariel D. Anbar, Laura E. Wasylenki, and Thomas G. Spiro*:** Density Functional Theory Analysis of Molybdenum Isotope Fractionation

Pages 12434−12438. There was a typographical error in eq 1. It should have been

$$ {}^{a}Q_{\mathrm{vib}} = \prod_i \frac{\mathrm{e}^{-h\nu_i/2kT}}{(1 - \mathrm{e}^{-h\nu_i/kT})} \tag{1}$$

The correct version of the equation was used in the actual calculations.

There was, however, a more serious error in eq 4, the correct version of which is[1,2]

$$\ln\left[\prod_i \left({}^{b}\nu_i/{}^{a}\nu_i\right)\right] = \ln\left[(m_a/m_b)^{3/2}(M_b/M_a)^{3/2}\left\{\prod_j \left(I_j^b/I_j^a\right)\right\}^{1/2}\right] \tag{4}$$

where $m_a$ and $m_b$ are atomic masses of isotopes $a$ and $b$, $M_a$ and $M_b$ are the molecular masses for isotopomers $a$ and $b$, and the $I_j$'s are the moments of inertia of the principal axes.

Using $\ln[\Pi_i({}^{95}\nu_i/{}^{97}\nu_i)]$ instead of the incorrect $\ln[(m_{97}/m_{95})^{3/2}(M_{95}/M_{97})^{3/2}]$ to calculate the reduced partition function ratios gives significantly different values for most of the isotope fractionation factors. The corrected values are listed in Table 1.

**TABLE 1: Mo Isotope Fraction Factors vs $MoO_4^{2-}$ at 25 °C for Candidate Molybdic Acid Structures, Calculated in the Gas Phase via DFT with the B3LYP Functional**

| complex | $\Delta^{97/95}\mathrm{Mo}_{\mathrm{MoA-MoO_4^{2-}}}$ (‰) |
|---|---|
| $MoO_3$ | −1.13 |
| $MoO_3(H_2O)$ | −0.46 |
| $MoO_3(H_2O)_2$ | −0.36 |
| $MoO_3(H_2O)_3$ | −0.38 |
| $MoO_2(OH)_2$ | +0.19 |
| $MoO_2(OH)_2(H_2O)$ | 0.00 |
| $MoO_2(OH)_2(H_2O)_2$ | −0.34 |
| $MoO(OH)_4$ | −0.31 |
| $MoO(OH)_4(H_2O)$ | −0.59 |
| $Mo(OH)_6$ | −0.58 |

In most cases the isotope fractionation factors were significantly smaller in magnitude than in our original report, but there were a couple that showed small increases in magnitude. None of the corrected isotope fractionation factors is close to the experimental value of −1.8‰. In our original calculations the species that had isotope fractionation factors vs $MoO_4^{2-}$ closest to the experimental value were $MoO_3(H_2O)_3$ and $MoO_3$, and they were equidistant from the experimental value. In the corrected calculations $MoO_3$, with an isotope fractionation factor vs $MoO_4^{2-}$ of −1.13‰, is the closest, but as discussed in our original report, it is very unlikely that it can exist as a discrete species in aqueous solution. The corrected results show that our previous conclusion, that $MoO_3(H_2O)_3$ was the likely structure of the species adsorbed on the surface of the manganese oxyhydroxide, was incorrect, as the isotope fractionation factor vs $MoO_4^{2-}$ of −0.38‰ is quite different from the experimental value.

Because none of the corrected isotope fractionation factors vs $MoO_4^{2-}$ for the Mo species considered are in good agreement with the experimental value, other explanations for the isotope fractionation between Mo in solution and adsorbed on manganese oxyhydroxides must be considered. The most likely explanations are (1) The adsorbed Mo takes on a structure that is significantly different from any species that exists in solution, and this drives the isotope fractionation. As we noted in the paper, the expected damping of Mo−O bending modes in the adsorbed species would shift the Mo isotope fractionation factor closer to the experimentally observed value. (2) Solvation effects, particularly directional solvent−solute interactions, could also be responsible for the some of the discrepancy between calculated and experimental results. Our original calculations showed that simple solvation models such as the polarizable continuum model were less accurate than the gas phase frequency calculations. There have been suggestions that explicit solvation models should improve the accuracy of the calculations[3,4] which would shed light on the important question of how significant these specific solvent interactions are.

### References and Notes

(1) Redlich, O. *Z. Phys. Chem.* **1935**, *28*, 371–382.

(2) Teller, E. quoted by Angus, W. R.; Bailey, C. R.; Hale, J. H.; Ingold, C. K.; Leckie, A. H.; Raisin, C. G.; Thompson, J. W.; Wilson, C. L. *J. Chem. Soc.*, **1936**, 971−987.

(3) Tossell, J. A. *Geochim. Cosmochim. Acta* **2005**, *69*, 2981–2993.

(4) Liu, Yun. *Geochim. Cosmochim. Acta* **2008**, *72*, A564.

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**W. Henry, C. G. Coates, C. Brady, K. L. Ronayne, P. Matousek, M. Towrie, S. W. Botchway, A. W. Parker, J. G. Vos, W. R. Browne,* and J. J. McGarvey*:** The Early Picosecond Photophysics of Ru(II) Polypyridyl Complexes: A Tale of Two Timescales

Pages 4537−4544. Reference to an important result reported by Damrauer and McCusker (Damrauer, N. H.; McCusker, J. K. *J. Phys. Chem. A* **1999**, *103*, 8440−8446), was omitted inadvertently. In their 1999 report, these authors reported a transient process with a 5 ps time constant in the femtosecond transient absorption (TA) spectroscopy of $[Ru(dmb)_3]^{2+}$ (where dmb = 4,4′-dimethyl-2,2′-bipyridyl). This process was assigned to vibrational cooling dynamics of the $^3$MLCT manifold (where MLCT = metal to ligand charge transfer). The authors noted that this was observed for $[Ru(bpy)_3]^{2+}$ (where bpy = 2,2′-bipyridyl) also. The omission of this point from the original text of the Henry et al. paper may lead to the inference that the model presented is in disagreement with the model proposed by the McCusker group for the earliest photophysical dynamics of $[Ru(bpy)_3]^{2+}$ based on TA studies. This is in fact not the case. The model advanced by the McCusker group concerning the sequence and time scale of the photophysical processes that follow excitation to the Franck−Condon (FC) $^1$MLCT state of $[Ru(bpy)_3]^{2+}$ is in full agreement with the conclusions of the Henry et al. paper. The model described in Figure 9 of the paper of Henry et al. is a summary of the results of that study and studies reported previously by several others, including the McCusker group. This includes the point that vibrational cooling and relaxation in the $^3$MLCT state, following ultrafast formation of the latter by intersystem crossing from the FC $^1$MLCT state, takes place over some 5−10 ps. The results from the TA studies by the McCusker group at 400 nm excitation are therefore very much in line with the time-resolved resonance Raman studies reported by Henry et al.

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