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COMMENTS

Comments on “Theoretical Studies of Ground and Excited Electronic States in a Series of Halide Rhenium(I) Bipyridine Complexes”[†]

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Complexes of the type [Re(L)(CO)$_3$(2,2′-bipyridine)]$^{n+}$ are much studied because of their interesting spectroscopic, photophysical, photochemical and electrochemical properties. They are widely used as building blocks of photoactive and/or electroactive supramolecules, probes and sensors. It is therefore important to understand their electronic structure and assign correctly their low-lying electronic transitions. It is equally important to critically assess the applicability of quantum chemical techniques to calculate ground- and excited-state properties of transition metal complexes.

Recently, Feng et al. have calculated vacuum electronic structures and transitions of a series of prototypical complexes [Re(Cl)(CO)$_3$(4,4′-R$_2$-2,2′-bipyridine)] (R = H, CH$_3$, C(O)OCH$_3$) and [Re(Cl)(CO)$_3$(5,5′-Br$_2$-2,2′-bipyridine)], using DFT and TD-DFT techniques, with a B3LYP functional and a LANL2DZ basis set.[1] Depending on the substituent, the lowest allowed electronic transition (osc. strength 0.031−0.037) was identified as predominantly HOMO−1 → LUMO and calculated in the range 2.21−1.95 eV, that is, 561−636 nm. Calculated energies of this transition are substantially lower as compared with the lowest absorption band, which occurs in the experimental spectra between 380 and 433 nm, as measured in CH$_3$CN or CH$_2$Cl$_2$. To achieve a satisfactory agreement between the TD-DFT calculated and experimental spectra, the authors have assigned the lowest absorption band to a higher-lying HOMO−4 → LUMO transition with an oscillator strength calculated between 0.081 and 0.124, neglecting any contribution from the lowest allowed HOMO−1 → LUMO transition to the absorption spectrum. Although the authors claim that all transitions with nonzero oscillator strengths were included, there is no sign of any band due to the HOMO−1 → LUMO transition in the simulated absorption spectra, despite its oscillator strength being about one-third of the HOMO−4 → LUMO transition.

Herein, we have recalculated electronic transitions of [Re(Cl)(CO)$_3$(bpy)] with identical functional and basis set as those used by Feng et al. The values reported in the Table 4 of ref 1 were reproduced while more low-intensity transitions were calculated. Using these transition energies and oscillator strengths, we have simulated the absorption spectrum, Figure 1. A band at about 560 nm originating in the HOMO−1 → LUMO transition is clearly seen, in contrast with the simulated spectrum reported in Feng’s paper (Figure 6).[1] It follows that the lowest experimental absorption band has to be assigned to the lowest allowed HOMO−1 → LUMO transition, despite its calculated energy being much lower than the experimental energy. In fact, it was shown before that TD-DFT frequently underestimates energies of electronic transitions that are accompanied by a substantial charge density redistribution.[2−6] For example, TD-DFT vacuum calculations of the complexes [Ru(X)(R)(CO)$_2$(diimine)] (X = Cl, Br, I, R = X, Me, SnPh$_3$, diimine = bpy or *N,N*′-bis-*i*Pr-1,4-diazabutadiene) have predicted their low-lying metal-to-ligand and ligand-to-ligand charge-transfer (MLCT, LLCT) transitions to occur at energies well below those of the lowest experimental absorption bands.[4−6] Moreover, calculated transition energies depend strongly on the DFT functional used.[2,3,6]

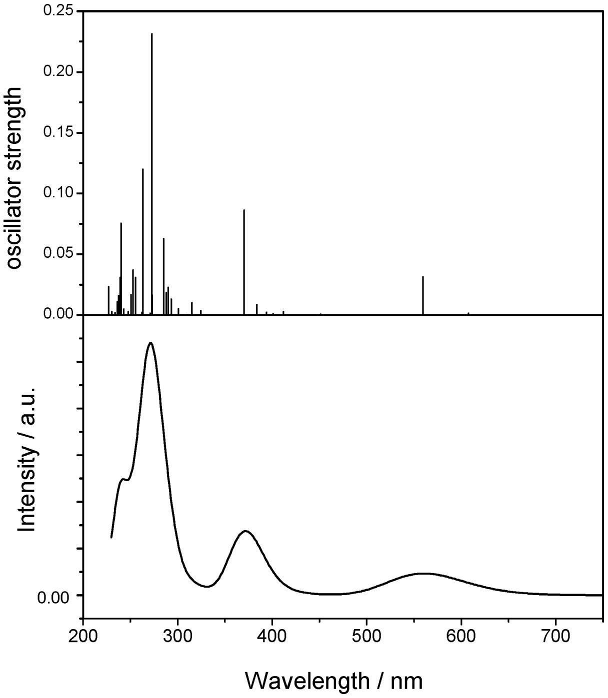

Figure 1. Electronic transitions calculated by the procedure used by Feng et al.[1] (top) and a corresponding simulated UV−vis absorption spectrum (bottom). The simulation was performed using the GaussSum[7] software. All calculated transitions are included. Gaussian shapes of the absorption bands are assumed. The fwhm value of 0.4 eV[8] used corresponds to typical experimental bandwidths of MLCT bands. Band areas are proportional to calculated oscillator strengths. A very similar spectrum with a well-developed ~560 nm band is obtained when only the transitions reported in Table 4 of Feng’s paper[1] are used and the Gaussian curves are plotted with the Origin 7.0 software.

To clarify the situation and assign the lowest absorption band of [Re(Cl)(CO)$_3$(bpy)], we have calculated its electronic transitions by TD-DFT (Gaussian 03), using cc-pvdz basis sets[9] and the PBE1PBE hybrid functional, which is composed of the Perdew, Burke, Ernzerhof[10] exchange and a correlation func-

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[†] The corresponding author of the original article was contacted and agrees with this Comment.

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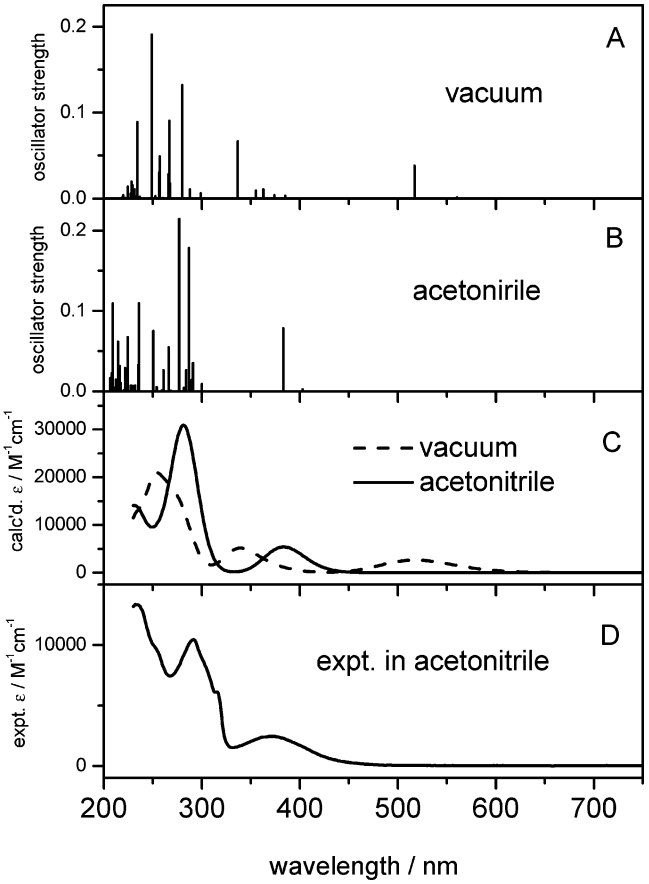

Figure 2. Electronic transitions of [Re(Cl)(CO)$_3$(bpy)] calculated in a vacuum (A) and in acetonitrile (B), simulated absorption spectra of [Re(Cl)(CO)$_3$(bpy)] calculated in a vacuum (C, dashed line) and in acetonitrile (C, full line), and experimental absorption spectrum measured in acetonitrile (D). Calculation: TD-DFT G03/PBE1PBE, CPCM model for the solvent. Simulation: All calculated transitions included. Gaussian shapes (fwhm = 0.4 eV cm^{-1})[8] of the absorption bands are assumed. Band areas are proportional to calculated oscillator strengths. Simulated using the GaussSum[7] software.

tional with 25% HF exchange. Calculations were performed both in a vacuum and in a CH$_3$CN solution, the latter being described by the conductor-like polarizable continuum model (CPCM). The results are presented in Figure 2. All transitions with a significant charge-transfer character shift to higher energies on going from vacuum to a CH$_3$CN solution. The simulated vacuum spectrum shows the lowest absorption band due to the HOMO−1 → LUMO transition at an unrealistically long wavelength, 518 nm, followed by a HOMO−4 → LUMO transitions at 340 nm. In CH$_3$CN, the simulated spectrum corresponds very well to the experimental one. It shows a band due to the HOMO−1 → LUMO transition at 383 nm, that is, very close to the lowest experimental band at 371 nm. The higher-lying HOMO−4 → LUMO transition shifts in CH$_3$CN to shorter wavelengths and merges with other, mostly bpy-localized, transitions to form a single absorption band calculated at 281 nm. The corresponding experimental band occurs at about 290 nm.

We conclude that the lowest absorption band of [Re(Cl)(CO)$_3$(bpy)] originates predominantly in the $a^1A' \rightarrow b^1A'$ (HOMO−1 → LUMO) transition. The HOMO−1 is Re−Cl π antibonding, with Re 5d and Cl 3p contributions of 52 and 22%, respectively, as calculated in CH$_3$CN. The LUMO is predominantly π^* bpy. The lowest allowed transition can thus be described as MLCT with a minor LLCT contribution. The next intense feature within the spectrum is composed of several bpy-localized intraligand transitions mixed with MLCT excitations, and the HOMO−4 → LUMO transition. This spectral assignment can be extended to other Re complexes studied in Feng's paper. On the methodological side, it follows that inclusion of the solvent environment in calculations is very important to achieve a realistic description of charge-transfer electronic transitions of low-valent transition metal complexes measured in solution.

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