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COMMUNICATION

Accurate yet Feasible Computations of Resonance Raman Spectra for Metal Complexes in Solution: $[\text{Ru}(\text{bpy})_3]^{2+}$ as a Case Study

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Herein we present a new and promising approach for the high-resolution modeling of vibrational Resonance Raman spectra of metal complexes in solution. The model explicitly includes Duschinsky couplings, solvent effects, and anharmonic corrections in a computational tool able to treat large molecular systems containing transition metals.

Ruthenium derivatives are of particular interest for their widespread applications in devices like sensors,¹ or solar cells.²⁻⁴ Examples of such systems are the polypyridine Ruthenium complexes, which have been extensively studied with both experimental and theoretical approaches.⁵⁻⁸ Due to their relative complexity, a detailed characterization often requires the combination of multiple spectroscopic approaches. The wealth of information generated in this case can be challenging to interpret, which makes the use of computational chemistry very appealing to understand the contributions of different origins (solvent, temperature, anharmonicity...) and facilitate the analysis of experimental results. Therefore, theoretical investigations have become a crucial area of development and reliable methodologies are emerging for effective yet reliable multi-frequency studies.

Nowadays, density functional theory (DFT) is routinely used to obtain electronic and vibrational information for a wide range of systems thanks to the ongoing development of theoretical tools and hardware capabilities, for instance to predict structure, spectroscopic or luminescent behaviors of small,⁹⁻¹¹ medium,¹²⁻¹⁸ and large (even multi-metallic) molecules.¹⁹⁻²² Thanks to the development of more efficient algorithms and novel methodologies, the range of applications and the size of investigable systems are in constant progress. Regarding more specifically computational spectroscopy applied to metal complexes, we recall the work of Vlcek Jr. and Zális, who focused on the possible applications of models rooted into the DFT and its time-dependent extension (TD-DFT) on d^6 metal complexes.²³ Moreover, some joint theoretical and experimental studies on the vibrational and electronic properties of Ruthenium derivatives have been reported in the last years.^{13,14,24-30}

Among the available spectroscopies, Resonance Raman (RR) has seen a growing interest over the years, both at theoretical and experimental levels, thanks to its ability to enhance selectively the

vibrational features of a specific region within a complex system. During the last decades, RR has been used in several research areas such as luminescent systems,^{31,32} biomolecules,^{33,34} large molecules, including multi-metallic ones and even clusters.³⁵⁻³⁷ RR spectra are also often used in conjunction with an empirical interpretation to characterize electronic excited states, assess the degree of metal-ligand delocalization, etc.^{38,39} From a theoretical point of view, RR is currently treated by mean of simplified models, either by ignoring the excited electronic state or by employing quite drastic approximations about its potential energy surface.^{40,41} Among these approximated models, the so-called 'short-time approximation' for isolated molecules^{42,43} leads to reasonable results when only normal modes involving the metal are of interest,⁴² but shows some limitations for more general situations.⁴³ A complete framework for the computation of RR spectra with full inclusion of all Albrecht terms,⁴⁴ together with solvent and leading anharmonic contributions has been recently developed in our group and applied to several organic molecules.⁴⁵ Here, we report its first and successful application to an inorganic metal complex, namely $[\text{Ru}(\text{bpy})_3]^{2+}$ (Figure 1). This complex has been characterized through several spectroscopic techniques leading to the collection of a large number of data, including a high-resolution Resonance Raman spectrum.⁴⁶ In the following we show that including all the additional contributions available for the time in our computational tool, it is now possible to reach a quantitative agreement between theory and experiment.

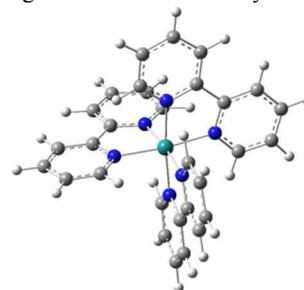


Figure 1. Molecular structure of $[\text{Ru}(\text{bpy})_3]^{2+}$.

All calculations have been performed at the DFT and TD-DFT levels of theory employing a development version of the GAUSSIAN

suite of programs⁴⁷ on the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex. On the grounds of several previous studies,^{29,48,49} we have chosen the B3PW91 functional.^{50–52} The associated basis set is the so-called LANL2DZ, including a pseudopotential for inner electrons of Ru and augmented with polarizations functions on C (d ; 0.587), N (d ; 0.736) and Ru (f ; 1.235).^{53–56} Bulk solvent effects (CH_3CN) have been taken into account by the PCM (Polarizable Continuum Model) model.^{57,58} Excitation energies and transition dipole moments from the electronic ground state, together with equilibrium geometry and harmonic frequencies for excited states (singlet for RR and triplet for phosphorescence) have been evaluated by means of TD-DFT.

The RR spectrum has been calculated starting from the sum-over-state expression of the polarizability tensor.^{44,45} The flexibility of the implementation allows the computation of RR spectra at different levels of approximation.⁵⁹ As a starting point, we recall that transition intensities are always calculated within the harmonic approximation and that, whatever the chosen model, the harmonic potential energy surface (PES) of the initial state is to be computed about its minimum. A first semi-quantitative analysis can be performed at the Vertical Gradient (VG) level.⁶⁰

In this model, the shape of the PESs of the ground and excited states are assumed to be the same, so that the calculation of the frequencies of the latter is unneeded. Furthermore, in VG, the PES is expanded about the equilibrium geometry of the ground state. While most theoretical spectra are calculated with those simplified models, it is often necessary to include other effects to reproduce accurately the experimental spectra. Therefore, the calculations have been carried out also with the more general Adiabatic Hessian approach (AH), in which the PES of the final state is more properly described, including mode mixing as well. Moreover, we can also take into account the first-order terms in the transition dipole moment expansion, which corresponds to the Herzberg-Teller (FCHT) approximation. This is equivalent to the inclusion of the B and C Albrecht terms in the expansion of the polarizability tensor, which are usually neglected in the analysis of RR spectra, especially for large molecules.⁴⁴

A further improvement of the theoretical results can be obtained with the inclusion of anharmonic effects. A complete anharmonic treatment (including intensity) is out of question due to the excessive cost. However, for the ground state, it is quite simple to choose a region of interest and to include complete anharmonic contributions for the modes falling in this part of the spectrum together with leading couplings to all the other modes.⁶¹ In the present case we have selected all the 71 modes within the 1000–1700 cm^{-1} wavenumber range (out of 177). The relative cost to compute each set of input data needed for the most complete RR calculations is reported in Figure 2.

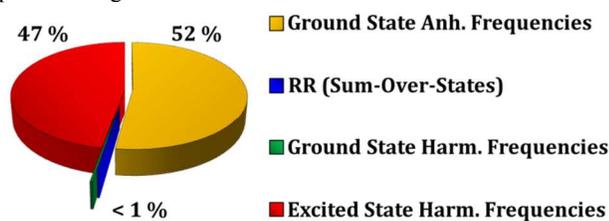


Figure 2. Percentage contributions of different computation steps (biproc Intel Xeon E5-2670 @2.6 GHz and 64 GB RAM).

It is noteworthy that the overall computer time is dominated by the evaluation of ground-state anharmonic and excited state harmonic frequencies, whereas the specific calculation of ground state harmonic frequencies and vibronic contributions has a negligible cost irrespective of further simplifications (VG or AH).

In order to further correct the peak intensities in the RR spectrum, it is necessary to account for the anharmonicity of the excited-state PES too. However, the lack of analytic force constants makes a direct approach too costly. Therefore, we have used our previously proposed method to extrapolate the anharmonic frequencies of the excited state by using those of the ground state and the Duschinsky transformation.⁶² Thanks to this procedure, it is possible to account for the leading effects of anharmonicity on both PESs without any additional computational burden. Finally, while RR spectra of metal complexes are usually recorded in solution, solvent effects are generally either neglected,⁴³ or coupled with simplified model in the simulation of RR spectra.⁶³ In contrast, bulk solvent effects are properly included in our simulations.

The optimization of the ground state without any symmetry constraint (C_1) leads to a minimum on the PES (no imaginary frequency), whose structure is in good agreement with the one reported by Biner *et al.*⁶⁴

TD-DFT calculations carried out on this geometry lead to two main transitions at 422 nm and 442 nm, which correspond to the well-known metal-to-ligand charge transfer (MLCT) bands, and are in a very good agreement with their experimental counterparts (*ca* 450 nm and the shoulder at *ca* 420 nm).^{65,66} Then, geometry optimization of the first excited triplet state has been performed using the same methodology leading to a computed phosphorescence wavelength of 578 nm. This value is slightly underestimated with respect to the observed one at 298 K (611 nm), but is in remarkable agreement with the one observed at 77 K (582 nm).⁶⁶ Although emission spectra are not of direct interest in the present context, a reliable estimation of different excited electronic states gives further confidence in the underlying quantum mechanical computations.

As mentioned above, evaluation of the harmonic frequencies of the ground state and of the energy gradient of the excited state at the optimized geometry of the ground electronic state, provides all the ingredients needed for evaluation of the RR spectrum in the VG approximation at the Franck-Condon (FC) level using the same excitation wavelength as the experimental one (457.8 nm). The only ‘empirical’ parameter entering our computation of the RR spectrum is the damping constant governing line-widths, which it is related to the half-width at half-maximum (HWHM) of the Lorentzian broadening to be applied to match the theoretical one-photon absorption spectrum to its experimental counterpart. For the sake of simplicity, we have chosen a value of 100 cm^{-1} , in agreement with previous work,⁴⁵ but we have also tested higher values of the damping constant with no significant changes at least for the region (1000–1700 cm^{-1}) of interest in the present context.

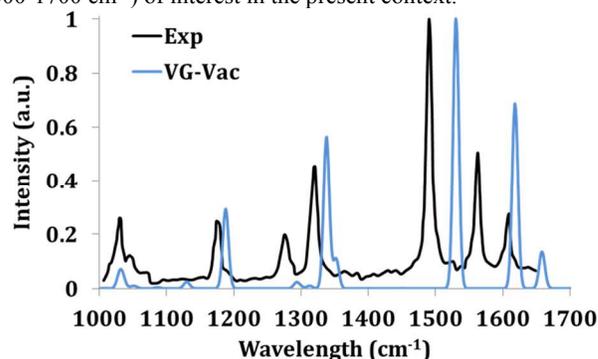


Figure 3. Comparison between the experimental (from ref. ⁴⁶) and theoretical (VG|FC in vacuum) RR spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$.

Experimental and computed (VG in vacuum) spectra are compared in Figure 3.⁴⁶ It is quite apparent that the general shape of the experimental spectrum is quite well reproduced together with the positions of bands below 1250 cm^{-1} . On the other hand, the relative

intensities of different peaks are not fully satisfactory and there is a general blue shift (by about 2-3%) of the band positions between 1250 and 1700 cm^{-1} . Thus, although the VG-FC simulation (which represents the current state-of-the-art in the field) matches at least qualitatively the experimental results, further effects have to be included in order to reach a quantitative agreement.

Figure 4 shows a comparison between the experimental and theoretical spectra calculated with AH method in solution (a) and with inclusion of anharmonic effects (b). Although Herzberg-Teller effects (B and C Albrecht terms) can be included in the computations, in the present case they lead to negligible modifications of the computed RR spectrum and have been, therefore, not explicitly shown (See SI). Note that the choice of the solvation regime in the computation of RR spectra is not trivial.⁴⁵ For adiabatic models, the equilibrium geometry of the excited state must be optimized, and the PCM cavity is displaced during the optimization process. Therefore, a fully equilibrium regime (in which both nuclear and electronic degrees of freedom of the solvent are assumed to be equilibrated for the calculation of the properties of both electronic states) is best-suited in this case.

It is quite apparent that inclusion of solvent effects improves the position of the peaks in the 1000-1200 cm^{-1} region with only a slight change in the band intensity over the complete spectrum. Furthermore, in the region 1300-1700 cm^{-1} , the inclusion of solvent effects together with Duschinsky coupling provides a better agreement concerning the intensity of the main peaks, but the effect is negligible for the position of those peaks.

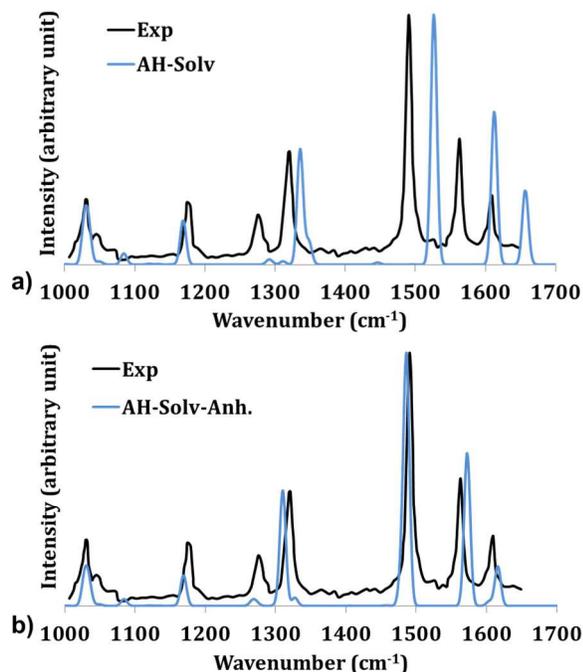


Figure 4. Experimental (from ref. ⁴⁶) and computed RR spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ at the AH level including solvent effects (a) and, also upon addition of anharmonic contributions (b).

Further non-negligible improvements are obtained when switching to the full AH method with inclusion of solvent and anharmonic effects in the region of 1250-1700 cm^{-1} . The significant displacements of several bands issuing from this more complete model leads to a fully satisfactory superposition between computed and experimental spectra, allowing, at the same time, an unambiguous assignment of all the bands.

Figure 5 shows a graphical representation of the composition of the computed normal modes at 1334, 1526, 1614 and 1656 cm^{-1} . The

most intense peak, at 1526 cm^{-1} , corresponds to the bending of the Ru-N bond coupled to the stretching of the C-C bond between the two pyridyl rings. The peak at 1614 cm^{-1} is related to the N-Ru-N bending in plane with respect to the connected pyridine group. The third peak, at 1656 cm^{-1} , can be assigned to the combination of the stretching of the Ru-N bond with a deformation of the bipyridyl ring and a stretching of the bond between them. Finally, the peak at 1334 cm^{-1} , corresponds mostly to the stretching of the C-C bond between the two rings. It is noteworthy that this is the only intense peak, which does not involve the Ru-N bond.

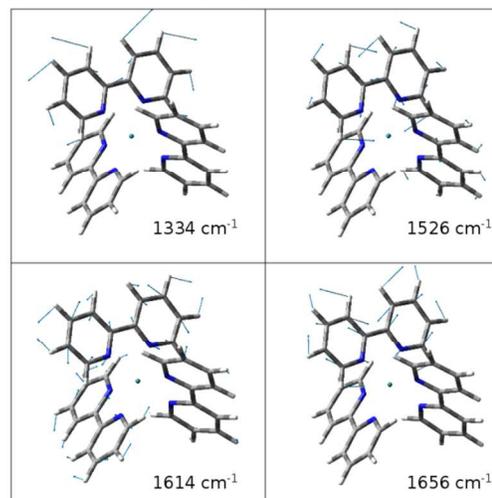


Figure 5. Graphical representation of the normal modes corresponding to the main peaks of the RR spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$. The Ru-N bonds have not been represented for the sake of clarity.

Conclusions

To conclude, a new computational protocol for the computation of RR spectra of metal complexes has led for the first time to nearly quantitative agreement with the experimental spectrum concerning band positions, global shape and intensities. Furthermore, assignment of the peaks to specific vibrations has been possible, thus allowing a consistent interpretation of the spectrum. From the one side, the results of our study point out that it is necessary to take into the proper account all possible effects in order to set up a quantitative approach. From the other side, the robustness and ease of use of the computational protocol together with its implementation in a widely available computer code allow to extend this kind of studies to other kinds of metal complexes. Of course, such an objective requires the extension of previous validation studies for organic systems to the IR and Raman spectra of metal complexes. Less “innocent” solvents (e.g. showing specific solute-solvent interactions) can be effectively treated by integrated discrete-continuum models.⁶⁷ Furthermore, new developments are under way in order to set up analytical second derivatives for excited states, thus dramatically reducing the computer time of this part of the calculation. Finally, joint experimental and theoretical studies are planned on other metal complexes to help their characterization at a deeper level of knowledge.

Notes and references

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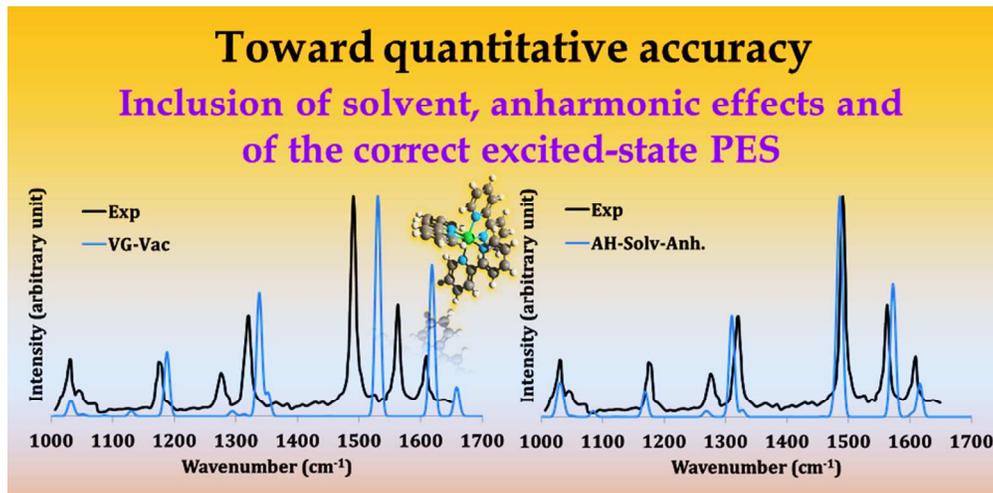
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Electronic Supplementary Information (ESI) available: Simulated FCHT RR spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$. See DOI: 10.1039/c000000x/

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