

Correction to “Analysis of Electronic States and Energy Level Structure of Uranyl in Compounds”

G. K. Liu

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This erratum makes several clarifying remarks and corrections:

- (i) The method adopted in the original paper, in which the two electron sf configuration is used to approximate the lowest excited states of uranyl derived from a $\sigma f_{\delta,\phi}$ configuration, is insufficient. First, the odd-parity sf atomic basis cannot represent the configurations responsible for the uranyl excited states, which are derived from the $\sigma_u \delta_u$ and $\sigma_u \phi_u$ configurations and are of even parity. Second, under the Coulomb electrostatic interaction, the sf configuration does not produce the same energy level splitting as that of $\sigma f_{\delta,\phi}$. Because the σ_u orbital has the leading compositions of $O2p_\sigma$ and $U5f_\sigma$, the Coulomb electrostatic interaction alone splits $\sigma f_{\delta,\phi}$ into four levels ($^1\Delta$, $^1\Phi$, $^3\Delta$, $^3\Phi$) instead of two expected in the sf basis. Although the correct number of energy levels is produced by the combination of a single term exchange interaction and spin–orbit coupling, the one-parameter Hamiltonian term representing the exchange interaction does not describe adequately the primary properties of electrostatic interaction in uranyl. The Hamiltonian parameter G^3 can provide only a simplified simulation of the Coulomb interaction. As a result the values of other parameters obtained in fitting the experimental data to other Hamiltonian terms are also affected, but to a less significant extent. A more appropriate approach to modeling the electronic interaction of uranyl should include p_σ and f_σ components in the wave functions.
- (ii) The crystal field operator $C_0^{(2)}$ has nonzero matrix elements between the diagonal terms such as those given in eq 7. The statement (on page 12421) concerning nonzero matrix elements for the $k = 2$ crystal field operators is incorrect. The reason to drop the term $B_0^2 C_0^{(2)}$ in the calculation of the crystal field splitting is that the value of the rank-2 parameter B_0^2 is much smaller than that of the rank-4 and rank-6 parameters. Therefore, as a common procedure in empirical fitting of crystal field splitting with a small number of observed energy levels, B_0^2 is excluded and its contribution is effectively taken account by B_0^4 and B_0^6 .
- (iii) The statement on page 12424 that implies using different spin–orbit coupling parameters in ref 9 is incorrect. The author intended to clarify that the spin–orbit coupling of an electron in $f_{\delta,\phi}$ states leads to a splitting into two energy levels with $J = 5/2$ and $7/2$, respectively, whereas in ref 9 the evaluation of spin–orbit coupling resulted in a splitting of $f_{\delta,\phi}$ into four levels.
- (iv) The experimental energy of the fourth excited state, given in Table 1 as $21\,233\text{ cm}^{-1}$, is not correct. In the cited source, ref 9, it is $21\,316\text{ cm}^{-1}$.

- (v) The statement (p 12424) that “a characteristic energy gap of typically 4000 cm^{-1} between two groups of absorption bands did not result from any ab initio calculations” is not true. In fact, recent calculations by Pierloot and van Besien (ref 22) produced a gap of 3306 cm^{-1} , extending from $23\,228$ to $26\,534\text{ cm}^{-1}$, which compares well with the experimental gap of 3472 cm^{-1} .

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