A Vibronic Coupling Hamiltonian to Describe the Ultrafast Excited State Dynamics of a Cu(Ⅰ)-Phenanthroline Complex

Gloria Capano, Thomas J. Penfold, Ursula Röthlisberger, and Ivano Tavernelli

Abstract: We present a model Hamiltonian to study the nonadiabatic dynamics of photoexcited [Cu(dmp)], (dmp = 2,9-dimethyl-1,10-phenanthroline). The relevant normal modes, identified by the magnitude of the first order coupling constants, correspond closely to those observed experimentally. The potential energy surfaces (PES) and nonadiabatic couplings for these modes are computed and provide a first interpretation of the nonadiabatic relaxation mechanism. The Hamiltonian incorporates both the low lying singlet and triplet states, which will make it possible to follow the dynamics from the photoexcitation event to the initial stages of intersystem crossing.

Keywords: Vibronic coupling Hamiltonian · Time-dependent density functional theory

1. Introduction

Transition metal complexes play a central role as photocatalysts and as sensitizers in dye-sensitized solar cells. Thus understanding their photodynamic properties is of fundamental as well as practical importance. Cu(Ⅰ)-phenanthroline complexes are a class of systems that has recently received increasing attention. These compounds exhibit many properties similar to the popular ruthenium polypyridines, but have a lower coordination number of 4, which permits larger structural distortions in the excited state. While this offers greater flexibility to fine tune their photophysical properties, it also gives rise to strong structure-dependent energetics and susceptibility to solvent effects, which has so far hampered their development.

Previous studies of the excited-state properties of Cu(Ⅰ)-phenanthrolines have focused upon understanding their strongly solvent-dependent excited-state lifetimes which are significantly quenched in electron-donating solvents. This has been attributed to the complexation of a solvent molecule to the metal center in the excited state, which becomes possible due to the pseudo Jahn-Teller (PJT) distortion of the ligands, exposing the copper ion to the solvent. However, using time-resolved X-ray absorption spectroscopy, combined with first-principles molecular dynamics simulations in explicit solvent, we have recently shown that this is not the case. Instead, the solvent interaction is transient and arises from a particular solvent structure that is also present in the electronic ground state.

To reduce the influence of the surrounding solvent and to prolong the excited-state lifetime, it is important that structural modifications of the phenanthroline-derived ligands are performed in such a way that they are able to disrupt the structure of the first solvation shell.

Importantly, these modifications not only affect the interaction with the solvent, but also the femtosecond (fs) dynamics that follow photoexcitation, characterized by couplings between multiple excited states leading to strong nonadiabatic effects. Ultrafast absorption and emission studies used to probe these photodynamics have focused upon the prototypical Cu(Ⅰ)-phenanthroline complex, [Cu(dmp),].,7 Tahara and co-workers concluded that upon photoexcitation, decay of the initially populated state occurs with a time constant of ≈45 fs. This is followed by two other processes of ≈60 fs and ≈7.4 ps, which were assigned to a PJT distortion (ligand flattening) and intersystem crossing, respectively. In a later study, they also probing the time-evolution in the lowest singlet Metal-Ligand Charge Transfer (MLCT) state, using the observed dynamics to predict the most important normal modes activated during the excited-state dynamics. Interestingly, they also reported that the S state exhibits a small energetic barrier leading to the PJT distortion. However, such a barrier is at odds with the spontaneous structural instability usually associated with JT type effects.

For a full understanding of the excited-state dynamics of such complexes, simulations provide an important tool. In this contribution we present a Vibronic Coupling Hamiltonian suitable for use in quantum nuclear dynamics to study the excited-state properties of [Cu(dmp),]. We identify the normal modes which are most relevant and discuss the calculated PES along these modes in relation to the excited-state dynamics. The Hamiltonian incorporates both the low lying singlet and triplet states, which makes it possible to probe the entire dynamics during the first picosecond (ps) after photoexcitation.

2. Theory

To describe the nonadiabatic dynamics of [Cu(dmp),] we use the Vibronic Coupling Hamiltonian, described in ref. [8],

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Briefly, an N state Hamiltonian, is expressed using an N×N matrix and expanded as a Taylor series around the Franck-Condon (FC) point \( Q_0 \):

\[
\hat{H} = \hat{H}_0 + \hat{W}^{(0)} + \hat{W}^{(1)} + \hat{W}^{(2)} \tag{1}
\]

The first term includes the kinetic energy operator and a harmonic term representing the ground state Hamiltonian. \( \hat{W}^{(0)} \) is the zeroth order diagonal coupling matrix which contains the vertical excited state energies at the FC geometry. The third term, \( \hat{W}^{(1)} \), contains the linear coupling elements expressed as:

\[
\hat{W}^{(1)}_{nn'} = \langle \phi_n | \frac{\partial \hat{H}_A}{\partial Q_i} | \phi_{n'} \rangle Q_i \tag{2}
\]

and

\[
\hat{W}^{(1)}_{nn'} = \langle \phi_n | \frac{\partial \hat{H}_A}{\partial Q_i} | \phi_{n'} \rangle Q_i \tag{3}
\]

where \( \phi \) are the electronic wavefunctions. The quantities within the Dirac brackets are the on-diagonal (Eqn. (2) and off-diagonal (Eqn. (3)) coupling constants, usually represented by \( \kappa(n) \) and \( \lambda(n,n') \), respectively. The on-diagonal terms are related to the derivative of the adiabatic PES with respect to the coordinates and represent the forces acting on the diabatic surface. The off-diagonal terms are the nonadiabatic couplings.

The second order (\( \hat{W}^{(2)} \)) nonadiabatic coupling terms are generally small and usually neglected, however the on-diagonal terms can play an important role and are expressed:

\[
\hat{W}^{(2)}_{nn} = \frac{1}{2} \sum_{i,j} \langle \phi_n | \frac{\partial^2 \hat{H}_A}{\partial Q_i \partial Q_j} | \phi_n \rangle Q_i Q_j \tag{4}
\]

In this case, the quantity within the Dirac brackets is usually referred to as \( \gamma(n) \). When \( Q = Q_0 \), the coupling occurs within a nuclear degree of freedom (DOF) and causes a change of frequency of the excited state potential. For \( Q \neq Q_0 \) (bilinear), coupling occurs between two nuclear DOFs and is responsible for intramolecular vibrational redistribution.

In the Hamiltonian in Eqn. (1), the number of expansion coefficients (i.e., \( \kappa \), \( \lambda \) and \( \gamma \)) can quickly become very large as the number of DOFs increases. To reduce computational cost, symmetry constraints may be used. For the linear terms, the expansion coefficients are non-zero only when the product of the irreducible representation of the electronic states and of the vibrational DOF is totally symmetric. For the \( D_2 \) point group relevant for the copper phenantroline complexes considered here we can write,

\[
\Gamma_n \times \Gamma_{Q_i} \times \Gamma_{n'} \supset \Gamma_A \tag{5}
\]

where \( \Gamma_n \) and \( \Gamma_{n'} \) are the irreducible representations of the states \( n \) and \( n' \) and \( \Gamma_A \) is the irreducible representation of normal mode \( Q \).

Table 1. Excitation energies (eV) and oscillator strength of the singlet and triplet states of \([\text{Cu(dmp)}]^{+}\) at the ground-state equilibrium geometry calculated using TD-DFT with the B3LYP functional.

<table>
<thead>
<tr>
<th>State</th>
<th>Symmetry</th>
<th>Energy [eV]</th>
<th>Oscillator Strength</th>
<th>Description*</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1B(_3)</td>
<td>2.44</td>
<td>0.0006</td>
<td>( d_{xz} \rightarrow \pi_{1}^* ), ( d_{xz} \rightarrow \pi_{2}^* )</td>
</tr>
<tr>
<td>S2</td>
<td>1A</td>
<td>2.51</td>
<td>0.0000</td>
<td>( d_{xz} \rightarrow \pi_{1}^* ), ( d_{xz} \rightarrow \pi_{2}^* )</td>
</tr>
<tr>
<td>S3</td>
<td>1B(_3)</td>
<td>2.70</td>
<td>0.1608</td>
<td>( d_{xz} \rightarrow \pi_{1}^* ), ( d_{xz} \rightarrow \pi_{2}^* )</td>
</tr>
<tr>
<td>T1</td>
<td>3A</td>
<td>2.27</td>
<td>-</td>
<td>( d_{xz} \rightarrow \pi_{1}^* )</td>
</tr>
<tr>
<td>T2</td>
<td>3A</td>
<td>2.31</td>
<td>-</td>
<td>( d_{xz} \rightarrow \pi_{1}^* )</td>
</tr>
<tr>
<td>T3</td>
<td>3B(_3)</td>
<td>2.33</td>
<td>-</td>
<td>( d_{xz} \rightarrow \pi_{1}^* )</td>
</tr>
<tr>
<td>T4</td>
<td>3B(_3)</td>
<td>2.37</td>
<td>-</td>
<td>( d_{xz} \rightarrow \pi_{1}^* )</td>
</tr>
</tbody>
</table>

*See Fig. 1 for a representation of the orbitals. The dominant characters of the electronic transitions are indicated.
find that the lowest energy structure has D₂ symmetry, giving rise to a small but siz-able splitting of these states. The S₁ state, whose transition from the ground state is dipole-allowed, has an energy of 2.70 eV and closely corresponds to the maximum observed in the experimental absorption spectra of [Cu(dmp)]⁺, 2.73 eV.\textsuperscript{(12)}

### 3.2 First-order Expansion Coefficients

The first-order terms arise from coupling of the electronic states to a specific nuclear DOF (Eqs (2) and (3)). Based on the magnitude of the linear coupling constants we have identified eight normal modes that are likely to be dominant in the initial photoexcited dynamics (Table 2). Although this clearly represents a significant reduction in the dimensionality of the investigated configuration space, the modes included closely correspond to those identified in the emission study of ref. \textsuperscript{[7b]}. Cuts through the PESs along some of the most important modes (ν₂₁, ν₁₉, ν₂₅, and ν₈) are depicted in Fig. 2.

Owing to symmetry, only modes ν₁₉ and ν₂₅ can yield non-zero on-diagonal linear coupling coefficients (κ). Indeed, both of these modes exhibit excited-state minima that are shifted with respect to the ground-state equilibrium position (an effect of on-diagonal linear coupling). For ν₁₉, this shift reflects a strengthening of the Cu–N bonds in the excited state, which is supported by experimental observations\textsuperscript{(6)} and is due to the π back-donation character of the ligands and the enhanced electrostatic interaction between metal and ligands following the charge transfer excitation.

Along ν₁₉, the S₂ and S₃ states also exhibit a shortening of the Cu–N bonds. In contrast the triplet states exhibit a profile more reminiscent of a PJT distortion with an asymmetric double minimum profile. This behavior is due to linear off-diagonal coupling between the T₁/T₂ and T₄/T₅ states (Table 3).

The modes ν₂₁ and ν₂₅ have b₃ symmetry and correspond to a flattening motion of the two ligands and to an off center movement of the Cu atom, respectively. The on-diagonal linear coupling coefficients (κ) are always zero by symmetry, however the off-diagonal expansion coefficients (λ) can be non-zero between states S₁/S₂ and S₃/S₄. As shown in Table 3 these modes strongly couple the S₁ and S₃ surfaces and are responsible for the PJT effects in [Cu(dmp)]⁺.\textsuperscript{[13]}. This effect is strongest in ν₂₁, where both the lowest singlet and triplet states are strongly characterized by double minima profiles located symmetrically with respect to the ground state equilibrium position, which arises from the aforementioned coupling. The effect is weaker for ν₁₉. Finally, as shown in Table

<table>
<thead>
<tr>
<th>Mode</th>
<th>Symmetry</th>
<th>Theory [cm⁻¹]</th>
<th>Expt. [cm⁻¹]</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₈</td>
<td>a</td>
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<td>125</td>
<td>Breathing</td>
</tr>
<tr>
<td>ν₁₉</td>
<td>b₃</td>
<td>193.61</td>
<td>191</td>
<td>Rocking</td>
</tr>
<tr>
<td>ν₂₁</td>
<td>b₃</td>
<td>247.61</td>
<td>240</td>
<td>Rocking</td>
</tr>
<tr>
<td>ν₂₅</td>
<td>a</td>
<td>270.85</td>
<td>290</td>
<td>Twist</td>
</tr>
<tr>
<td>ν₃₁</td>
<td>b₃</td>
<td>420.77</td>
<td>438</td>
<td>Bending</td>
</tr>
<tr>
<td>ν₄₁</td>
<td>b₃</td>
<td>502.65</td>
<td>–</td>
<td>Bending</td>
</tr>
<tr>
<td>ν₅₅</td>
<td>b₃</td>
<td>704.75</td>
<td>704</td>
<td>Rocking</td>
</tr>
<tr>
<td>ν₈₈</td>
<td>b₃</td>
<td>790.76</td>
<td>–</td>
<td>Rocking</td>
</tr>
</tbody>
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<td>Rocking</td>
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**Table 2. Symmetry and frequency (cm⁻¹) of the selected normal modes.** The normal modes were calculated using DFT within the approximation of the B3LYP functional. The experimental values are taken from ref. \textsuperscript{[6a]}.
3 we also find an off-diagonal expansion coefficient (λ) along the v25 coupling the S1 and S2 states. This offers the possibility for the wavepacket to relax directly from the initially populated state into the lowest singlet state, however given the large energy separation and the strong coupling between the S1 and S2 states, this pathway will likely provide only these a minor contribution to the overall dynamics.

### 4. Conclusions and Outlook

Using TDDFT, we have calculated a model Hamiltonian based upon the Vibronic Coupling ansatz. Our calculated PES show that at the equilibrium geometry, which possesses D2h symmetry, the optically bright state is the S0 MLCT state. Importantly, the two excited states which lie below S0 are very close in energy, and are strongly coupled. This means that the rate of internal conversion into the S1, S2, S3 states, which are weakly coupled and are separated by a larger energy gap. In addition, contrary to previous observations[7], the present PESs calculated in this work do not exhibit a barrier leading to the PTJ distortion in the excited state. The Hamiltonian derived in this work can be used, in conjunction with nuclear quantum dynamics simulations, to shed new insights into the ultrafast excited state dynamics of [Cu(dmp)+].

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