Coupled Electronic States in trans-Dioxo Complexes of Rhenium(V) and Osmium(VI) Probed by Near-Infrared and Visible Luminescence Spectroscopy

Carole Savoie and Christian Reber*

Contribution from the Département de chimie, Université de Montréal, Montréal QC H3C 3J7, Canada
Received September 13, 1999

Abstract: trans-Dioxo complexes of rhenium(V) and osmium(VI) with ethylenediamine, imidazole, and oxalate ancillary ligands show luminescence maxima varying between 620 and 900 nm. The resolved vibronic progressions of the rhenium complexes have intensity distributions that cannot be rationalized with harmonic potential energy surfaces. The broadband spectra of the osmium(VI) complexes also show deviations from the band shapes expected for a harmonic ground-state potential surface. We use the large variation of luminescence energies and the vibronic features to show the influence of excited electronic states on the ground-state potential energy surface. The vibronic structure and band envelopes of the luminescence spectra are calculated using the lowest energy adiabatic surface obtained from three interacting electronic states.

Introduction

The excited electronic states of a molecule are generally not considered to have a significant influence on its ground state properties, because they are well separated in energy from the ground state. We use a series of transition metal complexes to show that excited states in the visible and near-infrared spectral region do influence the ground state potential energy surface. Dramatic spectroscopic effects have previously been reported to arise from coupled excited states of transition metal compounds, leading to intensity borrowing,1 interference dips,2 or unusual spacings of resolved vibronic progressions,3 observations which have been rationalized in a consistent way with time dependent quantum mechanical models based on coupled potential energy surfaces.4 We use this theoretical approach in the following, but apply it to the study of ground state properties of trans-dioxo complexes of rhenium(V) and osmium(VI), a class of compounds whose photochemical and electrochemical properties have received considerable interest.5–12

The influence of the excited states on the ground-state potential surface is experimentally determined from low-temperature luminescence spectra of crystalline trans-dioxo complexes. The importance of interactions between electronic states for situations other than the well-studied Jahn–Teller13,14 or intervalence electron-transfer potentials15,16 has traditionally been neglected in the analysis and understanding of spectra and properties of transition metal compounds. Several recent reviews focus on such effects from a theoretical perspective and include detailed analyses of the dynamics for model systems such as diatomic and triatomic molecules.17,18 The photochemical consequences of coupled excited states for organic reactions have also been reviewed recently.19 We attempt to transfer some of these approaches to transition metal chemistry, which often involves molecules that are too complicated to be studied by full theoretical analyses. The title complexes allow us to benefit as much as possible from symmetry and different types of metal–ligand bonds.

We examine a series of trans-dioxo complexes of rhenium(V) and osmium(VI) with the [Xe]5d2 electron configuration and ethylenediamine, vinylimidazole, and carboxylate ancillary ligands, abbreviated as L in the following. These molecules show luminescence that can be tuned over a wide energy range through the use of different ancillary ligands. Their absorption and vibrational spectra are well studied, but their luminescence spectroscopy has received less attention, with the exception of trans-ReO2(pyridine)4+, a complex with a luminescence maximum at 650 nm and resolved vibronic structure,5,6 and a series of trans-dioxo complexes of osmium(VI) with cyanide or macrocyclic nitrogen donor ligands, which show luminescence maxima between 620 nm10 and 700 nm.9,20 We present and analyze previously unreported luminescence data for six trans-dioxo complexes.

The ground state of all title compounds has no orbital or spin degeneracy, an important prerequisite to observe subtle vibronic effects which are easily hidden in spectra consisting of a

superposition of transitions to final states arising from a degenerate ground-state split by spin–orbit coupling or low symmetry. The high symmetry allows us to apply crystal field theory to define the energies and metal–ligand bonding characteristics of the relevant excited states. The single and double metal–ligand bonds have well separated vibrational frequencies and normal coordinates that involve predominantly only one type of ligand, an important advantage for the analysis of the vibronic structure of the luminescence spectra. Metal–

oxo vibrational frequencies are higher than metal–ancillary ligand frequencies by approximately a factor of 4 and both modes are therefore easily identified in the vibronic structure of an electronic spectrum. A recent quantitative normal coordinate analysis of trans-OsO$_2$(oxalate)$_2$ and trans-OsO$_2$-(malonate)$_2$ concludes that the Os=O oscillators contribute between 98% and 100% to the metal–oxo coordinate and that the metal–ligand modes involving the ancillary ligands L have between 39% and 48% metal–L character, with the remaining contributions originating from oscillators centered on L.

We find that not only the lowest energy excited state influences the potential energy surface of the ground state. A model involving two excited states is necessary to calculate the vibronic structure of the luminescence spectra for our series of related molecules. Low-temperature optical spectroscopy provides a powerful approach to characterize interactions between electronic states, information not easily available from other experimental or theoretical techniques. We have applied absorption spectroscopy in a previous study and use luminescence spectroscopy in the following.

**Experimental Section**

All trans-dioxo complexes of rhenium(V) were prepared using literature methods. Both trans-ReO$_2$(ethylene diamine)$_2$Cl and trans-ReO$_2$(N,N,N,N'-tetramethylethylene diamine)$_2$Cl were prepared from solutions of ReCl$_3$(OEt)$_2$(PPh$_3$)$_2$ in absolute ethanol, to which an excess of the ethylene diamine ligand was added. After 1 h at reflux a yellow precipitate, which then was recrystallized several times from a methanol/water 1:1 mixture. trans-ReO$_2$(1-vinylimidazolide)$_2$ was prepared by adding an excess of the ligand to a suspension of ReO$_2$(Ph$_3$)$_2$ in methanol. The crystals obtained were filtered and washed with toluene. Both trans-OsO$_2$(en)$_2$Cl and trans-OsO$_2$(oxalate)$_2$(NBu$_4$)$_2$ were prepared according to literature methods. K$_2$Os$_2$O$_4$·2H$_2$O (Strem Chemicals) and recrystallized from ethanol/ether. The ancillary ligands ethylene diamine, N,N,N,N',N'-tetramethylethylenediamine, 1-vinylimidazolide, and oxalate will be abbreviated as en, tmen, vi-im, and ox in the following and we will use only the formula of the transition metal complex without the counterion for brevity. The purity of all compounds was checked by IR, Raman, and electronic spectroscopy.

The luminescence instrumentation has been described in detail previously. A Xe lamp filtered through a copper sulfate solution and Schott BG18 or UG11 filters was used as excitation source. The sample was cooled in a helium gas-flow cryostat (Oxford Instruments CF 1204). The emitted light was dispersed through a 0.75 m monochromator (Spex 170M) and detected with a photomultiplier (Hamamatsu R406 or R928) or a Ge near-infrared detector (Applied Detector Corporation 403UL). All luminescence spectra were corrected for detector response by calibration with a calibrated reference tungsten lamp (Oriel 63350), using the procedure described in detail previously. Luminescence lifetimes were measured with an excimer laser (XeCl, 308 nm) as excitation source and detected with a Hamamatsu R406 photomultiplier. The time-dependent intensities were stored with a digital oscilloscope (Tektronix TDS380). Absorption spectra were measured with a Varian Cary 5E spectrometer.

**Spectroscopic Results**

Crystals of all trans-dioxo complexes used for this study show luminescence at low temperatures. The spectra of trans-ReO$_2$-(vi-im)$_2$+, trans-ReO$_2$(en)$_2$+, and trans-ReO$_2$(tmen)$_2$+ are presented in Figure 1. It is remarkable that these closely related complexes show band maxima separated by 3700 cm$^{-1}$ (10 K).

![Figure 1. Solid-state luminescence spectra of trans-ReO$_2$(tmen)$_2$Cl (10 K, bottom trace), trans-ReO$_2$(en)$_2$Cl (15 K, middle trace), and trans-ReO$_2$(1-vinylimidazolide)$_2$ (6 K, top trace).](image)

**Table 1. Summary of Spectroscopic Data from Low-temperature Crystal Spectra of trans-Dioxo Complexes**

<table>
<thead>
<tr>
<th>Complex</th>
<th>lum. max. [cm$^{-1}$]</th>
<th>lum. origin [cm$^{-1}$]</th>
<th>lum. lifetime [µs]</th>
<th>$\hbar\omega_{3\rightarrow0}$ [cm$^{-1}$]</th>
<th>$\hbar\omega_{3\rightarrow1}$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ReO$_2$(en)$_2$+</td>
<td>12190</td>
<td>14200</td>
<td>1.6 (10 K)</td>
<td>880$^\circ$</td>
<td>210$^\circ$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0 (80 K)</td>
<td>899$^\circ$</td>
<td>260$^\circ$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>795$^\circ$</td>
<td></td>
</tr>
<tr>
<td>ReO$_2$(tmen)$_2$+</td>
<td>15910</td>
<td>17660</td>
<td>62 (10 K)</td>
<td>890$^\circ$</td>
<td>200$^\circ$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>60 (100 K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>42 (250 K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ReO$_2$(vi-im)$_2$+</td>
<td>13310</td>
<td>14700</td>
<td>0.89 (10 K)</td>
<td>885$^\circ$</td>
<td>175$^\circ$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.82 (100 K)</td>
<td>912$^\circ$</td>
<td>236$^\circ$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.40 (250 K)</td>
<td>726$^\circ$</td>
<td>270$^\circ$</td>
</tr>
<tr>
<td>OsO$_2$(en)$_2$+</td>
<td>13550</td>
<td>15200</td>
<td>0.89 (10 K)</td>
<td>912$^\circ$</td>
<td>236$^\circ$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.82 (100 K)</td>
<td>726$^\circ$</td>
<td>270$^\circ$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.40 (250 K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OsO$_2$(ox)$_2$+</td>
<td>11050$^c$</td>
<td>12600</td>
<td>0.36 (16 K)</td>
<td>907$^d$</td>
<td>561$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.32 (80 K)</td>
<td>910$^d$</td>
<td>569$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.20 (120 K)</td>
<td>730$^c$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Luminescence. $^b$ Raman. $^c$ Absorption (E$_g$ excited state). $^d$ Raman, refs 20 and 21. $^e$ trans-OsO$_2$(malonate)$_2$ shows a weak luminescence band with a maximum at 1600 cm$^{-1}$ (10 K).

lopes and intensity distribution along the main progression of the spectra in Figure 1 are similar to the literature spectrum of trans-ReO2(pyr- dine)22+ and the spectra in Figure 1 are in good agreement with low-frequency Raman transitions in Table 1. The luminescence lifetime of ReO2(tmen)2+ is 62 µs at 10 K, similar to the 68 µs lifetime reported at low temperature for ReO2(pyr-didine)2+ and longer by a factor of 50 than the 1.6 µs lifetime of ReO2(en)2+ at 10 K. This difference is most likely due to more efficient nonradiative relaxation processes for complexes with low energy emission bands, such as ReO2(en)2+. Similar lifetimes between 1 and 3 µs have been determined before for a series of trans-ReO2(R-imidazole)+ complexes with emissions in the near-infrared.

Figure 2 shows the luminescence spectra of trans-OsO2(en)2Cl2 (10 and 100 K, bottom traces) and trans-OsO2(ox)(NBu4)2 (13 and 80 K, top traces). The abscissa scale is identical with that in Figure 1.

Discussion

Totally Symmetric Electronic States of trans-Dioxo Complexes. In this section, we identify excited electronic states with the same symmetry as the ground state and define a model for the ground-state potential energy surface that includes interactions with the excited states. The d-orbitals of a trans-dioxo complex with D4h point group symmetry and the z axis parallel to the metal–oxo bond split into b2g (dz2), e2g (dxy, dxz, dyz), b1u (d2x2−y2), and a1g (dz2−r2) in increasing order of energy.6,34 We will only consider electronic states arising from (b2g)2(e2g)m orbital configurations, (n, m: 0, 1, 2; n + m = 2). The ground state of all trans-dioxo compounds studied here is 1A1g and arises from the (b2g)2 electron configuration. Spin–orbit coupling is an important effect in complexes of third-row transition metals, and we will therefore use interactions between spin–orbit states of A1g symmetry. Their spin and orbit symmetry and electron configurations are given in Figure 3. The lowest-energy excited A1g state is a spin–orbit level of the 3Eg crystal field state with the (b2g)(e2g) electron configuration. It is not the emitting state, as the B1g and B2g spin–orbit levels are lower in energy for all title complexes.6,34 The second A1g excited state within our model is the 1A1g state arising from the (e2g)3 electron configuration.34 These three states interact through off-diagonal matrix elements involving spin–orbit coupling and interelectronic repulsion. Their electronic energies are obtained as eigenvalues of:

\[ V_{A_1g} = \begin{bmatrix} E_1 & V_{12} & V_{13} \\ V_{12} & E_2 & V_{23} \\ V_{13} & V_{23} & E_3 \end{bmatrix} \]

The diagonal elements E_i are given in the literature34 in terms of crystal field theory (CF) using the angular overlap formalism:

\[ E_{1C} = E\left(\frac{1}{2}, A_{1g}, b_{2g}^2\right) = 3K_{dy} = 3(3B + C) \]

\[ E_{2C} = E\left(\frac{3}{2}, E_g, b_{2g} b_{2g}\right) = \Delta_n = 2(e_{\pi}(O) - e_{\pi}(L)) \]

\[ E_{3C} = E\left(\frac{5}{2}, A_{1g}, e_{2g}^2\right) = 2\Delta_n + 4K_{dy} \]

Empirical values for the two crystal field parameters \( \Delta_n \) and


Electronic states are indicated in idealized potential energy surfaces for trans-Dioxo Complexes of Re(V) and Os(VI) 

Figure 3. Potential energy surfaces for trans-ReO$_2$(1-vinylimidazole)$_2^+$ along the rhenium–oxo (a) and rhenium–(1-vinylimidazole) (b) normal coordinates. Electronic states are indicated in idealized $D_3h$ symmetry and their orbital configurations are given. Adiabatic potential energy surfaces that include coupling between electronic states are given as dotted lines, as calculated from eq 1. The arrow denotes the luminescence transition from the lowest energy spin–orbit coupling constant $\tilde{\zeta}$. The numerical values of $V_i$ in Table 2 are in this range and will be used to calculate the effects of the two excited states on the ground-state potential surface. The off-diagonal matrix elements are treated as constants in the following. The diagonal elements correspond to harmonic potential energy surfaces with vibrational frequencies and positions of their minima along the normal coordinate axes determined from luminescence, absorption, and Raman spectra.

Calculation of Luminescence Spectra. The matrix in eq 1 represents the energies of the three $A_{1g}$ electronic states at the ground-state equilibrium geometry and the values of $E_1$, $E_2$, and $E_3$ given by eqs 2–4 do not vary as a function of molecular structure. It is essential to realize that the energy minima of the excited states correspond to molecular structures that are different from the ground-state equilibrium geometry. $E_1$, $E_2$, and $E_3$ represent therefore potential energy surfaces in a model that allows us to calculate spectra. We use the harmonic potential surfaces given in eqs 5–7 as a function of the metal–oxo ($Q_{M-O}$) and metal–L ($Q_{M-L}$) normal coordinates.

$$
E_1 = E_1^{CF} + \frac{k_{M-O}}{2}Q_{M-O}^2 + \frac{k_{M-L}}{2}Q_{M-L}^2
$$

$$
E_2 = E_2^{CF} + \frac{k_{M-O}}{2}(Q_{M-O}^2 - 2Q_{M-O}\Delta Q_{M-O}) + \frac{k_{M-L}}{2}(Q_{M-L}^2 - 2Q_{M-L}\Delta Q_{M-L})
$$

$$
E_3 = E_3^{CF} + \frac{k_{M-O}^2}{2k_{M-O}}(Q_{M-O}^2 - 4Q_{M-O}\Delta Q_{M-O}) + \frac{k_{M-L}^2}{2k_{M-L}}(Q_{M-L}^2 - 4Q_{M-L}\Delta Q_{M-L})
$$

The force constants $k_i$ in eqs 5–7 are calculated from the experimental vibrational frequencies in Table 1. The energy $E_{calc}(A_{1g}^3E_g)$ obtained from the crystal field calculation compares favorably to the first absorption maxima of the rhenium complexes. The potential minima for both excited states $E_2$ and $E_3$ are defined by $\Delta Q_{M-O}$ and $\Delta Q_{M-L}$. These two parameters are obtained from the comparison of calculated and experimental luminescence and absorption spectra. Metal–oxo bond length changes are obtained as $\Delta Q_{M-O}=\sqrt{2}$. The orbital configurations of the two lowest energy electronic states and the ground and excited-state vibrational frequencies in Table 1 define the signs of these bond length changes. The excitation of a molecule to its $A_{1g}$ ($3E_g$) excited state ($E_3$) increases electron density in the $\pi$ antibonding $e_g$ orbitals oriented toward the oxo ligands. The metal–oxo vibrational energy of this excited state decreases to approximately 90% of the ground-state value, and we expect the bond length to increase. The values of $\Delta Q_{M-O}$ given in Table 2 are similar for all complexes, reflecting their almost identical metal–oxo bonding. In the $A_{1g}^3E_g$ excited state electron density is removed from the $\pi$ antibonding $b_{2g}$ orbital oriented

---

Note: The text contains mathematical equations and references, which are not rendered here due to the limitations of the text conversion process. The full context and source of the information can be found in the referenced literature.
toward the ancillary ligands, and the M–L vibrational frequency of the excited state increases to 120% of the ground-state value, leading to a bond length decrease and to the negative values of the ΔQ_{M–L} in Table 2.

The highest energy A_{1g} state (3 A_{1g}, e_{g}^2 configuration) cannot be observed spectroscopically, but it can be characterized with eqs 1–5 and with reasonable estimates for its force constant and for the position of its potential minimum along the coordinates Q. We assume in eq 7 that its ΔQ values correspond to the double of those obtained for the A_{1g}(E_{g}) state, where only one electron is excited into the e_{g} orbital. We estimate vibrational frequencies that change by a factor of k_{l}/k_{1} from the values obtained for the A_{1g}(E_{g}) excited state. Figure 3 shows the harmonic potentials in eqs 5–7 as a function of both relevant normal coordinates. The excited-state potentials cause a flattening of the ground-state surface at positive values of Q_{Re}=0 and negative values of Q_{M–L}. The higher energy excited state in eq 1 effectively represents both high-energy crystal field states or totally symmetric charge transfer states. Qualitative experimental evidence for this excited state is observed in the absorption spectrum of trans-ReO_{2}(en)_{2}^{2+}, which shows a weak band with a resolved progression in the Re=O mode starting at approximately 28000 cm^{-1}, possibly corresponding to the second excited state in our model and confirming our assumption of a large offset of its potential energy minimum along Q_{Re}=0. In other compounds, this transition is masked by more intense transitions to ungerade parity excited states. The contour lines in Figure 4a show the potential surface for a harmonic ground state, calculated from eq 1 with V_{12} = V_{13} = V_{23} = 0. The contour diagram in Figure 4b is calculated for the lowest energy adiabatic surface obtained from eq 1 with the nonzero coupling constants V_{ij} given in Table 2 for trans-ReO_{2}(vi-im)_{2}^{2+}, again illustrating the flattening caused by the excited electronic states.

The analytical expression for the ground-state potential surface, corresponding to the lowest-energy eigenvalue of eq 1 with the diagonal elements of the matrix given by eqs 5–7, contains many terms of the form k_{l}Q_{M}=0Q_{M–L} (m = 0, n ≤ 6). These terms lead to potential energy surfaces such as Figure 4b where the Q_{M}=0 and Q_{M–L} coordinates can no longer be separated. The influence of terms with m = n = 1 and m = 2, n = 1 on electronic spectra has been studied in detail for hexafluoroacetacetonato(dimethylgold(III)) and values of k_{l} have been determined from fits to experimental spectra. In our model, both the values of m and n and the magnitude of k_{l} for each coupling term are defined by the spectroscopic parameters in Tables 1 and 2. The coupling between the coordinates Q_{M} and Q_{M–L} is an effect of the interacting electronic states of the title compounds.

We use the time-dependent theory of emission spectroscopy built on vibronic origins are experimentally observed to have intensity distributions identical with those on pure copy^{39,40} for our calculations. This approach allows us to calculate spectra for all models within the same framework. The emission spectrum is given by:

$$I_{\text{em}}(\omega) = C_{\omega} |\langle \psi | \phi(t) \rangle|^{2} e^{-\Gamma t^{2} + iE_{\omega}t \tau} dt$$

(8)

ϕ represents the nuclear wave function of the molecule at t = 0 on the ground-state potential surface. The most important ingredient determining the vibrionic structure and band shape of the luminescence spectrum is the autocorrelation function ⟨ϕ|ϕ(t)⟩ of the wave packet evolving on the ground-state potential surface. Γ is a phenomenological damping factor adjusted to reproduce the resolution of the experimental spectra and E_{ω0} is the energy of the electronic origin, given in Table 1 for the title compounds. We assume a harmonic surface for the emitting state and make the Condon approximation for all calculations, using a transition dipole that is independent of Q_{M}=0 and Q_{M–L}. This assumption is justified because progressions built on vibronic origins are experimentally observed to have intensity distributions identical with those on pure


Savoie and Reber

Table 2. Summary of Parameters for the Calculation of Spectra of trans-Dioxo Complexes

<table>
<thead>
<tr>
<th></th>
<th>ReO_{2}(vi-im)_{2}^{2+}</th>
<th>ReO_{2}(en)_{2}^{2+}</th>
<th>ReO_{2}(men)_{2}^{2+}</th>
<th>OsO_{2}(ox)_{2}^{2+}</th>
<th>OsO_{2}(en)_{2}^{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔQ [cm^{-1}]</td>
<td>10970</td>
<td>22000</td>
<td>22000</td>
<td>4000</td>
<td>0</td>
</tr>
<tr>
<td>K_{ij} [cm^{-1}]</td>
<td>2000</td>
<td>3100</td>
<td>2000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ζ [cm^{-1}]</td>
<td>3000</td>
<td>3000</td>
<td>3000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>V_{12} [cm^{-1}]</td>
<td>2160</td>
<td>420</td>
<td>2250</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>V_{13} [cm^{-1}]</td>
<td>2690</td>
<td>441</td>
<td>2980</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>V_{23} [cm^{-1}]</td>
<td>4600</td>
<td>4620</td>
<td>4820</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>E_{ij}(A_{1g},E_{g}) [cm^{-1}]</td>
<td>15670</td>
<td>15700</td>
<td>18490</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>E_{ij}(A_{1g},A_{1g}) [cm^{-1}]</td>
<td>41890</td>
<td>48560</td>
<td>47860</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ΔQ_{Re=0} [Å ]</td>
<td>0.11</td>
<td>0.13</td>
<td>0.12</td>
<td>0.085</td>
<td>0.10</td>
</tr>
<tr>
<td>ΔQ_{M–L} [Å ]</td>
<td>-0.08</td>
<td>-0.11</td>
<td>-0.08</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>Γ [cm^{-1}]</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>350</td>
<td>350</td>
</tr>
</tbody>
</table>

Figure 4. Ground-state potential energy surface for trans-ReO_{2}(1-vinylimidazole)_{2}^{2+}: (a) diabatic surface and (b) lowest adiabatic surface obtained from eq 1. The dots indicate the position of the emitting state potential minimum. The energy minimum of both contour diagrams is at 0 cm^{-1} and contour lines are shown at intervals of 2000 cm^{-1}.


electronic origins in many transition metal compounds with inversion symmetry.\textsuperscript{41} The crystal structures of the ethylenediamine and oxalate complexes have a center of inversion at the metal site.\textsuperscript{21,24,28} The luminescence spectra of trans-ReO\textsubscript{2}(tmen)\textsuperscript{3+}, trans-ReO\textsubscript{2}(en)\textsuperscript{2+}, trans-OsO\textsubscript{2}(en)\textsuperscript{2+}, and trans-OsO\textsubscript{2}(ox)\textsuperscript{2+} are therefore superpositions of spectra built on vibronic origins that are too close in energy to be resolved in our experiments. The crystallographic point group symmetry of the trans-ReO\textsubscript{2}(R-imidazole)\textsuperscript{3+} compounds does not retain the inversion center,\textsuperscript{36} relaxing the parity selection rule and leading to a weakly allowed electronic transition in addition to progressions built on vibronic origins. This superposition is a likely cause of the limited resolution of the luminescence spectra, in contrast to the allowed oxo \( \rightarrow \) metal charge-transfer absorption bands, where line widths of less than 20 cm\(^{-1}\) are observed for some of the title compounds.\textsuperscript{20,29,33}

The time-dependent wave function \( \phi(t) \) in eq 8 is calculated on a two-dimensional grid representing the ground-state potential surface with the split operator algorithm developed by Feit and Fleck.\textsuperscript{42}

\[ \phi(t + \Delta t) = e^{i(\Delta t\mathbf{M})V^2} e^{-i\Delta tV^i} e^{i(\Delta t\mathbf{M})V^2} \phi(t) + O((\Delta t)^3) \] \hspace{1cm} (9)

Equations 8 and 9 allow us to calculate the autocorrelation function \( \langle \phi(t) \phi(t) \rangle \) and the luminescence spectrum.

**Luminescence Spectra from Harmonic Potential Energy Surfaces.** Harmonic potentials provide an excellent starting point for the analysis of vibronic structure in electronic spectra of transition metal compounds and have been extensively used to calculate spectra for a large number of transition metal complexes and organometallic molecules.\textsuperscript{40,43} We use them first to calculate the resolved luminescence spectra for the trans-dioxo complexes of rhenium(V) shown in Figure 1. The vibrational energies of the ground and emitting state potentials are determined from luminescence, Raman, and absorption spectra and are summarized in Table 1. A calculated luminescence spectrum based on harmonic surfaces is given in the literature for trans-ReO\textsubscript{2}(py)\textsuperscript{4+} and is in perfect agreement with the experimental spectrum.\textsuperscript{6} The positions of the minima along the normal coordinates are the only adjustable parameters and absolute values of 0.07 and 0.03 Å are obtained for the rhenium-\( \pi \)-oxo and rhenium-\( \pi \)-pyridine bond length changes, respectively.\textsuperscript{6} The corresponding changes along the normal coordinates \( \Delta Q_{\text{Re}=0} \) and \( \Delta Q_{\text{Re}=1} \) are 0.10 and 0.06 Å, respectively. The literature luminescence spectrum of trans-OsO\textsubscript{2}(CN)\textsubscript{4}\textsuperscript{2−} shows weakly resolved vibronic structure with a separation between peaks corresponding to the Raman active Os=O mode.\textsuperscript{9,20} We estimate a value of 0.10 Å for \( \Delta Q_{\text{Os}=0} \) from the literature spectra, very similar to the values reported in Table 2 for the two trans-dioxo complexes of osmium(VI) in Figure 2. Calculations based on harmonic potentials are shown in Figures 5, 7, and 8 for all title compounds. The parameters used for the calculations are summarized in Table 2.

There are two important discrepancies between experimental spectra and calculations based on harmonic potentials. Both arise from the terms coupling the coordinates \( Q_{\text{M}=0} \) and \( Q_{\text{M}=1} \) as a consequence of the interactions between the ground and excited electronic states. The first difference is indicated by the sloping lines on top of the experimental and calculated spectra in Figures 4a, 5, and 6.


influenced by all three $A_{1g}$ electronic states defined in eq 1. But we found that the adjustable parameter $k$ state potential and fitting the adjustable parameter in the following the model outlined in the first section to rationalize the spectra observed for the rhenium(V) complexes in Figure 1. We have previously reported a phenomenological model that was sufficient to quantitatively describe the nonreplica vibronic pattern of a complex, $trans$-$\text{ReO}_2(1\text{-methylimidazole})_4^{2+}$, by adding a single $k_o\hbar_\text{Re}-\hbar\text{Re}_{L}$ term coupling the two normal modes to the harmonic ground-state potential and fitting the adjustable parameter $k_o$. This coupling constant was found to be smaller by approximately 2 orders of magnitude than the rhenium–oxo and rhenium–$L$ vibrational energies. The phenomenological model does not allow us to rationalize the presence or absence of nonreplica patterns in the luminescence spectra of the closely related rhenium complexes presented here and reported previously, but we found that the adjustable parameter $k_o$ is largest for low-energy luminescence spectra, a qualitative correlation that has inspired us to develop the model described here.

Figure 5 shows a detailed comparison between spectra calculated from several models and the experimental spectrum of $trans$-$\text{ReO}_2(\text{vi-im})_4^{2+}$. The top trace in both sections is the experimental spectrum, followed by the spectrum calculated from the lowest adiabatic potential in eq 1 and the spectrum calculated from harmonic potential surfaces.

ReO$_2$Ln$^+$ ($n = 2, 4$) complexes with low-energy emission is influenced by all three $A_{1g}$ electronic states defined in eq 1. We use in the following the model outlined in the first section of the discussion to rationalize the spectra observed for the rhenium(V) complexes in Figure 1. We have previously reported a phenomenological model that was sufficient to quantitatively describe the nonreplica vibronic pattern of one complex, $trans$-$\text{ReO}_2(1\text{-methylimidazole})_4^{2+}$, by adding a single $k_0\hbar_\text{Re}-\hbar\text{Re}_{L}$ term coupling the two normal modes to the harmonic ground-state potential and fitting the adjustable parameter $k_0$. This coupling constant was found to be smaller by approximately 2 orders of magnitude than the rhenium–oxo and rhenium–$L$ vibrational energies. The phenomenological model does not allow us to rationalize the presence or absence of nonreplica patterns in the luminescence spectra of the closely related rhenium complexes presented here and reported previously, but we found that the adjustable parameter $k_0$ is largest for low-energy luminescence spectra, a qualitative correlation that has inspired us to develop the model described here.

Figure 5 shows a detailed comparison between spectra calculated from several models and the experimental spectrum of $trans$-$\text{ReO}_2(\text{vi-im})_4^{2+}$ (top trace). The spectrum corresponding to the full three-level model given in eq 1 and Figures 3 and 4 provides the best overall fit and is shown directly below the experimental spectrum. The harmonic spectrum (bottom) does not reproduce the variation of the vibronic structure along the main progression at all, because all interactions with excited states are neglected. This is obvious from a comparison of the sloping lines above the first and fourth members of the main progression in both the experimental and calculated spectra shown in Figure 5. The spectra calculated from models with only two coupled levels are shown as the third and fourth traces in Figure 5 and do not lead to a variation of the shape of each member of the main progression that matches the experiment. Even increasing the only remaining coupling constant $V_{12}$ or $V_{13}$ in these models does not result in calculated spectra that show as good an agreement with experiment as the spectrum from the full calculation with eq 1. The effect of two excited states with different potential energy minima along $Q_o$ on the ground-state potential surface appears to be essential. The comparison in Figure 5 shows that the full model in eq 1 has to be used to quantitatively rationalize the observed vibronic structure.

Figure 6 illustrates the influence of the vibronic line width and inhomogeneous broadening on the calculated luminescence spectrum of $trans$-$\text{ReO}_2(\text{vi-im})_4^{2+}$. The bottom and middle traces are calculated with the same model as the best fit spectrum shown in Figure 5, but with damping factors $\Gamma$ of 10 and 60 cm$^{-1}$ for the high- and low-resolution spectra, respectively. These calculated spectra show nonreplica patterns very similar to the best fit in Figure 5, indicating that this effect does not depend on the bandwidth of individual vibronic lines. The resolution and background of the experimental luminescence spectra are most likely determined by inhomogeneous broadening. The top spectrum in Figure 6 illustrates the result of a weighted addition of spectra displaced along the abscissa axis, shown as the sum of the best fit spectrum from Figure 5 (weight 30%) and best fit spectra displaced by $\pm 70$ cm$^{-1}$ (15% each), $\pm 140$ cm$^{-1}$ (7% each), $\pm 210$ cm$^{-1}$ (4% each), $\pm 280$ cm$^{-1}$ (4% each), and $\pm 350$ cm$^{-1}$ (4% each). This calculated spectrum provides a good reproduction of the background intensity between the members of the main progression in the experimental spectrum in Figure 5 and it retains the vibronic intensity distribution of the best fit calculation. The comparison of all spectra indicates that the intensity variations along the main progression are not significantly affected by line broadening or by an unresolved background.

The lowest adiabatic surface is sufficient to calculate spectra because only negligible wave packet amplitude extends to the region of the avoided crossing between the potential surfaces illustrated in Figure 3. The energy difference between the ground-state minimum and the initial position of the wave packet, indicated by the black dots in Figure 4, is 2470 cm$^{-1}$ for the harmonic surface in Figure 4a and 2030 cm$^{-1}$ for the potential in Figure 4b. The difference of 440 cm$^{-1}$ between these two energies is due to coupling between the ground and excited electronic states, as derived with our model from the low-temperature luminescence spectra. The difference is obvious from Figure 4, where the dot indicating the emitting state minimum is outside the innermost (2000 cm$^{-1}$) contour line for the harmonic potential in Figure 4a, but intersects this contour line for the potential including coupling in Figure 4b. The terms coupling normal coordinates cause wave packet dynamics on the potential energy surface in Figure 4b that can no longer be separated into independent $Q_{L}=0$ and $Q_{L}=1$ dynamics, as has been illustrated in detail for a two-dimensional potential surface $V(Q_o,Q_i)$ with a single $k_0\hbar_0 Q_o Q_i$ coupling term.$^{46}$ The same approach was applied to the ethylenediamine and tetramethylethylenediamine compounds and leads to satisfactory spectra calculated with eq 1, as illustrated in Figure 7. The calculated spectra show the importance of the energy difference.

---


between the electronic states: the effect is easily seen in the experimental luminescence spectrum of trans-OsO₂(en)₂²⁺, but it is much less obvious for the tetramethylethylenediamine complex. The parameters used for the two complexes are very similar, with the exception of the interelectronic repulsion parameter, $K_{xy}$, which is significantly larger for the ethylenediamine complex.

The values determined for $\Delta Q_i$ in Table 2 are very similar for the three rhenium complexes, but the detailed vibronic structure of their luminescence spectra varies and the spectra do not have the same overall bandwidths: the spectrum of trans-ReO₂(en)₂²⁺ is obtained from a one-dimensional harmonic potential surface and shown as the bottom trace in part a. The calculated spectrum of trans-OsO₂(en)₂²⁻ based on harmonic potential energy surfaces is shown as a dotted line in part b. The spectrum calculated from a model including coupling between two potential surfaces is given as a solid line (bottom trace in part b).

Figure 8. Calculated and experimental luminescence spectra of (a) trans-OsO₂(en)₂²⁺ and (b) trans-OsO₂(ox)₂²⁻. The top traces in both sections denote the experimental spectrum. The calculated spectrum of trans-OsO₂(en)₂²⁺ is obtained from a one-dimensional harmonic potential surface and shown as the bottom trace in part a. The calculated spectrum of trans-OsO₂(ox)₂²⁻ based on harmonic potential energy surfaces is shown as a dotted line in part b. The spectrum calculated from a model including coupling between two potential surfaces is given as a solid line (bottom trace in part b).

The unresolved band shapes of the trans-ReO₂(en)₂²⁺, but it is much less obvious for the tetramethylethylenediamine complex. The parameters used for the two complexes are very similar, with the exception of the interelectronic repulsion parameter, $K_{xy}$, which is significantly larger for the ethylenediamine complex.

The values determined for $\Delta Q_i$ in Table 2 are very similar for the three rhenium complexes, but the detailed vibronic structure of their luminescence spectra varies and the spectra do not have the same overall bandwidths: the spectrum of the ethylenediamine complex is narrower than the spectrum of trans-ReO₂(tmen)⁺⁺, which has its maximum at higher energy. The same trend is observed for trans-dioxo complexes of osmium(VI) and discussed in the following section. The model in eq 1 involving three coupled electronic states therefore provides a complete and quantitative explanation for the observed spectroscopic effects.

Band Shapes of trans-Dioxo Complexes of Osmium(VI). The unresolved band shapes of the trans-OsO₂L₂ complexes in Figure 2 also show distinct evidence for interacting ground and excited electronic states. We calculate spectra for a simplified model including only one normal coordinate, the osmium–oxo mode $Q_{Os-O}$. The spectrum of trans-OsO₂(en)₂²⁺ resulting from a harmonic ground state potential surface is shown in Figure 8a. Both the shape of the calculated band and its width are in very good agreement with the experimental spectrum. The only adjustable parameter is $\Delta Q_{Os-O}$, reported in Table 2. Our value of 0.10 Å is within the range of literature values given as 0.10–0.12 Å for trans-OsO₂(CN)₂²⁻.

The spectrum of trans-OsO₂(ox)₂²⁻ is compared to the calculation based on a harmonic potential energy surface in Figure 8b (dotted line). The high-energy onset of the calculated spectrum is steeper than observed experimentally and the low-energy decrease of the calculated intensity occurs slower than in the experimental spectrum. It is not possible to simultaneously remove both discrepancies with a harmonic ground-state surface. The experimental band shapes at 10 and 80 K are very similar and differ from a Poisson envelope. The constant luminescence lifetimes across the band shape indicate that the envelope is not due to two or more overlapping harmonic spectra. The value of 0.085 Å for $\Delta Q_{Os-O}$ obtained from the fit is smallest among the values in Table 2, possibly related to the osmium–oxo bond length of trans-OsO₂(ox)₂²⁻ which is 0.03 Å shorter than in trans-OsO₂(en)₂²⁺ or due to the competition between metal–oxo and metal–oxalate $\pi$ bonding.

We improve our model by including interactions between the ground state and the lowest energy excited state, involving a single coupling constant $V_{12}$. The energy of this excited state is obtained from the absorption and luminescence spectra and given in Table 2. The calculated spectrum shown as a solid line in Figure 8b (bottom trace) is obtained from the upper left 2×2 section of the matrix in eq 1 by adjusting $V_{12}$. Increasing its value leads to a narrower calculated band shape with a steeper decrease of the intensity at low energies and improves the agreement with the experiment, as shown in Figure 8b. A qualitatively similar change in the band envelope as a consequence of coupling is observed for the low-energy emission of the rhenium compounds in Figures 5 and 7b. The remaining discrepancies between experimental and calculated band shapes are most likely due to the limitation to only one excited state interacting with the ground state of the osmium(VI) complexes, unlike the rhenium compounds, where the full model with two excited states in eq 1 was used. The unresolved luminescence spectra and the limited crystal field absorption data of the osmium(VI) complexes do not provide sufficient experimental information to define all the parameters necessary for a model involving three electronic states.

The reason for the narrowing of the band envelope is evident from a comparison of the autocorrelation functions $\langle \phi(0)\phi(t) \rangle$ in eq 8 obtained for harmonic ground-state potentials and for the surfaces including coupling to excited states. At the initial position of the wave packet, the harmonic ground-state potential of each title compound has a steeper slope than the lowest adiabatic surface arising from the coupled model, as illustrated for trans-ReO₂(vi-im)⁺⁺ in Figures 3 and 4. The slope of the surface region explored by the wave packet at short times determines the initial decrease of the autocorrelation function. A rapid decrease is calculated from harmonic surfaces as illustrated by the dotted lines in Figures 9a and 9b for trans-OsO₂(ox)₂²⁻ and trans-ReO₂(en)₂⁺⁺, respectively. These autocorrelations lead to a broad Poisson band envelope. The adiabatic surfaces are flattened in the region below the emitting state minimum and we calculate a slower decrease of the autocorrelation, shown as solid lines in Figures 9a and 9b, leading to the narrower band envelopes and deviations from a Poisson band shape illustrated for trans-OsO₂(ox)₂²⁻ in Figure 8b and for trans-ReO₂(en)₂⁺⁺ in Figure 7b.

The autocorrelation functions for the two calculated spectra of trans-ReO₂(en)₂⁺⁺ in Figure 7a are compared over a longer time period in Figure 9c. Autocorrelation maxima occur every 37.9 fs on the harmonic ground-state surface, shown as a dotted line in Figure 9c. This time interval leads to a constant energy separation of 880 cm⁻¹ between the calculated maxima of the main progression. It is obvious that the recurrences occur later in time for the autocorrelation calculated with the adiabatic surface including coupling (solid line in Figure 9c) than for the
autocorrelation obtained with the harmonic surface. The difference is 1.0 fs for the first recurrence, which corresponds to an energy interval of 857 cm$^{-1}$, and increases to 4.6 fs for the fifth peak in Figure 9c. These longer times lead to maxima of the main progression which occur at slightly lower energy than those of the spectrum resulting from a harmonic surface. The time differences between maxima of the autocorrelation shown as a solid line in Figure 9c are not constant for the adiabatic potential defined in eq 1 and lead to energy differences between members of the main progression that vary across the spectrum. These properties of the autocorrelation function cause the distinct intensity variations indicated by the sloping lines in Figures 5 and 7: the maximum intensity of the first member of the main progression occurs later in its series of low-frequency peaks than for the fourth member of the main progression, which has its maximum intensity at the beginning of its cluster of low-frequency bands. The nonreplica pattern is clearly illustrated by the autocorrelation recurrences, which occur at longer times on the potential surface obtained from the full model in eq 1, illustrated for one compound in Figure 4b. Figure 9d illustrates the differences between autocorrelations from potentials including coupling to excited states and harmonic surfaces for trans-ReO$_2$(en)$_2$$^+$ (solid line) and trans-ReO$_2$(tmen)$_2$$^+$ (dotted line). The initial positive difference leads to the narrower band envelope and the shift of the autocorrelation recurrences causes the characteristic negative and positive autocorrelation differences at each recurrence. The comparison in Figure 9d shows that similar effects are observed for both compounds, but that they are much stronger for the complex with the lower energy emission, represented by the solid line in Figure 9d, again illustrating the influence of the excited electronic states on the ground-state potential energy surface. The model defined in eq 1 rationalizes the vibronic structure and luminescence band shapes for many 5d$^2$ configured trans-dioxo compounds and gives a quantitative description of the ground-state potential energy surfaces for the title compounds.

**Conclusion**

The detailed comparison of luminescence spectra of trans-dioxo complexes allows us to determine the influence of excited electronic states on the ground-state potential energy surface. The resolved vibronic structure in luminescence spectra can be used to calculate this effect, but even the shape of unresolved band envelopes provides experimental evidence for coupling between the electronic ground and excited states.

**Acknowledgment.** This work was made possible by grants from the Natural Sciences and Engineering Research Council (Canada). We acknowledge contributions from Sandrine Stanislas, Andreea Vuica, Steve Masson, and Thierry Wamser.

JA993305Q