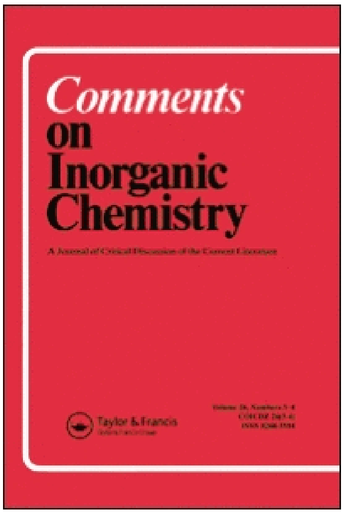

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PRESSURE-INDUCED CHANGE OF *d-d* LUMINESCENCE ENERGIES, VIBRONIC STRUCTURE AND BAND INTENSITIES IN TRANSITION METAL COMPLEXES

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PRESSURE-INDUCED CHANGE OF *d-d* LUMINESCENCE ENERGIES, VIBRONIC STRUCTURE AND BAND INTENSITIES IN TRANSITION METAL COMPLEXES

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The effects of hydrostatic pressure on the luminescence spectra of tetragonal transition metal complexes with nondegenerate electronic ground states are analyzed quantitatively by means of models based on potential energy surfaces defined along normal coordinates. Pressure-induced changes of intensity distributions within vibronic progressions, band maxima, electronic origins and relaxation rates are discussed for metal-oxo complexes of rhenium(V) and molybdenum(IV) (d^2 electron configuration) and for square-planar complexes of palladium(II) and platinum(II) (d^8 electron configuration).

Keywords: Luminescence spectroscopy, d-d transitions, pressure, metal-oxo complexes, square-planar complexes, molybdenum(IV), palladium(II), platinum(II), rhenium(V)

1. INTRODUCTION

High external pressure provides an important pathway to a wide variety of solid-state structural changes and allows us to tune physical properties

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for many different materials, as described in a number of extensive reviews with detailed bibliographies covering applications in chemistry, materials science and physics, as well as the experimental methodology, in particular for spectroscopic measurements.[1–7]

Transition metal complexes are particularly attractive for the study of pressure effects, due to their high symmetry and electronic structure with degenerate and nondegenerate electronic states. Luminescence and absorption spectra of many transition metal compounds, including organometallic molecules, have been measured and pressure-induced variations have been reported for the energies of their band maxima.[1,3,4,6,7] Excited states with different multiplicities are often close in energy, as illustrated by numerous studies of octahedral chromium(III) complexes, where an emitting state crossover from a quartet to a doublet state has been observed.[6] The corresponding change from a triplet to a singlet emitting state for an octahedral vanadium(III) complex was recently reported.[8] Many literature studies focus on pressure-induced spectroscopic effects caused by ground-state metal-ligand bond length changes, illustrated for example by spin-crossover complexes, where pressure can lead to very large metal-ligand bond length changes and even to crystallographic phase transitions.[9,10] Large spectroscopic changes have been observed as a consequence of a few intermolecular effects, involving, for example, the stacking of square-planar d^8 complexes,[11] where pressure-dependent luminescence and triboluminescence phenomena have been compared.[12] Pressure effects on intermolecular distances in luminescent gold(I) cyanides have been reported to lead to significant red shifts due to shorter metal-metal distances.[6,13] A middle-ground between intra- and intermolecular effects of pressure is occupied by exchange-coupled polymetallic complexes[5,14,15] and materials of interest as molecular magnets.[16] Phenomena such as piezochromism, mechanochromism and their characterization through luminescence spectroscopy and other properties such as electrical conductivity measurements have been reviewed recently.[17–19] There are many effects where small changes to the environment of transition metal compounds create large changes of their properties, reported as tribochromism[20] and vapochromism.[21,22] Several of the compounds showing these phenomena can be probed by luminescence spectroscopy and adjustable external pressure provides an important tool to study and control such effects.

This comment addresses an apparent gap in the literature: on the one hand, structural changes occupy a prominent place in high-pressure research; on the other hand, the vast majority of literature reports on high-pressure luminescence and absorption spectroscopy focus on band maxima and rationalize the observed variations entirely in terms of electronic energy levels, neglecting effects due to pressure-induced changes of the structural differences between the initial and final states of the transition. The traditional approach allows transitions to be classified based on the pressure-induced shifts of band maxima,[3,4,23,24] but more detailed comparisons have to take into account the vibronic nature of electronic transitions, leading to resolved structure and broad bands for many transition metal compounds. In ambient-pressure spectroscopy, often carried out at low temperature, the vibronic spectra obtained with different spectroscopic techniques have been quantitatively analyzed with theoretical models[25–29] and the chemical and photochemical consequences of excited state distortions have been discussed.[26,30] Only a small number of recent studies link these two aspects and determine pressure-dependent structural changes between the ground and excited states of transition metal complexes, for example in octahedral halide complexes of chromium(III)[31] and vanadium(III)[8], where luminescence spectra were used, and in permangante, where pressure-dependent absorption and resonance Raman spectra have been analyzed.[32]

Theoretical work on pressure-dependent electronic spectra is based on potential energy surfaces. Traditionally, assumptions are made that lead to calculated variations of band maxima and widths using quantities that are not obvious to determine experimentally, such as local compressibilities and assumptions on the variation of crystal-field parameters with metal-ligand bond distance.[33–35] Most often, experimental data with sufficient detail to determine potential energy surfaces was not available for these studies. Recent work based on electronic structure calculations shows interesting trends for relatively simple transition metal complexes, such as the octahedral VCl_6^{3-} anion,[36] and new general approaches have been described,[37] but not yet applied to transition metal complexes.

In the following, we summarize recent work on the combination of experimental and calculated spectra based on potential energy surfaces defined by adjustable parameters. Resolved vibronic structure is often observed for the examples presented, providing key information for the application of straightforward theoretical models. Two types of tetragonal complexes are explored: first, d^2-configured metal-oxo complexes, and second, square planar complexes of d^8-configured transition metal ions.

2. ONE-DIMENSIONAL NORMAL COORDINATE MODEL

The potential energy surfaces for the initial and final states of a transition are a key aspect of any model used to calculate electronic spectra. All examples discussed in the following involve transition metal complexes with nondegenerate electronic ground states, leading to luminescence spectra arising from a transition to a single electronic state. The simplest quantitative model involves two harmonic potential energy curves along a single normal coordinate, as illustrated in Figure 1. The highest-energy transition in this model is the electronic origin of the luminescence spectrum, denoted as E_{00}. The luminescence band maximum is at E_{max}, also given in Figure 1. The potential energy minima are offset by an amount ΔQ_i along the normal coordinate Q_i. The final

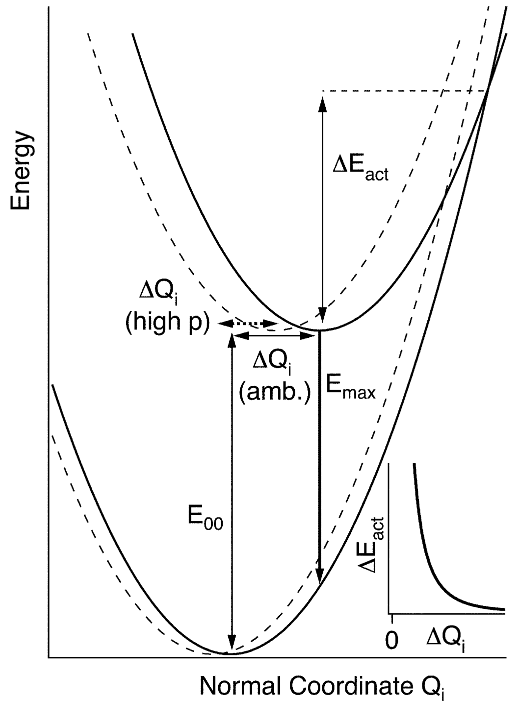

Figure 1. Potential energy curves at ambient pressure (solid) and at high pressure (dotted) for the ground and emitting states along a single normal coordinate Q_i. The spectroscopic parameters E_{00}, E_{max}, ΔQ_i and ΔE_{act} are defined. The only change at high pressure is a decrease of ΔQ_i. The inset shows the variation of the activation energy ΔE_{act} with ΔQ_i.

parameter of interest is the activation energy ΔE_{act}, which, in a simple classical view, determines the nonradiative relaxation rate constant: If it is high, the nonradiative relaxation processes are expected to be inefficient. The change of these four parameters with pressure will be analyzed from luminescence spectra for the transition metal complexes discussed in the following. The only other quantities needed to define the curves in Figure 1 are the vibrational frequencies of the mode associated with the normal coordinate Q_i in the ground and emitting states. The ground state frequencies are found to change by very small amounts from pressure-dependent Raman spectra, and such frequency changes do not have a significant effect on the luminescence spectra.

The model in Figure 1 is chosen for a substantial offset ΔQ_i and for a situation where the emitting-state potential energy minimum is at a larger value of Q_i than the ground state minimum, corresponding to weaker metal-ligand bonds in the emitting state. For this case, it is easy to qualitatively estimate the effect of an external pressure on ΔQ_i: Its magnitude is expected to decrease because pressure affects the emitting-state minimum more strongly than the ground state minimum, as illustrated by the dotted potential energy curves in Figure 1. This model therefore corresponds to a complex for which ΔQ_i decreases under high pressure, as indicated in Figure 1 by ΔQ_i (high pressure), which is set to a smaller value than ΔQ_i at ambient pressure. In order to obtain the dotted potential energy curves, the value of ΔQ_i was decreased by 9%, a value comparable to the 10 to 15% decreases of offsets ΔQ_i reported in the literature for halide complexes of chromium(III) between ambient pressure and 50 kbar.[31] Changes of the energies E_{00} and E_{max} are also expected with pressure. Their magnitudes and signs depend on the specific bonding situation and will be discussed in the following. The influence of pressure on the activation energy ΔE_{act} is shown in the inset to Figure 1: As ΔQ_i decreases, the activation energy increases strongly.

Calculated luminescence spectra for both sets of potential energy curves in Figure 1 are shown in Figure 2 at high and low resolution. Such calculations are easily carried out for harmonic and anharmonic potential energy surfaces.[25–29] The spectra shown as solid traces correspond to the ambient-pressure potential energy curves denoted by solid curves in Figure 1. A long progression is observed as a consequence of the large offset ΔQ_i. The members of the progression are separated by the ground-state vibrational frequency of the mode with normal coordinate Q_i and the intensity distribution within the progression depends strongly on

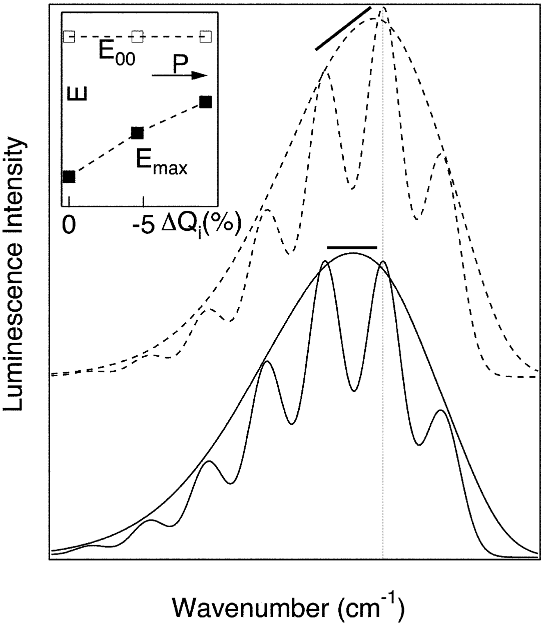

Figure 2. Luminescence spectra calculated from the potential energy curves in Figure 1. Spectra at ambient pressure are given by solid lines, those at high pressure by dotted lines. The bars above the spectra illustrate the change in vibronic intensities resulting from a decrease of ΔQ_i in Figure 1. The inset shows the variation of E_{00} and E_{max} obtained from the calculated spectra.

the magnitude of ΔQ_i. Such progressions are observed for many transition metal complexes, most often at low temperature. The decrease of ΔQ_i in Figure 1 leads to the spectra shown as dotted traces in Figure 2. The energies of the maxima forming the resolved progression are independent of the magnitude of ΔQ_i, as illustrated by the dotted vertical line, but the intensity distribution within the progression changes significantly, showing an increase for the high-energy members of the progression and a decrease for the maxima at lower energy. The change of ΔQ_i with pressure can be determined by fitting calculated spectra as shown in Figure 2 to experimental spectra with resolved vibronic structure. Typically, ΔQ_i and E_{00} are treated as adjustable parameters, defining E_{max} and ΔE_{act}. At lower resolution, only an unresolved band with a single maximum is observed, as illustrated by the low-resolution envelopes in Figure 2. The maximum E_{max} of the spectrum at high pressure, shown as a dotted trace, is closer to the vertical dotted line than the maximum of the ambient pressure spectrum, denoted by the solid trace. The decrease of ΔQ_i with pressure therefore leads to a blue-shift of the luminescence band maximum, as shown in the inset to Figure 2. The energy of the electronic origin E_{00} does not change with ΔQ_i, and as all other quantities defining the model in Figure 1 are at identical values for the calculated spectra, E_{00} is constant in the inset to Figure 2. The increase of E_{max} indicates that an interpretation of band maxima with pressure in terms of purely electronic models can be fallible: a pressure-induced shift of E_{max} occurs even if the electronic energy difference between the ground- and emitting states, defining the electronic origin E_{00}, does not change. Vibronic effects, such as the decrease of the energy difference between E_{00} and E_{max} in the inset to Figure 2, need to be considered. The model in Figure 1 can be used to obtain quantitative parameter values from experimental spectra, as illustrated in the following.

3. PRESSURE EFFECTS ON VIBRONIC PROGRESSIONS AND BAND ENERGIES: METAL-OXO COMPLEXES

The luminescence spectra of many different metal-oxo complexes have been reported and they often show distinct progressions in the metal-oxo stretching mode due to large offsets $\Delta Q_{metal\text{-}oxo}$ between the minima of the potential energy surfaces of the ground and emitting states along the metal-oxo normal coordinate.[38–44] In the following, we discuss the pressure effects on room-temperature luminescence spectra of *trans*-dioxo rhenium(V) and mono-oxo molybdenum(IV) complexes, both containing metal centers with a d^2 electron configuration. All spectra were measured using a Raman microscope spectrometer with the 514.5 and 488.0 nm excitation lines of an argon ion laser. A diamond anvil cell was used to control the hydrostatic pressure on the sample crystals and ruby luminescence was used for pressure calibration. The luminescence bands of the metal-oxo complexes discussed here are in the visible and near-infrared spectral regions and often show a dominant progression involving the metal-oxo stretching mode with a frequency of approximately 900 cm^{-1}.

The highest occupied and lowest unoccupied orbitals of these complexes arise from the t_{2g} orbitals in the O_h point group. The metal-oxo bonds are conventionally used to define the molecular z axis, leading to the occupied d_{xy} orbital (b_{2g} in D_{4h} point group symmetry), lower in energy than the empty $d_{xz,yz}$ (e_g in D_{4h} point group symmetry) orbitals.[38–44] Many complexes with different ancillary ligands show almost identical rhenium-oxo bond lengths of 1.765 Å, varying by only 0.001 Å for *trans*-dioxo complexes of rhenium(V) with ethylenediamine, pyridine and 1-methylimidazole ligands in the xy plane.[45,46]

Figure 3 shows the pressure-dependent luminescence spectra of *trans*-$ReO_2(py)_4I$ and *trans*-$ReO_2(tmen)_2Cl$ at room temperature.[47–49] The abbreviations py and tmen denote pyridine and tetramethylethylenediamine ligands, respectively. The progression in the metal-oxo mode is clearly visible in both spectra. As pressure increases, the intensity distribution within the progression changes toward higher intensities for the members of the progression at high energy. This is the change expected for a pressure-induced decrease in the offset $\Delta Q_{O=Re=O}$ along the metal-oxo coordinate, as discussed in the preceding section and shown in

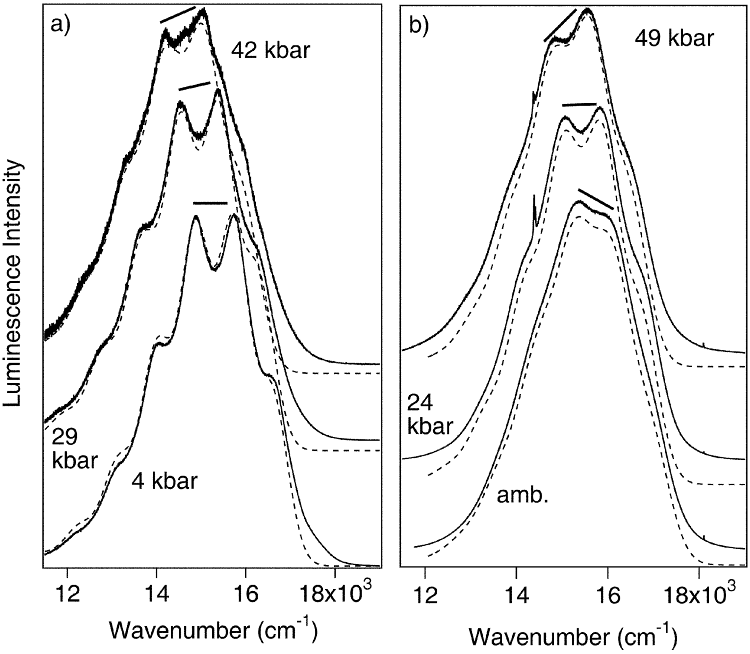

Figure 3. Experimental (solid lines) and calculated (dotted lines) pressure-dependent luminescence spectra of *trans*-$ReO_2(py)_4I$ (a) and *trans*-$ReO_2(tmen)_2Cl$ (b) at room temperature. Traces are offset along the ordinate for clarity and all spectra are normalized to identical areas.

Figure 2. The overall change between ambient pressure and approximately 40 kbar is larger for *trans*-$ReO_2(tmen)_2Cl$ than for *trans*-$ReO_2(py)_4I$, as illustrated by the sloping lines above the spectra in Figure 3. In addition, a red shift of the entire luminescence band is observed as pressure increases, another consequence of the pressure-induced compression of metal-ligand bonds. The rhenium-nitrogen single bonds are weaker and therefore more affected by pressure than the metal-oxo double bonds. These large bond length changes lead to stronger electrostatic crystal-field changes for the filled d_{xy} orbital involving the metal-nitrogen bonds and to a higher destabilization than for the empty $d_{xz,yz}$ orbitals involved in the metal-oxo double bonds, whose energy is less affected by pressure. In the molecular orbital view, the metal-nitrogen π-antibonding character of the d_{xy} HOMO orbital leads to a strong increase of the energy with pressure, dominating the energy increase of the metal-oxo π-antibonding $d_{xz,yz}$ LUMO orbitals and resulting in a red-shift of the luminescence band.

Spectra calculated with one-dimensional potential energy curves along the rhenium-oxo coordinate are shown as dotted lines in Figure 3. They reproduce the experimental data precisely and lead to a quantitative determination of the parameters E_{00}, E_{max} and $\Delta Q_{O=Re=O}$ for each pressure at which a spectrum was measured. The variations were found to be linear over the pressure range studied, and the slopes determined for the series of metal-oxo complexes compared here are summarized in Table 1. The band maxima E_{max} were determined from the calculated spectra by broadening each vibronic transition, as illustrated for the band envelopes in Figure 2. The pressure-induced variations of the parameters are illustrated in Figure 4 and show significant differences between these two compounds with similar ambient-pressure luminescence properties. The band maxima for *trans*-$ReO_2(py)_4I$ show a much stronger red shift of $-15.7\,cm^{-1}/kbar$ than for *trans*-$ReO_2(tmen)_2Cl$, where a shift of $-4.6\,cm^{-1}/kbar$ is obtained. The electronic origins for both compounds show a stronger red-shift than the band maxima: $-17.6\,cm^{-1}/kbar$ and $-8.4\,cm^{-1}/kbar$ for *trans*-$ReO_2(py)_4I$ and *trans*-$ReO_2(tmen)_2Cl$, respectively. This pressure-induced decrease of the energy difference between E_{00} and E_{max} again corresponds to the expectation for a decrease of $\Delta Q_{O=Re=O}$, illustrated in the inset to Figure 2. This decrease, illustrated by the difference of the slopes for E_{00} and E_{max} in Figure 4, is approximately twice as large for *trans*-$ReO_2(tmen)_2Cl$ than for *trans*-$ReO_2(py)_4I$. Both the intensity distributions and the energies

Table 1. Pressure dependence of room-temperature luminescence parameters for metal-oxo complexes obtained from fits of calculated spectra to experimental spectra. Luminescence band maxima E_{max}, their pressure-induced changes and those of electronic origins E_{00}, offsets ΔQ_i along the metal-oxo stretching normal coordinate and metal-oxo Raman frequencies are given

Compound	E_{max} (cm^{-1}) $\pm\Delta E_{max}/\Delta p$ (cm^{-1}/kbar)	$\Delta E_{00}/\Delta p$ (cm^{-1}/kbar)	$\Delta Q/\Delta p$ (Å/kbar^{-1})	$\hbar\omega_{metal\text{-}oxo}$ (cm^{-1}) $+\Delta\hbar\omega/\Delta p$ (cm^{-1}/kbar)
ReO$_2$(py)$_4$I[a]	15360–15.7	–17.6	$-0.6 \cdot 10^{-4}$	$905 + 0.53$
ReO$_2$(tmen)$_2$Cl[b,c]	15590–4.6	–8.4	$-1.9 \cdot 10^{-4}$	$868 + 0.42$
ReO$_2$(en)$_2$Cl[b,c]	13780–6.8	–12.0	$-2.5 \cdot 10^{-4}$	$898 + 0.37$
MoOCl(CN-*t*-Bu)$_4$ BPh$_4$[d]	$11950 + 12.0$	n/a	≈ 0[e]	$954 + 0.24$
MoOF(py)$_4$BPh$_4$[d]	13000–7.5	n/a	n/a	$953 + 0.18$

[a] Ref.[49]

[b] Ref.[48]

[c] Ref.[50]

[d] Ref.[51]

[e] Estimated from the spectra in Fig. 5.

obtained from the calculated spectra indicate a decrease of $\Delta Q_{O=Re=O}$ with increasing pressure. The magnitude of this decrease for the two *trans*-dioxo complexes is compared in Figure 4b. The slopes differ by a factor of three and $\Delta Q_{O=Re=O}$ values at 40 kbar are smaller by 7% and 2% than the ambient pressure values for *trans*-ReO$_2$(tmen)$_2$Cl and *trans*-ReO$_2$(py)$_4$I, respectively. The larger decrease for *trans*-ReO$_2$(tmen)$_2$Cl is qualitatively obvious from the more prominent change in intensity distribution within the progression, illustrated in Figure 3 over an identical pressure range for both compounds.

The different variations of $\Delta Q_{O=Re=O}$ with pressure for the two complexes in Figure 3 can be rationalized qualitatively from the effects of coupling between the ground state and excited states of identical symmetry. This effect is significant for *trans*-ReO$_2$(tmen)$_2^+$, but small for *trans*-ReO$_2$(py)$_4^+$.[44,48] It has been shown to more strongly influence lower-energy luminescence bands,[43,44] and therefore a larger pressure-induced variation of $\Delta Q_{O=Re=O}$ is expected for complexes such as *trans*-ReO$_2$(en)$_2^+$, where the pressure-induced decrease of the energy difference between E_{00} and E_{max} is more pronounced than for the *trans*-dioxo complexes with higher-energy luminescence bands in Figures 3 and 4, leading

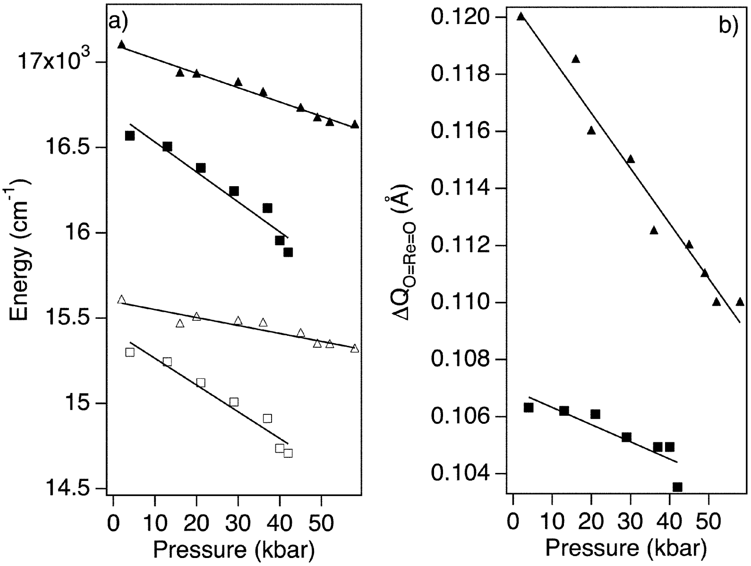

Figure 4. Pressure-induced variations of luminescence parameters for *trans*-ReO$_2$(py)$_4$I (squares) and *trans*-ReO$_2$(tmen)$_2$Cl (triangles). (a) Band maxima E$_{max}$ (open symbols) and electronic origins E$_{00}$ (solid symbols), (b) $\Delta Q_{O=Re=O}$. The slopes of the solid lines are summarized in Table 1.

to a decrease of $\Delta Q_{O=Re=O}$ larger by 25% than for *trans*-ReO$_2$ (tmen)$_2^+$, as summarized in Table 1. In addition to the luminescence energy, the size of the offset between ground- and emitting–state potential energy minima along the rhenium-ancillary ligand stretching coordinate also appears to influence the magnitude of the pressure-induced decrease of $\Delta Q_{O=Re=O}$. It is intuitively appealing to assume that large, monodentate ligands, such as pyridine, are more strongly affected by external pressure than compact, chelating ligands such as tetramethylethylenediamine, leading to the stronger red shift for *trans*-ReO$_2$(py)$_4$I, but this correlation is too simplistic, as a *trans*-dioxo complex with monodentate imidazole ligands shows a very small red-shift of the luminescence band maximum E$_{max}$ by only –2 cm^{-1}/kbar.[50] Pressure-dependent luminescence spectra reveal the important influence of the ancillary ligand, but it is obvious that a larger set of compounds needs to be studied in order to rationalize all observed effects. The comparison of the experimental and calculated luminescence spectra in Figure 3 leads to quantitative values for the parameters defining the ground- and emitting–state potential energy curves in Figure 3. The pressure-induced variations of $\Delta Q_{O=Re=O}$ and E_{00} or E_{max} are shown to be independent: a larger change of $\Delta Q_{O=Re=O}$ is observed for *trans*-ReO_2 $(tmen)_2Cl$ than for *trans*-$ReO_2(py)_4I$, but the inverse order is obtained for the red-shifts of E_{00} and E_{max}.

Mono-oxo complexes of d^2-configured metals provide an interesting comparison to *trans*-dioxo compounds. An illustrative example are molybdenum(IV) complexes, several of which have been shown in the past to be luminescent with easily discernible Mo-oxo progressions dominating the low-temperature spectra.[41,42,51] Vibronic progressions in the metal-oxo mode are shorter for mono-oxo compounds than for trans-dioxo complexes of both second and third row d-block metal ions. [41,42,44,51,52] Figure 5 shows the pressure-dependent luminescence spectra of MoOCl(CN-*t*-Bu)$_4$BPh$_4$. At ambient pressure, the first and second members of the progression in the Mo-oxo modes are visible as a shoulder at approximately 12700 cm^{-1} and as the overall maximum. Their relative intensities show no pressure-induced variation within

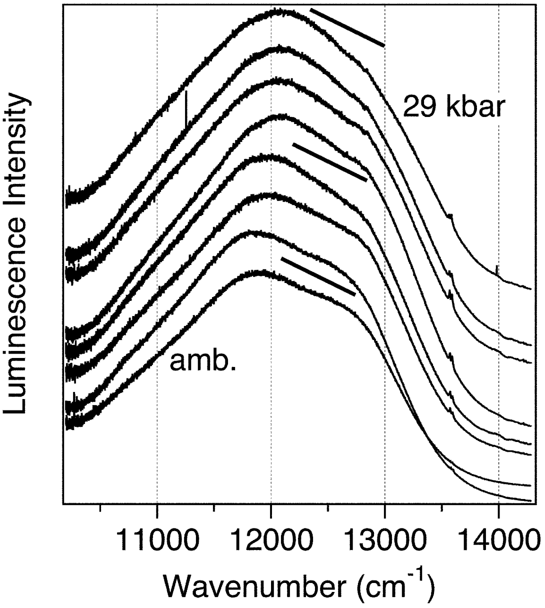

Figure 5. Pressure-dependent luminescence spectra of MoOCl(CN-*t*-Bu)$_4$BPh$_4$ at room temperature. The solid bars indicate the negligible variation of the intensity distribution within the vibronic progression in the Mo-oxo vibrational mode.

experimental accuracy, as indicated by the sloped lines in Figure 5, in contrast to the spectra in Figure 3, where a change is easily observed. This indicates that the offset $\Delta Q_{\text{Mo-oxo}}$ changes very little over the pressure range in Figure 5, an important difference between the *trans*-dioxo and mono-oxo moieties.

The band maximum in Figure 5 shows a blue shift of $+12\,\text{cm}^{-1}/\text{kbar}$ with pressure, in contrast to all *trans*-dioxo complexes in Figure 3 and Table 1, where a red-shift is observed. This is a consequence of the strong π-acceptor character of the isocyanide ligands. Their π-bonding interactions with the metal d_{xy} orbital lead to a decrease in energy as the Mo–C bonds are compressed. A mono-oxo complex with pyridine ancillary ligands, $MoOF(py)_4BPh_4$, shows a pressure-induced red shift of $-7.5\,\text{cm}^{-1}/\text{kbar}$ for its band maximum, similar to the *trans*-dioxo complex of rhenium(V) with pyridine ligands. The overview in this section is intended to illustrate that the predominantly metal-centered *d-d* transitions of metal-oxo complexes are well suited to a detailed exploration of pressure-induced luminescence effects caused by different metal-ligand bonds.

4. PRESSURE-INDUCED INCREASE OF LUMINESCENCE INTENSITIES: SQUARE-PLANAR COMPLEXES

The pressure-dependent luminescence spectra of a variety of square-planar complexes of platinum(II) have been studied.[11, 53–55] In the following, we focus on complexes with sulfur ligator atoms and *d-d* luminescence transitions. All crystal structures show metal-metal distances longer than 8 Å and no stacking of luminophores along the z axis, defined as the fourfold axis of the square-planar luminophore.[55,56]

The series of complexes compared in the following are $M(SCN)_4^{2-}$ and $M(SeCN)_4^{2-}$, where M denotes palladium(II) and platinum(II). Low-temperature luminescence spectra show rich resolved vibronic structure with progressions involving the totally symmetric M-S stretching modes, as well as the nontotally symmetric stretching mode and the S-M-S bending mode.[53,54,57] The lowest-energy electronic transition from the singlet ground state to a triplet excited state involves the population of the σ-antibonding $d_{x^2-y^2}$ orbital and leads to a large change in metal-ligand bonding, giving rise to the vibronic structure of the luminescence spectra and to an expected blue shift of the luminescence band maximum with pressure. Room-temperature luminescence spectra are

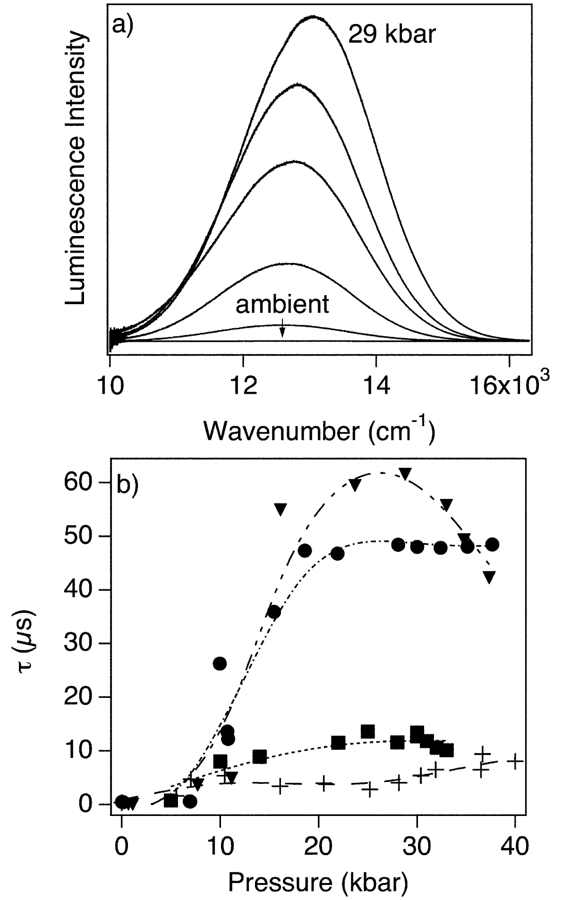

Figure 6. (a) Pressure–dependent luminescence spectra of $Pd(SCN)_4(n\text{-}Bu_4N)_2$ at room temperature. (b) Pressure-dependent luminescence lifetimes for $Pd(SCN)_4(n\text{-}Bu_4N)_2$ (circles), $Pd(SeCN)_4(n\text{-}Bu_4N)_2$ (triangles), $Pt(SCN)_4(n\text{-}Bu_4N)_2$ (squares) and $Pt(SeCN)_4$ $(n\text{-}Bu_4N)_2$ (crosses).

shown for $Pd(SCN)_4^{2-}$ in Figure 6a. In contrast to the metal-oxo complexes discussed in the preceding section, no vibronic structure is resolved. The band maximum shows a pressure-induced blue shift of $+29\,cm^{-1}$/kbar, similar in magnitude to the shifts observed for octahedral halide complexes of first-row transition metals.[8,31] The most obvious pressure effect is the dramatic increase of the luminescence intensity shown in Figure 6a.[54] The ambient-pressure luminescence is very weak, and temperature-dependent spectra and lifetimes indicate that nonradiative relaxation processes dominate the excited-state deactivation at room temperature. External pressure leads to more competitive radiative rates, resulting in more intense luminescence. The pressure dependent luminescence lifetimes in Figure 6b for all four compounds in this series show a distinct increase of the lifetime as pressure increases, indicating that nonradiative relaxation rates decrease substantially with pressure.[53] At the highest pressures in Figure 6b, intensities and lifetimes decrease, likely an indication of efficient energy-transfer among the closer-spaced complexes to quenching traps or pressure-induced imperfections. The increase of both luminescence intensities and lifetimes with pressure appears to be more pronounced for the palladium(II) complexes than for their platinum(II) analogs, as illustrated in Figure 6b, a difference that can not be correlated with other phenomenological quantities, such as the pressure-induced shifts of the luminescence maxima. These shifts are $+24\,\mathrm{cm}^{-1}$/kbar and $+29\,\mathrm{cm}^{-1}$/kbar for $Pt(SCN)_4^{2-}$ and $Pd(SCN)_4^{2-}$, respectively, but despite their similar blueshifts, very different enhancements of the luminescence intensities and lifetimes are observed for these two complexes in Figure 6b, indicating that the variation of other quantities, in particular the offsets ΔQ_i in Figure 1, are of importance.

The schematic view in Figure 1 is useful to qualitatively rationalize the pressure-induced decrease of the nonradiative relaxation rate. In the square-planar complexes, a decrease of ΔQ_i along several coordinates is expected as pressure increases, leading to a large increase of the activation energy ΔE_{act}, the classical barrier for nonradiative relaxation. This increase is strongly nonlinear, as illustrated in the inset to Figure 1. The ambient-pressure offsets ΔQ_i can be determined for all compounds from low-temperature spectra with resolved vibronic structure. These are an important ingredient to models for nonradiative relaxation rates, in addition to vibrational frequencies of the modes associated to these normal coordinates. Temperature-dependent luminescence lifetimes lead to best-fit values for the adjustable parameters of established theoretical models for the nonradiative relaxation rate constants, qualitatively corresponding to the energy barrier ΔE_{act} in Figure 1 and the pre-exponential factor and in the classical activation energy picture.[53] From this set of parameters, the variation of the nonradiative rate constant as the offsets ΔQ_i decrease is easily calculated without additional parameters. This variation is shown in Figure 7 for the four complexes as a function of

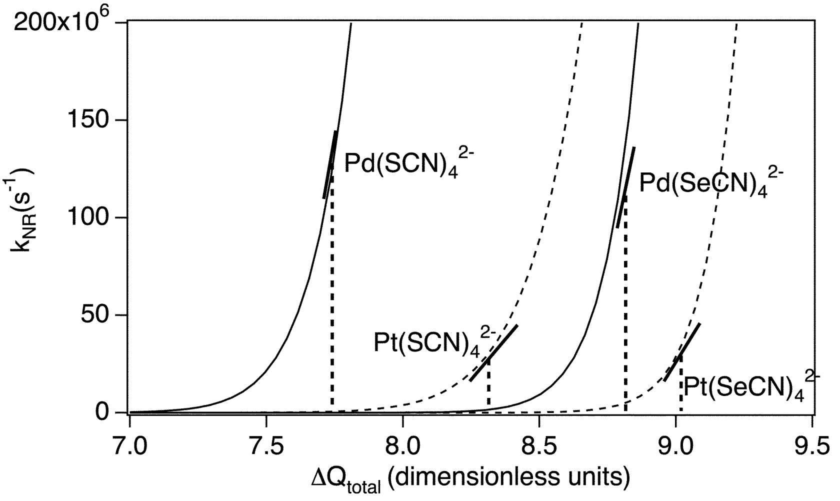

Figure 7. Variation of the nonradiative relaxation rate constant as a function of total offset between ground– and emitting–state potential energy minima for square-planar complexes.

the sum of all ΔQ_i values. External pressure causes a small decrease of ΔQ_{total}, and the slopes for each complex in Figure 7 indicate the magnitude of the variation of luminescence intensities and lifetimes. This simple approach immediately reveals larger slopes for both palladium(II) complexes than for their platinum(II) analogs. The pressure-dependent luminescence intensities and lifetimes provide therefore a detailed view on excited-state relaxation, not accessible from ambient-pressure data alone and again emphasizing the importance of the offsets ΔQ_i, whose variation is neglected in purely electronic models.

The influence of individual offsets ΔQ_i on the increases of luminescence intensities and lifetimes still has to be explored in detail for these square-planar complexes. A first step in this direction are complexes with chelating ligands. Figure 8 shows luminescence spectra of the Pd(pyrrole-*N*-carbodithioate)$_2$ complex. Its luminescence energy and bandwidth are very similar to those of $Pd(SCN)_4^{2-}$, confirming that it originates from a *d-d* transition. An obvious increase of the luminescence intensity is observed, but it is less pronounced than for the monodentate ligands in Figure 6a. It appears therefore that normal coordinates such as S-M-S bending that are "blocked" by the bidentate ligand play a significant role in the observed pressure effect. The changes in luminescence properties arising from intramolecular effects through

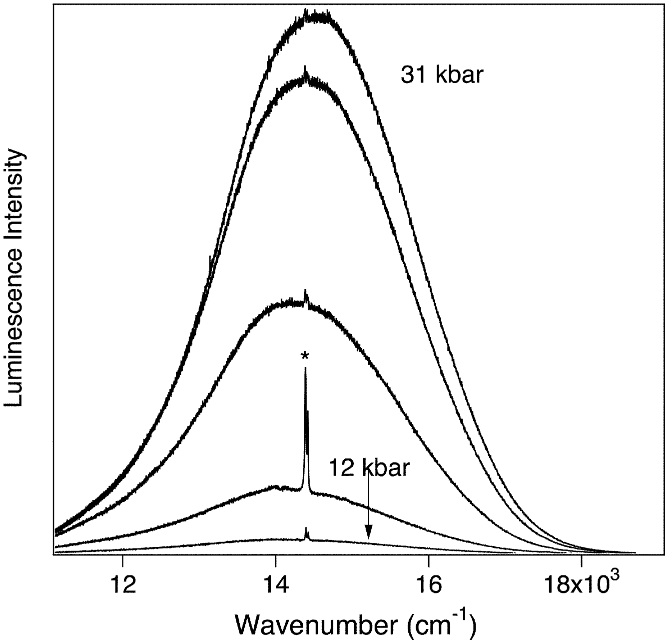

Figure 8. Pressure-dependent luminescence spectra of Pd(pyrrole-*N*-carbodithioate)$_2$ at room temperature. The asterisk denotes ruby luminescence used to calibrate the hydrostatic pressure in the diamond anvil cell.

external pressure can again be rationalized in the context of the model defined in Figure 1.

5. CONCLUSIONS AND OUTLOOK

The previous sections illustrate how detailed insight on intramolecular effects can be gained from pressure-dependent luminescence spectra. The exploration of such effects has become very accessible, due to sensitive detection with microscope spectrometers combined to established, versatile diamond anvil cells. An interesting direction of future research is to explore new intermolecular interactions to amplify the spectroscopic effects induced by pressure. Such studies will most likely require a combination of pressure-dependent spectroscopy and crystallography. Pioneering work in this area has been carried out for salts of $Au(CN)_2^-$[6,13] and $Pt(CN)_4^{2-}$.[11] Other gold(I) compounds with simpler structures also appear to be promising, as illustrated in Figure 9 for Au$_2$(pyrrole-*N*-carbodithioate)$_2$, a

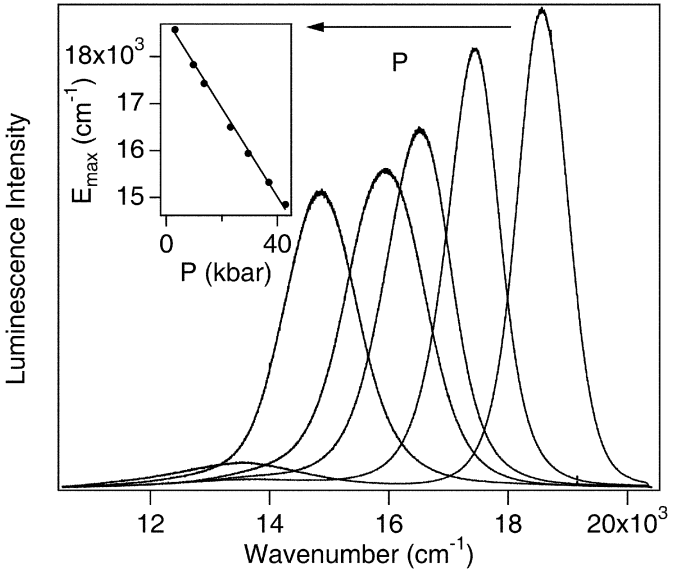

Figure 9. Pressure-dependent luminescence spectra of Au_2(pyrrole-*N*-carbodithioate$)_2$. The inset shows the variation of the band maximum with pressure.

compound with bimetallic units bridged by two ligands.[22,58] A large pressure-induced red shift of the band maximum by approximately $-100\,cm^{-1}$/kbar is observed, as shown in the inset to Figure 9, indicating that intriguing pressure effects occur for compounds other than the established cyanide complexes of late transition metal ions.

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