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# Comments on Inorganic Chemistry: A Journal of Critical Discussion of the Current Literature

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# RAMAN SPECTROSCOPY OF TRANSITION METAL COMPLEXES: MOLECULAR VIBRATIONAL FREQUENCIES, PHASE TRANSITIONS, ISOMERS, AND ELECTRONIC STRUCTURE

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# RAMAN SPECTROSCOPY OF TRANSITION METAL COMPLEXES: MOLECULAR VIBRATIONAL FREQUENCIES, PHASE TRANSITIONS, ISOMERS, AND ELECTRONIC STRUCTURE

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Raman spectroscopy is less commonly used than infrared absorption spectroscopy for the vibrational characterization of inorganic compounds, but its applications have significantly increased over the past decade due to high-performance instrumentation. This Comment describes the use of Raman spectroscopy for the characterization of inorganic compounds. We illustrate the application of Raman techniques with the spectra of a series of classic transition metal complexes recorded at variable temperature and pressure. Illustrative examples include [Ni(NH<sub>3</sub>)<sub>6</sub>]X<sub>2</sub> compounds (X=Cl<sup>-</sup> or [NO<sub>3</sub>]<sup>-</sup>), thermochromic squareplanar or tetrahedral [CuCl<sub>4</sub>]<sup>2-</sup> complexes, the *cis* and *trans* [Cu(glycinasquare-planar [Pt(dithiocarbamate)<sub>2</sub>]  $to_{2} \cdot H_{2}O$  complexes, and [Pd(dithiocarbamate)<sub>2</sub>] complexes, as well as metal-oxo and trans-dioxo complexes of metals with the d<sup>2</sup> electron configuration, such as molybdenum(IV), rhenium(V), and osmium(VI). The variation of the symmetric metal-ligand stretching frequencies with temperature or pressure is presented. Resonance Raman spectroscopy provides a detailed characterization of the electronic structure for the [Ru(BQDI)(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] complex with the observation of overtones and combination bands at the excitation wavelength of 488 nm. Time-dependent theoretical calculations for the [Ru(BQDI)(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] complex are used to rationalize the resonance Raman intensities and to determine excited-state properties.

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Molecular lanthanide clusters are used to illustrate the applications of Raman spectroscopy to polymetallic complexes.

*Keywords*: lanthanide clusters, phase transition, polymetallic complexes, Raman spectroscopy, resonance Raman spectroscopy, thermochromism, transition metal complexes, variable pressure spectroscopy, variable temperature spectroscopy

#### 1. INTRODUCTION

Vibrational spectroscopy is commonly used to characterize transition metal complexes and organometallic compounds. The two main techniques are infrared and Raman spectroscopy, with the former better known and more frequently applied, as illustrated for example by the substantial number of references to the infrared data in Nakamoto's books<sup>[1,2]</sup> and other compilations.<sup>[3,4]</sup> This preference is mainly due to widely available. sensitive, easy-to-use IR and FTIR spectrometers, concisely summarized by Harris and Bertolucci in their book on symmetry and spectroscopy published in 1978:<sup>[5]</sup> "At present, instrumentation of IR spectroscopy is generally more sensitive than that of Raman spectroscopy in terms of the amount of signal one can get from a given amount of sample. This was not the case before about 1950 when Raman spectroscopy was the better developed of the two techniques, and it may not be the case too long in the future." Over the past decade, Raman spectroscopy has indeed again become a frequently used technique for the characterization of many inorganic compounds.<sup>[6-13]</sup> This renewed interest is due to a new generation of optics and CCD detectors enabling chemists to record very weak signals with excellent signal/noise ratios. Advances in laser technology and the design of very efficient filters to eliminate elastically scattered excitation light are additional important instrumental developments that have made Raman spectroscopy more versatile and data acquisition more efficient. The technique is non-destructive and requires only minimal sample preparation, in particular for solid inorganic compounds. Overviews and detailed descriptions of practical aspects are given elsewhere.[14-20]

In this Comment, we illustrate the application of Raman techniques to a series of transition metal complexes. A number of spectra recorded at variable temperature and pressure are presented to build on the textbook literature, where often only spectra of simple solvent molecules are presented and discussed. Our choice of examples is intended to bridge the gap between introductory descriptions of Raman spectroscopy and the research inorganic literature, where often highly specialized topics, such as resonance Raman intensities, are used to gain insight.

Raman spectra recorded at variable temperature and pressure provide quantitative insight on frequency variations, leading to detailed information ranging from molecular electronic structure to solid-state phase transitions. The first two examples presented in the following are the variable-temperature Raman spectra of octahedral  $[Ni(NH_3)_6]^{2+}$ complexes crystallized as chloride and nitrate salts.<sup>[21-31]</sup> The Stokes and anti-Stokes Raman spectra are presented for one of the compounds, allowing for a comparison usually only given for the simplest molecules, such as CCl<sub>4</sub>.<sup>[11,12]</sup> An easily visible structural phase transition occurs for thermochromic square-planar or tetrahedral [CuCl<sub>4</sub>]<sup>2-</sup> complexes. We present Raman spectra at variable temperature for the well-known thermochromism phenomenon of  $(DEA)_2[CuCl_4]$  (DEA = diethylammonium).<sup>[32-39]</sup> A comparison of infrared and Raman spectra is presented for the *cis* and *trans* [Cu(glycinato)<sub>2</sub>] · H<sub>2</sub>O complexes.<sup>[40-42]</sup> The trans [Cu(glycinato)<sub>2</sub>] · H<sub>2</sub>O compound shows only the symmetric or the antisymmetric stretching mode, according to the IR and Raman selection rules, but both modes are observed in the cis isomer.

Variable-pressure Raman spectra of square-planar [Pt(dithiocarbamate)<sub>2</sub>] and [Pd(dithiocarbamate)<sub>2</sub>] complexes<sup>[43]</sup> illustrate the effect of external pressure on  $\nu$ (M-S) stretching frequencies. A series of *trans*-dioxo complexes, [OsO<sub>2</sub>(ethylenediamine)<sub>2</sub>]Cl<sub>2</sub>, [ReO<sub>2</sub>(ethylenediamine)<sub>2</sub>]Cl and [ReO<sub>2</sub>(tetramethylethylenediamine)<sub>2</sub>]Cl, show short metal-oxygen double bonds. The variation of the  $\nu_s$ (O=M = O) symmetric stretching frequency at variable pressures is presented,<sup>[44-48]</sup> and compared to monooxo complexes of Mo<sup>IV</sup> and Re<sup>V.[48,49]</sup>

Resonance Raman spectroscopy provides detailed insight on the electronic structure for complexes with an intense absorption band at the excitation wavelength used.<sup>[50-54]</sup> A well-suited example is the [Ru(BQDI)(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] complex, with BQDI = *o*-benzoquinonediimine, whose Raman spectrum shows many overtones and combination bands.<sup>[55,56]</sup> Time-dependent theoretical calculations allow the excited-state characteristics to be determined quantitatively.

Polymetallic complexes are a focus of modern coordination chemistry. Raman spectroscopy can be used to characterize lanthanide clusters with interesting magnetic properties, as shown with the concluding examples.

#### 2. RAMAN SPECTROSCOPY AT VARIABLE TEMPERATURE

#### 2.1. Hexaamine Nickel(II) Nitrate Complexes: [Ni(NH<sub>3</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub>

Octahedral transition metal complexes are abundant and the symmetry of their vibrational modes with Raman or infrared activity is easily established.<sup>[11]</sup> We choose the  $[Ni(NH_3)_6]^{2+}$  complex as a representative example. Figure 1 shows both the conventional Stokes Raman spectra at variable temperature, where scattered light with energies lower than the excitation energy is recorded, and also anti-Stokes Raman spectra, where scattered light with energies higher than the excitation energy is recorded. The absolute frequency in cm<sup>-1</sup> is shown on the top horizontal axis (excitation energy 20492 cm<sup>-1</sup>) in order to clearly show the relationship between excitation wavelength, Stokes and anti-Stokes Raman shifts. Intensities of anti-Stokes Raman transitions depend on thermal populations of excited vibrational levels, leading to very weak signals at low temperature, in



Figure 1. Temperature dependence of the Raman spectra of  $[Ni(NH_3)_6](NO_3)_2$  showing both the Stokes (a) and anti-Stokes (b) portions of the spectra (excitation wavelength 488 nm, corresponding to 20492 cm<sup>-1</sup>). The evolution of the  $\nu_1(NO_3^-)$  stretching intensity with temperature (anti-Stokes) is shown (c). All Raman spectra are normalized on the most intense band. Raman shifts of the Stokes spectra are given as negative numbers.

particular for high-frequency modes. The most intense band in the Stokes spectra arise from the nitrate group at approximately  $1050 \text{ cm}^{-1}$ . The corresponding transition in the anti-Stokes spectra is much weaker at all temperatures and is not detected at 80 K, the lowest temperature in Figure 1. At low temperature, only the low-frequency bands are observable, as illustrated in Figure 1(b). The spectra also show bands at low frequencies, for example the characteristic symmetric stretching mode of the octahedral [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> complex, identified as  $\nu_s$ (Ni-N) in Figure 1, near 400 cm<sup>-1</sup>.<sup>[24,27]</sup> At temperatures higher than 120 K, the intense, characteristic bands of the nitrate group at approximately 710 cm<sup>-1</sup> and 1050 cm<sup>-1</sup> appear and their intensities increase with temperature. The intensity of the Raman band near 1050 cm<sup>-1</sup> is shown in Figure 1(c) and can be fitted using:

$$f(T) = C \times \frac{e^{\left(-\frac{1050}{kT}\right)}}{1 + e^{\left(-\frac{1050}{kT}\right)}}$$
(1)

In Equation (1),  $k = 0.69509 \text{ cm}^{-1}/\text{K}$ , the Boltzmann constant, and C is an adjustable scaling factor.

This example shows that both Stokes and anti-Stokes spectra are easy to record and can be used to determine the main vibrational frequencies, e.g., for the  $\nu_s$ (Ni-N) symmetric stretching mode of octahedral  $[Ni(NH_3)_6]^{2+}$  complexes.

# 2.2. Hexaamine Nickel(II) Chloride Complexes: [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub>

This example is again focusing on the  $[Ni(NH_3)_6]^{2+}$  complex, but crystallized with a different anion, Cl<sup>-</sup>. The Stokes Raman spectra of a large region including high frequencies up to 4000 cm<sup>-1</sup> are given in Figure 2(a). The chloride salt does not show the characteristic bands of the nitrate group, easily discernible in Figure 1. As in the case of the nitrate salt, the  $\nu_s$ (Ni-N) symmetric stretching mode with a frequency of approximately 400 cm<sup>-1</sup> can be identified and is shown in detail in Figure 2(c). A characteristic intense band corresponding to the  $\delta_{as}$ (NH<sub>3</sub>) antisymmetric bending mode is identifiable at approximately 1585 cm<sup>-1</sup>. Its linewidth f(T) increases with temperature, as shown in Figure 2(b). This increase can be analyzed by a least-squares fit using Equation (2), given by the dotted line in Figure 2(b):<sup>[57,58]</sup>

$$\mathbf{f}(\mathbf{T}) = \mathbf{A} + \mathbf{B} \times \mathbf{T} + \mathbf{C} \times \mathbf{e}^{\frac{-\mathbf{D}}{\mathbf{k}\mathbf{T}}}$$
(2)

In this equation,  $k = 0.69509 \text{ cm}^{-1}/\text{K}$  denotes the Boltzmann constant and A, B, C, and D are adjustable parameters. The least-squares



Figure 2. Raman spectra of  $[Ni(NH_3)_6]Cl_2$  at variable temperature (a) and evolution of the linewidth for the  $\delta_{as}(NH_3)$  antisymmetric deformation mode with temperature (b and c) (excitation wavelength 488 nm). All Raman spectra are normalized on the most intense band. According to convention, only the Stokes region of the Raman spectra is shown and all Raman shifts are given as positive numbers.

fit leads to values of  $30 \text{ cm}^{-1}$  for A,  $-0.32 \text{ cm}^{-1}/\text{K}$  for B, 275 cm<sup>-1</sup> for C, and 124 cm<sup>-1</sup> for D. The nonlinear increase of the width defines the values for C and D. The latter is an estimate for the frequency of low-energy, possibly delocalized modes involving the [NH<sub>3</sub>] ligands.

At high frequencies, it is possible to identify the symmetric and antisymmetric stretching modes of [NH<sub>3</sub>] ligands between 3000 cm<sup>-1</sup> and 3600 cm<sup>-1</sup> (E<sub>g</sub>  $\nu_s$ (N-H) = 3160 cm<sup>-1</sup>, A<sub>Ig</sub>  $\nu_s$ (N-H) = 3250 cm<sup>-1</sup> and T<sub>2g</sub>  $\nu_{as}$ (N-H) = 3320 cm<sup>-1</sup>). One of these frequencies is very close to the double of the  $\delta_{as}$ (NH<sub>3</sub>) frequency of 1585 cm<sup>-1</sup>. It is therefore possible that overtones involving the 1585 cm<sup>-1</sup> mode are involved, gaining intensity through a Fermi resonance.<sup>[24]</sup>

# 2.3. Comparison of the ν<sub>s</sub>(Ni-N) Symmetric Stretching Frequencies for [Ni(NH<sub>3</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub> and [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub>

The transitions corresponding to  $\nu_s$ (Ni-N) symmetric stretching modes for both salts in Figures 1 and 2 are identified. In the chloride salt, we note the presence of a narrow, symmetric band with a linear shift of its maximum by  $7 \text{ cm}^{-1}$  between 80 K and 300 K to lower frequencies  $(-0.03 \text{ cm}^{-1}/\text{K})$ , a sign of a slight structural variation, as illustrated in Figure 3(b).

For the nitrate salt, the situation is not as straightforward. At 80 K, an asymmetric band with a single maximum is observed, as shown in Figure 3(a). On increasing temperature to approximately from 120 K to 200 K, a broader band appears, possibly a superposition of several, slightly different  $\nu_s$ (Ni-N) bands for inequivalent complexes. At 240 K, the maximum shifts to higher frequencies and the band remains asymmetric at 300 K, becoming symmetric at 350 K. It is therefore impossible in this case to give a simple trend of the evolution of the  $\nu_s$ (Ni-N) symmetric stretching frequency with temperature, in contrast to the chloride salt.

Solid-state phase transitions have been reported for the nitrate salt.<sup>[23,25,27,28]</sup> The nitrate salt can exist in three solid modifications: I – cubic F, II – cubic P, and III – orthorhombic. The mechanism of the I $\rightarrow$ II and II $\rightarrow$ III transformations has been discussed.<sup>[23,25]</sup> The



Figure 3. Temperature-dependent Raman spectra showing the shift of the  $\nu_s$ (Ni-N) symmetric stretching frequency of [Ni(NH<sub>3</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub> (a) and [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub> (b) (excitation wavelength 488 nm). All Raman spectra are normalized on the most intense band.

I – cubic F and II – cubic P phases consist of flat triangular  $[NO_3]^-$  and octahedral  $[Ni(NH_3)_6]^{2+}$  units interlocking into a CaF<sub>2</sub>-type arrangement. In the II – cubic P phase, it is assumed that the  $[NO_3]^-$  ions execute significant torsional oscillations and reorientations in the crystal structure, which is a modification of the I – Cubic F phase. The phase transition leading to the III – orthorhombic phase may be a result of an orientational ordering of the  $[NO_3]^-$  in the crystal lattice. The study of the nitrate salt by X-ray powder diffraction at variable temperature shows a cycle of phase transitions with the formation of pure or mixed phases by heating or cooling. The phase transitions are observed through shifts of Bragg peaks, but mainly by splittings and the appearance of several new Bragg peaks, characteristic for a new phase.

Below 104 K, only Phase III was identified by X-ray diffraction. The Raman spectrum at 80 K therefore corresponds to a pure phase. Between 104 K and 230 K, two phases are potentially present, and the Raman spectra at 120 K, 160 K, 200 K correspond to this mixture. Between 230 K and 246 K, a single phase II is obtained, which may correspond to the Raman spectrum recorded at 240 K. Between 246 K and 256 K, a new mixture was shown with phases I and II, but no Raman spectrum has been recorded in this temperature range. Beyond 256 K, only phase I exists, corresponding to the Raman spectra recorded at 300 K and at 350 K.

#### 2.4. Thermochromic Tetrachlorocuprate Complexes

The third example illustrates the application of Raman spectroscopy to phase transitions involving changes of molecular structure, in contrast to the phase transitions involving packing changes presented in the preceding section. A phase transition involving the modification of the molecular structure has been documented for several  $[CuCl_4]^{2-}$  complexes.<sup>[32-39]</sup> These changes in molecular structure may occur as the result of external factors such as temperature, pressure, or photo-excitation. Both intramolecular and intermolecular effects play a role in the change of chromophore geometry. Intramolecular effects impact the geometry directly, but the intermolecular interactions can stabilize the chromophore in a different conformation in the structural packing. A temperature change can lead to a reorganized structural packing with different intermolecular contacts. The  $[CuCl_4]^{2-}$  complexes show a strong thermochromism, with compounds such as (DEA)<sub>2</sub>[CuCl<sub>4</sub>] that change color by heating. The

chromophore structure passes from approximately square planar with a green color to approximately tetrahedral with a yellow color at  $45^{\circ}$ C. Raman spectroscopy allows one to distinguish between the two forms.

The Raman spectra of five complexes have been recorded and are summarized in Figure 4: (DEA)<sub>2</sub>[CuCl<sub>4</sub>] ( $T_d$ ), (DEA)<sub>2</sub>[CuCl<sub>4</sub>] ( $D_{4h}$ ), Cs<sub>2</sub>[CuCl<sub>4</sub>] ( $T_d$ ), (DMA)<sub>3</sub>[CuCl<sub>5</sub>] ( $T_d$ ) and (DMA)<sub>2</sub>[CuCl<sub>4</sub>] ( $T_d$ ). We observe a  $\nu_s$ (Cu-Cl) (A<sub>1</sub>) symmetric stretching frequency at 281 cm<sup>-1</sup> and a T<sub>2</sub> frequency at 223 cm<sup>-1</sup> for the high-temperature (DEA)<sub>2</sub>[CuCl<sub>4</sub>] phase. In the room-temperature (DEA)<sub>2</sub>[CuCl<sub>4</sub>] phase, the A<sub>1</sub> symmetric stretching frequency and the T<sub>2</sub> frequency are 277 cm<sup>-1</sup> and 188 cm<sup>-1</sup>, respectively.

A series of measurements on the (DEA)<sub>2</sub>[CuCl<sub>4</sub>] compound starting with the high-temperature phase and slowly cooling to room temperature shows a continuous decrease of the T<sub>2</sub> frequency from approximately 220 cm<sup>-1</sup>. The frequency for the room-temperature phase is 188 cm<sup>-1</sup>. Table 1 summarizes vibrational frequencies for the five compounds and particularly for the two (DEA)<sub>2</sub>CuCl<sub>4</sub> phases, where values A<sub>1</sub> of the A<sub>1</sub> symmetric stretching frequency and the T<sub>2</sub> frequency obtained from Raman spectra are compared to literature values from infrared spectra. Figure 4(b) shows the variations of the  $\nu_s$ (Cu-Cl) symmetric stretching frequencies with the *trans* Cl-Cu-Cl angle in the [CuCl<sub>4</sub>]<sup>2-</sup> complexes. We note that, for the (DEA)<sub>2</sub>[CuCl<sub>4</sub>] compounds, there are complexes with different *trans* 



Figure 4. Raman spectra of  $[CuCl_4]^{2-}$  complexes with different counterions (a) (excitation wavelength 514 nm). All Raman spectra are normalized on the most intense band. Correlation between the  $\nu_s$ (Cu-Cl) symmetric stretching frequency and the *trans* Cl-Cu-Cl angles (b) with values of 180° for the perfect square-planar and 109.5° for the perfect tetrahedral structures. Ligand abbreviations: DEA = diethylammonium and DMA = dimethylammonium.

Compound	<i>trans</i> angle (°)	Raman A <sub>1</sub> frequency (cm <sup>-1</sup> )	Raman T <sub>2</sub> frequency (cm <sup>-1</sup> )	Infrared A <sub>1</sub> frequency (cm <sup>-1</sup> )	Infrared T <sub>2</sub> frequency (cm <sup>-1</sup> )
$(DEA)_2[CuCl_4](T_d)$	135–147	281	223	295	220
$(DEA)_2[CuCl_4] (D_{4h})$	145-179	277	188	282	186
Cs <sub>2</sub> [CuCl <sub>4</sub> ]	124	291	267	292	257
(DMA) <sub>3</sub> [CuCl <sub>5</sub> ]	136	284	239	295	230
(DMA) <sub>2</sub> [CuCl <sub>4</sub> ]	/	284	246	/	/

Table 1. Comparison of the *trans* Cl-Cu-Cl angles, the  $\nu_s$ (Cu-Cl) symmetric stretching frequency A<sub>1</sub> and the T<sub>2</sub> frequency, obtained by Raman spectra and from the infrared literature

Ligand abbreviation: DEA = diethylammonium and DMA = dimethylammonium.

Cl-Cu-Cl angles, and the angles are given between the minimum and maximum values  $(135-147^{\circ} T_{d} \text{ and } 145-179^{\circ} D_{4h})$ . The example spectra show that it is possible to probe structural phase transitions through the  $\nu_{s}$ (M-L) symmetric stretching frequency. These thermochromic compounds have also been studied at variable pressure with visible absorption spectroscopy and a pressure-induced phase transition (piezochromism) has been observed,<sup>[59]</sup> corresponding to a variation of the chromophore geometry between square planar, tetrahedral or intermediate, as pressure increases.

In contrast to the  $[CuCl_4]^{2-}$  complexes, where the main structural change involves the *trans* angle, other complexes can present a phase transition where bond lengths change significantly. A well-known example are spin crossover compounds such as Fe(phen)<sub>2</sub>(NCS)<sub>2</sub>.<sup>[60,61]</sup> This complex shows a sudden change of the  $\nu$ (C-N) Raman stretching frequency of the [NCS]<sup>-</sup> ligands from 2070 cm<sup>-1</sup> at 300 K to 2114 cm<sup>-1</sup> at 100 K, a change of 44 cm<sup>-1</sup> indicating the spin crossover from the high-spin state to low-spin state. This frequency change reflects the different structures of the high-spin and low-spin forms of this complex: the Fe-N(NCS) bond lengths range between 2.057(4) Å and 2.199(3) Å at room temperature for the high-spin state, and between 1.958(4) Å and 2.014(4) Å at lower temperature (130 K) for the low-spin state, corresponding to a strong compression of the octahedral complex.<sup>[62]</sup>

#### 2.5. The cis and trans lsomers of [Cu(Glycinato)<sub>2</sub>] · H<sub>2</sub>O

*Cis* and *trans* isomers popular in inorganic teaching laboratories are the *cis*  $[Cu(glycinato)_2] \cdot H_2O$  and *trans*- $[Cu(glycinato)_2] \cdot H_2O$  complexes

with  $C_{2v}$  and  $C_{2h}$  point group symmetry, respectively. Their Raman and IR spectra are shown in Figure 5. The selection rules for the *trans* isomer indicate that Raman active modes will be infrared inactive and inversely, leading to Raman active  $A_g$  and  $B_g$  modes that are infrared inactive while the  $A_u$  and  $B_u$  vibrational modes are infrared active but Raman inactive. This comparison illustrates the benefit of combining infrared and Raman spectra. However, the measurement of IR spectra below approximately 350 cm<sup>-1</sup> is difficult or impossible due to the absorption of KBr optics. In contrast, Raman spectra can be easily recorded at low frequencies allowing access to the region below 350 cm<sup>-1</sup>, corresponding essentially to the  $\nu$ (M-L) stretching modes. The Raman spectra in Figure 5 have higher resolution across the entire frequency range and well-defined peaks, while the infrared spectra show several intense, broad bands corresponding to overlapping transitions. A notable example occurs in



Figure 5. Temperature dependence of Raman spectra (bottom) and room-temperature infrared spectra (top) of *cis* and *trans*  $[Cu(glycinato)_2] \cdot H_2O$  (excitation wavelength 488 nm). All Raman spectra are normalized on the most intense band.

the region between  $3100 \text{ cm}^{-1}$  and  $3400 \text{ cm}^{-1}$ , where the distinction between different modes is much more obvious in the Raman spectra. The presence of intense transitions due to  $\nu$ (O-H) stretching modes between  $3000 \text{ cm}^{-1}$  and  $3500 \text{ cm}^{-1}$  complicates the analyses of the infrared spectra, illustrating a practical advantage of Raman spectroscopy in this frequency range for samples containing O-H groups. The well-defined peaks observed at  $3170 \text{ cm}^{-1}$ ,  $3255 \text{ cm}^{-1}$ ,  $3340 \text{ cm}^{-1}$  for the *cis* compound and  $3210 \text{ cm}^{-1}$ ,  $3260 \text{ cm}^{-1}$ ,  $3310 \text{ cm}^{-1}$  for the *trans* compound in the Raman spectra coincide with the maxima at  $3160 \text{ cm}^{-1}$ ,  $3250 \text{ cm}^{-1}$ , and  $3320 \text{ cm}^{-1}$  assigned as  $\nu$ (N-H) stretching modes for [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> in Figure 2. The comparison in Figure 5 therefore allows us to distinguish between  $\nu$ (O-H) and  $\nu$ (N-H) stretching modes with very similar vibrational frequencies.

Figure 6 shows a detailed view of the low-frequency region. The analysis of the metal-ligand stretching modes of the *cis*-[Cu(glycinato)<sub>2</sub>] · H<sub>2</sub>O compound is straightforward. The Raman spectra recorded at 80 K show the  $\nu_s$ (Cu-O) symmetric stretching frequency at 282 cm<sup>-1</sup>, the  $\nu_{as}$ (Cu-O) antisymmetric stretching frequency at 340 cm<sup>-1</sup>, the  $\nu_s$ (Cu-N)



Figure 6. Temperature dependence of Raman spectra between  $100 \text{ cm}^{-1}$  and  $600 \text{ cm}^{-1}$  of *cis* (bottom) and *trans* (top) [Cu(glycinato)<sub>2</sub>]  $\cdot$  H<sub>2</sub>O (a), and infrared spectra between 300 and 600 cm<sup>-1</sup> of *cis* (solid line) and *trans* (dashed line) [Cu(glycinato)<sub>2</sub>]  $\cdot$  H<sub>2</sub>O (b). All Raman spectra are normalized on the most intense band.

symmetric stretching frequency at 459 cm<sup>-1</sup>, and the  $\nu_{as}$ (Cu-N) antisymmetric stretching frequency at 481 cm<sup>-1</sup>. In the infrared spectrum recorded at 293 K, the  $\nu_s$ (Cu-O) symmetric stretching frequency is not observable, but the  $\nu_{as}$ (Cu-O) antisymmetric stretching frequency is 334 cm<sup>-1</sup>, the  $\nu_s$ (Cu-N) symmetric stretching frequency is observed at 457 cm<sup>-1</sup>, the  $\nu_{as}$ (Cu-N) antisymmetric stretching frequency at 477 cm<sup>-1</sup>, frequencies identical within experimental precision to those obtained from the Raman spectra. The spectra of the *trans* compound are different from the *cis* isomer, and the analysis is more delicate. The Raman spectra recorded at 309 cm<sup>-1</sup> and 469 cm<sup>-1</sup>, respectively. In contrast, the infrared spectra recorded at 293 K show only the  $\nu_{as}$ (Cu-O) and  $\nu_{as}$ (Cu-O) and  $\nu_{as}$ (Cu-N) antisymmetric stretching modes at 334 cm<sup>-1</sup> and 482 cm<sup>-1</sup>, respectively.

All data for the *cis* and *trans*  $[Cu(glycinato)_2] \cdot H_2O$  compounds are summarized in Table 2, providing detailed and IR or Raman activities for the two isomers.

The best-known set of *cis-trans* stereoisomers are those of  $[PtCl_2(NH_3)_2]$  because of the anti-tumor activity of the *cis* isomer. The Raman and IR spectra of the metal-ligand stretching modes show patterns similar to the  $[Cu(glycinato)_2]$  isomers presented above. The IR spectra of the two  $[PtCl_2(NH_3)_2]$  isomers and their palladium(II) analogs were reported decades ago,<sup>[63,64]</sup> with the *cis* isomer having four infrared-active metal-ligand stretching modes, as expected for its  $C_{2v}$  point group

Compound	Raman vibrational frequency (cm <sup>-1</sup> )	Infrared vibrational frequency (cm <sup>-1</sup> )	Assignment	Mode	Raman* Activity	Infrared* Activity
Cis [Cu(glycinato) <sub>2</sub> ]	282	/	ν <sub>s</sub> (Cu-O)	$A_1$	А	А
$H_2O(C_{2v})$	459	457	$\nu_s$ (Cu-N)			
	340	334	ν <sub>as</sub> (Cu-O)	$B_1$	Α	Α
	481	477	$\nu_{as}$ (Cu-N)			
Trans [Cu(glycinato) <sub>2</sub> ] ·	309	/	ν <sub>s</sub> (Cu-O)	$A_{g}$	Α	Ι
$H_2O(C_{2h})$	469	/	$\nu_s$ (Cu-N)	5		
	/	334	ν <sub>as</sub> (Cu-O)	$\mathbf{B}_{\mathbf{u}}$	Ι	А
	/	482	$\nu_{as}$ (Cu-N)			

Table 2. Comparison between the *cis* and *trans*  $[Cu(glycinato)_2] \cdot H_2O$ ; activity on the Raman and infrared spectra

 $^{*}A = active and I = inactive.$ 

symmetry. Their frequencies are  $324 \text{ cm}^{-1}$  and  $317 \text{ cm}^{-1}$  for the symmetric and  $\nu_{as}$ (Pt-Cl) antisymmetric stretching modes, along with  $517 \text{ cm}^{-1}$  and  $508 \text{ cm}^{-1}$  for the symmetric and  $\nu_{as}$ (Pt-N) antisymmetric stretching modes. The frequency differences between symmetric and antisymmetric modes are smaller than for the [Cu(glycinato)<sub>2</sub>] complex. The *trans* isomer with D<sub>2h</sub> point group symmetry shows only two infrared active metal-ligand stretching modes, corresponding to the antisymmetric stretching modes. The symmetric stretching modes are Raman active.<sup>[65–67]</sup> Detailed Raman spectra have been reported recently, and these highquality vibrational spectra are used as benchmark data for theoretical modeling aimed at drug development, emphasizing the importance of both Raman and infrared spectroscopy.<sup>[67]</sup>

# 3. RAMAN SPECTROSCOPY AT VARIABLE PRESSURE

# 3.1. Dithiocarbamate Complexes of Platinum(II) and Palladium(II)

Raman spectroscopy at variable pressure provides insight on subtle changes of bond lengths and other structural parameters. In addition to vibrational frequencies, trends are obtained through pressure variation, leading to additional information relevant to electronic structure, intermolecular effects, or other aspects. Representative examples are the Raman spectra of platinum(II) and palladium(II) dithiocarbamate complexes shown in Figure 7.<sup>[43]</sup> The spectra are well resolved and have a very high signal to noise ratio. All Raman bands shift to higher frequencies with increasing pressure. The  $\nu$ (M-S) symmetric stretching frequency for platinum(II) and palladium(II) complexes is easily identified at  $323 \text{ cm}^{-1}$  and  $300 \text{ cm}^{-1}$ , respectively, as is the  $\delta_s(SCS)$  symmetric bending mode of the dithiocarbamate ligands at  $464 \text{ cm}^{-1}$  and  $455 \text{ cm}^{-1}$ , assigned in Figure 7. The pressure dependence of  $\nu$ (M-S) is characterized by slopes of  $+0.35 \text{ cm}^{-1}/\text{kbar}$  and  $+0.37 \text{ cm}^{-1}/\text{kbar}$  for the platinum(II) and palladium(II) complexes, respectively. These values are identical within experimental precision and are in the typical range for metalligand single bonds. The  $\delta_s(SCS)$  symmetric bending frequencies vary by  $+0.44 \text{ cm}^{-1}/\text{kbar}$  and  $+0.47 \text{ cm}^{-1}/\text{kbar}$  for the [Pt(PDTC)<sub>2</sub>] and [Pd(PDTC)<sub>2</sub>] complexes, respectively, a stronger modification than observed for the stretching mode. This trend is observed for many compounds, illustrated, e.g., by  $K_2[PtCl_4]$ , where the infrared active  $\nu(Pt-Cl)$ 



Figure 7. Pressure dependence of Raman spectra of  $[Pt(PDTC)_2]$  (a) and  $[Pd(PDTC)_2]$  (b) between 150 cm<sup>-1</sup> and 600 cm<sup>-1</sup>. Ligand abbreviation: PDTC = pyrrolidine-*N*-dithiocarbamate.

stretching frequency varies by  $+0.25 \text{ cm}^{-1}/\text{kbar}$  and the  $\delta_s$ (ClPtCl) symmetric bending frequency by  $+0.46 \text{ cm}^{-1}/\text{kbar}$ .<sup>[20]</sup> Many factors contribute to pressure variations of vibrational frequencies, including packing, compressibility, bond strength, and steric effects.

Temperature effects on frequencies are much smaller. The  $\nu$ (M-S) frequencies decrease with increasing temperature by  $-0.02 \text{ cm}^{-1}/\text{K}$  for both complexes. In contrast, the  $\delta_s$ (SCS) frequencies are almost insensitive to temperature, with variations of less than 0.005 cm<sup>-1</sup>/K for the two compounds.

# 3.2. Metal-Oxo Multiple Bonds: *trans*-Dioxo Complexes of Osmium(VI) and Rhenium(V)

*Trans*-dioxo complexes of  $5d^2$  metal ions such as rhenium(V) or osmium(VI) have been extensively studied. Their metal-oxo bond lengths are very similar, illustrated by the values of 1.74(1) Å and 1.765(7) Å for *trans*-[OsO<sub>2</sub>(en)]<sup>2+[68]</sup> and *trans*-[ReO<sub>2</sub>(en)]<sup>+</sup>,<sup>[69]</sup> respectively. The electronic structure of these complexes depends on the metal ion and on the nature of the ancillary ligands. The  $\nu_s$ (O=M = O) symmetric stretching frequencies for metal-ligand double bonds are observed at much higher frequencies than the corresponding frequencies for metal-ligand

single bonds and frequencies for complexes with nearly identical metaloxo bond lengths can be easily distinguished, as illustrated in Figure 8 by the frequency difference of  $20 \text{ cm}^{-1}$  between *trans*-[OsO<sub>2</sub>(en)]<sup>2+</sup> and *trans*-[ReO<sub>2</sub>(en)]<sup>+</sup>, respectively.

The two compounds with N, N, N, N', N'-ethylenediamine ancillary ligands show a very similar pressure variation of their metal-oxo stretching modes, as illustrated in Figure 8. We observe a linear shift of the band maximum of the  $\nu_s$ (O=Os = O) or  $\nu_s$ (O=Re = O) symmetric stretching frequency by +0.29 cm<sup>-1</sup>/kbar and +0.37 cm<sup>-1</sup>/kbar for the osmium(VI) and rhenium(V) complexes, respectively, shown in Figure 9. The symmetric stretching frequency is higher in the case of the osmium(VI) compound, and stretching frequencies of the metal-oxo double bonds change significantly less with pressure than stretching frequencies involving metal-ligand single bonds.

A *trans*-dioxo complex with substituted ethylenediamine ligands, the N, N, N', N'-tetramethylethylenediamine complex of rhenium(V), shows a slightly lower metal-oxo stretching frequency, illustrated in Figure 9, than the *trans*-dioxo complexes with unsubstituted ethylenediamine ligands



Figure 8. Pressure dependence of Raman spectra in the region of the  $\nu_s(O=M=O)$  symmetric stretching frequency of  $[OsO_2(en)]Cl_2$  (a) and  $[ReO_2(en)]Cl$  (b). Ligand abbreviation: en = N, N, N, N'-ethylenediamine.



Figure 9. Pressure dependence of Raman spectra in the region of the  $\nu_s(O=Re=O)$  symmetric stretching frequency for [ReO<sub>2</sub>(tmen)]Cl (a). Pressure-induced shifts of the  $\nu_s(O=M=O)$  symmetric stretching frequency of three *trans*-dioxo compounds (b). Compounds are identified by the following symbols: circles for [OsO<sub>2</sub>(en)]Cl<sub>2</sub> (•), squares for [ReO<sub>2</sub>(en)]Cl (**■**) and triangles for [ReO<sub>2</sub>(tmen)]Cl (**▲**). Ligand abbreviations: en = N, N, N, N-ethylenediamine and tmen = N, N, N, N-tetramethylethylenediamine.

shown in figure 8. The variation by  $[+0.42 \text{ cm}^{-1}/\text{kbar}]$  of the  $\nu_s(O=Re=O)$  frequency with pressure is very similar to the trends for complexes with unsubstituted ethylenediamine ligands. For these three examples, the highest frequency shows the smallest variation with pressure, an intuitively appealing correlation that needs to be confirmed with additional compounds. We note also that the spectra at the highest pressure (above 35 kbar) have broader bands, indicating a deterioration of the sample crystal by the high pressure.

# 3.3. Metal-Oxo Multiple Bonds: Mono-Oxo Complexes of Molybdenum(IV) and Rhenium(V)

Mono-oxo complexes have often shorter metal-oxo bond lengths and higher metal-oxo stretching frequencies than the *trans*-dioxo complexes discussed in the preceding section. Two mono-oxo compounds,  $[MoOCl (CN-t-Bu)_4]BPh_4^{[49]}$  and  $[ReO(Br)_3(dppe)]$ ,<sup>[48]</sup> have been studied by

Raman spectroscopy at variable pressure. The region of the metal-oxo stretching mode is shown in Figure 10. The  $\nu_s(Mo\equiv O)$  and  $\nu_s(Re\equiv O)$  symmetric stretching frequencies are easily identifiable in the Raman spectra and are higher in frequency by approximately  $50 \text{ cm}^{-1}$  than the  $\nu_s(O=Os=O)$  or  $\nu_s(O=Re=O)$  symmetric stretching frequencies for *trans*-dioxo complexes.

The molybdenum(IV) complex in Figure 10(a) shows a linear variation of the  $\nu_s(Mo\equiv O)$  symmetric stretching frequency up to 31 kbar with a slope of  $+0.24 \text{ cm}^{-1}/\text{kbar}$ . At higher pressures, the spectra are less resolved and the Raman bands become significantly broader, a consequence of the deterioration of the sample crystal by high pressure. The band maxima are at significantly lower frequencies, an effect rationalized with pressure-induced changes in the *cis*-O-Mo-L angles.<sup>[49]</sup> For the rhenium(V) oxo compound, the peak at a Raman shift of approximately 981 cm<sup>-1</sup> is assigned as the metal-oxo stretching mode and shows a significant change with the pressure, as illustrated in Figure 10(b). Again, at the highest pressures shown, the band maximum shifts to lower frequencies and broadening occurs.



Figure 10. Pressure dependence of Raman spectra of the  $\nu_s(M\equiv O)$  symmetric stretching band of [MoOCl(CN-*t*-Bu)<sub>4</sub>]BPh<sub>4</sub> (a) and [ReO(Br)<sub>3</sub>(dppe)] (b). Ligand abbreviation: dppe = 1,2-diphenylphosphinoethane.

Table 3 summarizes the symmetric stretching frequencies for single  $\nu_s(M-L)$ , double  $\nu_s(O=M=O)$ , and triple  $\nu_s(M\equiv O)$  bonds illustrated by the examples in this section. Frequencies increase with the multiple bond character, the bond strength, and the bond length ( $d_{A-B}>d_{A=B}>d_{A=B}$ ), leading to the following qualitative classification:  $\nu_s(M-L)$  (275-500 cm<sup>-1</sup>)  $<<\nu_s(O=M=O)$  (840–920 cm<sup>-1</sup>)  $<\nu_s(M\equiv O)$  (950–1000 cm<sup>-1</sup>).

The pressure dependence of these frequencies appears to be inversely proportional to their formal bond order, with variations of  $\nu_s$ (M-L) of +0.35–0.68 cm<sup>-1</sup>/kbar larger than those for  $\nu_s$ (O=M=O) of+0.29– 0.42 cm<sup>-1</sup>/kbar and the smallest variations observed for formal  $\nu_s$ (M=O) triple bonds, where frequencies increase by +0.24–0.27 cm<sup>-1</sup>/kbar.

The frequencies presented in Table 3 are observed for complexes with different coordination geometries: octahedral for  $[Ni(NH_3)_6]X_2$ ,  $[ReOBr_3(dppe)]$ ,  $[MoOCl(CN-t-Bu)_4]BPh_4$ ,  $[OsO_2(en)_2]Cl_2$ ,  $[ReO_2(en)_2]$ Cl and  $[ReO_2(tmen)_2]Cl$ , tetrahedral for  $(DEA)[CuCl_4]$  and  $K[MnO_4]$ , and square-planar for  $(DEA)[CuCl_4]$ ,  $[Pt(PDTC)_2]$  and  $[Pd(PDTC)_2]$ .

Bond type	$ u_{\rm s}({ m M-X}) $ Stretching	Compound	Vibrational frequency (cm <sup>-1</sup> )	Temperature dependence (cm <sup>-1</sup> /K)	Pressure dependence (cm <sup>-1</sup> /kbar)
Single	$\nu_{s}$ (Cu-Cl)	(DEA)[CuCl <sub>4</sub> ]	277	/	/
		$(D_{4h})$	281		
		$(DEA)[CuCl_4](T_d)$			
	$\nu_{\rm s}$ (Ni-N)	[Ni(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>2</sub>	374	-0.03	/
	$\nu_{s}$ (Pt-S)	[Pt(SCN) <sub>4</sub> ](n-Bu <sub>4</sub> N) <sub>2</sub>	303	/	+0.60
	ν <b>s(Pd-S)</b>	[Pd(SCN) <sub>4</sub> ]( <i>n</i> -Bu <sub>4</sub> N) <sub>2</sub>	274	/	+0.68
	ν <b>(Pt-S)</b>	[Pt(PDTC) <sub>2</sub> ]	323	-0.02	+0.35
	ν <b>(Pd-S)</b>	[Pd(PDTC) <sub>2</sub> ]	300	-0.02	+0.37
Double	ν <sub>s</sub> (O=Os=O)	$[OsO_2(en)_2]Cl_2$	918	/	+0.29
	$\nu_{s}(O=Re=O)$	[ReO <sub>2</sub> (en) <sub>2</sub> ]Cl	898	/	+0.37
		[ReO <sub>2</sub> (tmen) <sub>2</sub> ]Cl	868		+0.42
	ν <sub>s</sub> (O=Mn=O)	K[MnO <sub>4</sub> ]	845	/	+0.32
Triple	ν <sub>s</sub> (Re≡O)	[ReO(Br) <sub>3</sub> (dppe)]	981	/	+0.27
	ν <b>₅(Mo≡O)</b>	[MoOCl(CN-t-	954	/	+0.24
		Bu) <sub>4</sub> ]BPh <sub>4</sub>			

Table 3. Summary of temperature-induced and pressure-induced shifts of selected Raman frequencies

DEA = diethylammonium; PDTC = pyrrolidine-N-dithiocarbamate; en = N, N, N', N'-ethylenediamine; tmen = N, N, N', N'-tetramethylethylenediamine and dppe = 1,2-diphenylphosphinoethane.

# 4. RESONANCE RAMAN SPECTROSCOPY: THE EXAMPLE OF A RUTHENIUM(II) BENZOQUINONE COMPLEX

A resonance Raman spectrum of  $[Ru(BQDI)(NH_3)_2Cl_2]$  (BQDI = *o*-benzoquinonediimine) was recorded with an excitation wavelength near the lowest-energy intense absorption maximum observed at approximately 20000 cm<sup>-1</sup> with a molar absorptivity  $\varepsilon$  of 10000 M<sup>-1</sup>cm<sup>-1</sup> close to the excitation wavelength of 488 nm.<sup>[55,56]</sup> In the resonance Raman spectrum in Figure 11, many overtones and combination bands identified by the labels I, II, III are observed. The off-resonance Raman spectrum was recorded with an excitation wavelength of 785 nm or approximately 12700 cm<sup>-1</sup> to compare to the resonance Raman spectra. Each band observed in the off-resonance spectra corresponds to a fundamental transition, and overtones and combination bands are too weak to be observable without resonance enhancements, as illustrated in Figure 11.

A total of 18 experimental vibrational frequencies can be identified for [Ru(BQDI)(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>].<sup>[55]</sup> The comparison of resonance and offresonance Raman spectra shows that all bands observed at Raman shift



Figure 11. Comparison of the resonance Raman spectrum (top, excitation wavelength 488 nm) to the off-resonance Raman (bottom, excitation wavelength 785 nm) for [Ru(BQ-DI)(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]. The series of overtones and combination bands (identified by the labels I, II, III) are identified in the resonance Raman spectrum. The two Raman spectra are normalized on the most intense band. Ligand abbreviation: BQDI = o-benzoquinonediimine.

higher than 1700 cm<sup>-1</sup> correspond to resonance-enhanced overtones or combination bands. All bands observed in the resonance Raman spectra not corresponding to the fundamental frequencies are therefore assigned as overtones or combination bands involving several vibrational quanta.

In the Raman spectra of  $[Ru(BQDI)(NH_3)_2Cl_2]$ , the distinction between the fundamental frequencies and overtones or combination bands is straightforward, as shown in Figure 11. The Raman shifts of approximately 2000 cm<sup>-1</sup> and 2600 cm<sup>-1</sup> corresponding to the labeled regions II and III in the resonance Raman spectrum are not fundamental, transitions, and their spacing of approximately 650 cm<sup>-1</sup> coincides with the Raman shift of the most intense band in the resonance Raman spectrum, observed at 655 cm<sup>-1</sup> in [Ru(BQDI)(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and assigned to a Ru-BQDI mode from DFT calculations.<sup>[55,56]</sup> The high relative intensity of the transition at 655 cm<sup>-1</sup> shows that the largest distortions between the ground-state and the excited-state structures occur along the normal coordinates of this mode. The bands in regions II and III are combination bands of fundamental frequencies with this mode.

In contrast, the assignment of all bands observed in region I is more complicated, as the fundamental bands and the first overtone of the most intense fundamental occur at Raman shifts of approximately  $1300 \text{ cm}^{-1}$ , requiring calculated spectra to identify individual modes. DFT and other electronic structure calculations are a powerful and rapid method to perform normal coordinate analyses and to calculate off-resonance Raman spectra,<sup>[55,56,67,70,71]</sup> but the discussion of these other approaches is beyond the scope of this Comment.

The resonance Raman intensities can be calculated easily using the time-dependant approach described by Heller and associates and applied to metal complexes by the Zink group.<sup>[50–54,67,72]</sup> The simplest approach is based on a single electronic excited state and the Raman scattering cross-section  $I_{i \to f}$  is given by:

$$I_{i\to f} \propto \omega_I \omega_S^3 [\alpha_{fi}] \times [\alpha_{fi}]$$
(3)

with

$$[\alpha_{fl}] = \frac{i}{\hbar} \int_0^\infty \langle \phi_f | \phi(t) \rangle \cdot e^{-iE_{00}t - \Gamma t} \cdot e^{i(\omega_i + \omega_I)t} dt$$
(4)

where  $\Gamma$  is a constant damping factor (in cm<sup>-1</sup>),  $\hbar\omega_i$  is the zero-point energy of the ground electronic potential energy surface and  $\hbar\omega_I$  is the

energy of the incident radiation.  $\langle \phi_f/\phi(t) \rangle$  is the autocorrelation function, which takes a simple analytical form if it is assumed that (a) the force constants are the same in both ground and excited states, (b) the potential energy surfaces are harmonic, (c) the transition dipole moment is independent of the normal coordinates, and (d) the normal coordinates are not coupled:

$$\begin{aligned} \langle \phi_f | \phi(t) \rangle &= \prod_k \left\{ \exp\left[ -\frac{\Delta_k^2}{2} (1 - \exp(-i\omega_k t)) - \frac{i\omega_k t}{2} \right] \\ &\times (1 - \exp(-i\omega_k t))^{n_k} \times \frac{(-1)^{n_k} \Delta_k^{n_k}}{(2^{n_k} n_k!)^{1/2}} \right\} \end{aligned}$$
(5)

In Equation (5),  $\omega_k$  and  $\Delta_k$  denote the wavenumber (in cm) and the difference between potential energy minima of the ground and excited states along the *k*th normal coordinate, respectively, and is the vibrational quantum number of the *k*th normal mode in the ground electronic state. As an example, the combination band  $(2n_1 + n_2)$  in a three mode case would have  $n_1 = 2$ ,  $n_2 = 1$ , and  $n_3 = 0$ . Equation (3) can be used to calculate the excitation profile for each fundamental, harmonic, and combination band involved in the resonance Raman spectrum. The intensity ratio of fundamentals to overtones can be calculated and  $\Delta_k$  values adjusted until a good fit is obtained, as illustrated in Figure 12. The approach consists of adjusting the ratio of intensities between calculated profiles for different modes by fitting the displacements  $\Delta_k^{n_k}$  in Equation (5) until the ratios of calculated intensities are in agreement with the experiment.

The calculated intensities are compared in Figure 12 to the experimental resonance Raman spectra for  $[Ru(BQDI)(NH_3)_2Cl_2]$ . These calculations can involve all fundamental modes identified in the experimental Raman spectra but, in this case, the analysis of  $[Ru(BQDI)(NH_3)_2Cl_2]$  has been simplified to include only the five modes appearing in overtones and combination bands. Figure 12 shows a very good agreement between calculated and experimental intensities of the resonance Raman spectra. The intensities of overtones and combination bands are also reproduced well, as illustrated for the first overtone of the  $650 \text{ cm}^{-1}$  mode. These intensities depend strongly on excited-state characteristics and provide an important additional criterion to compare model calculations and experimental spectra. A sample model calculation documenting this sensitivity is illustrated in Figure 13(a) with the



Figure 12. Comparison of calculated (solid) and experimental (dotted) resonance Raman spectra (excitation wavelength 488 nm) for  $[Ru(BQDI)(NH_3)_2Cl_2]$ . Ligand abbreviation: BQDI = *o*-benzoquinonediimine.



Figure 13. Illustration of the ground and excited states with different  $\Delta$  values used to calculate resonance Raman spectra from this one-dimensional model with a vibrational frequency of 655 cm<sup>-1</sup> (a). (b) Calculated resonance Raman spectra resulting from the one-dimensional model in (a) with  $\Delta = 1.8$  (•),  $\Delta = 2.0$  (**1**) and  $\Delta = 2.2$  (**1**) for an excitation wavelength  $\lambda_0 = 488$  nm. Ligand abbreviation: BQDI = *o*-benzoquinonediimine.

fundamental and the first four overtone transitions for the [Ru(BQDI) (NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] complex represented by the two downward arrows. The ground and excited-state harmonic potential energy curves are defined using  $\Delta = 2$ ,  $E_{00} = 17250$  cm<sup>-1</sup>,  $\Gamma = 150$  cm<sup>-1</sup>, and a single vibrational frequency of 655 cm<sup>-1</sup>.

Calculated Resonance Raman spectra of  $[Ru(BQDI)(NH_3)_2Cl_2]$  for three different values of  $\Delta$  are presented in Figure 13(b). The calculated intensities vary strongly for the three  $\Delta$  values of 1.8 (•), 2.0 ( $\blacksquare$ ) and 2.2 ( $\blacktriangle$ ) at the excitation wavelength of 488 nm or 20492 cm<sup>-1</sup>. The intensities of fundamentals and overtones or combination bands depend very strongly on the choice of  $\Delta$ , allowing this parameter to be estimated even in the absence of a full resonance Raman excitation profile. This example illustrates key characteristics of resonance Raman spectra, namely the intensity increase for certain fundamental, overtone, and combination bands and shows how excited-state properties can be determined.

# 5. RAMAN SPECTRA OF POLYMETALLIC COMPLEXES ILLUSTRATED BY LANTHANIDE CLUSTERS

Raman spectroscopy has been used to study polymetallic complexes, in particular complexes with metal-metal bonds, where recording spectra at frequencies lower than 300 cm<sup>-1</sup> is of key importance.<sup>[7,73–75]</sup> Recent work in this area has illustrated the advantage of using calculated spectra from electronic structure calculations, in particular DFT, in order to



Figure 14. Schematic structures of polymetallic lanthanide clusters.  $Ln_5 = [Ln(III)_5 (dbm)_{10}(\mu_3-OH)_4(\mu_4-OH)]$ ,  $Ln_8 = [Ln(III)_8(thd)_{10}(\mu_4-O)_1(\mu_3-OH)_{12}]$ , and  $Ln_9 = [Ln(III)_9 (acac)_{16}(\mu_3-OH)_8(\mu_4-O)_1(\mu_4-OH)] \cdot H_2O$ . Ligand abbreviation: Hdbm = dibenzoylmethane, Hthd = 2,2,6,6-tetramethylheptane-3,5-dione and Hacac = acetylacetone.

assign frequencies to vibrational modes and to correlate bond strengths with structural parameters.

A category of polymetalllic complexes of interest are lanthanide clusters with intricate molecular magnetic properties.<sup>[76-78]</sup> These systems are not usually characterized by vibrational spectroscopy, even though their Raman spectra reveal distinct characteristics, as illustrated by the series of clusters shown in Figure 14.<sup>[79,80]</sup> The compounds contain five, eight, or nine lanthanide ions, bridged by acetylacetonato ligands, with the variation of ligand substituents leading to the different numbers of metal ions in the cluster.

Figure 15 shows a comparison of a monometallic chromium(III) acetylacetonato complex, a type of compound extensively used in the



Figure 15. Raman spectra of acetylacetonato complexes. (a)  $Cr(thd)_3$ ; (b)  $Ln_8$  ([Ln(III)<sub>8</sub> (thd)<sub>10</sub>( $\mu_4$ -O)<sub>1</sub>( $\mu_3$ -OH)<sub>12</sub>]) for different lanthanide centers. Ligand abbreviation: Hthd = 2, 2,6,6-tetramethylheptane-3,5-dione.

past as a model to explore photochemical properties,<sup>[72,81]</sup> and still studied as a model for femtosecond dynamics involving multiple excited electronic states.<sup>[82]</sup> The most intense peak of its Raman spectrum shown in Figure 15(a), at 480 cm<sup>-1</sup>, is assigned to the  $\nu$ (Cr-O) symmetric stretching mode, with most of the other peaks due to modes of the (2,2,6,6-tetramethylheptane-3,5-dione) Hthd ligand. Figure 15(b) shows a series of Raman spectra of the octanuclear clusters illustrated in Figure 13(b), with different lanthanide centers. The frequencies observed coincide with those of the mononuclear complex, with the exception of the intense metal-ligand mode for the chromium(III) compound. They are therefore ligand-centered modes, with characteristic  $\nu$ (C=C) and  $\nu$ (C=O) acetylacetonato modes observed at approximately 930 cm<sup>-1</sup> and in the 1400 cm<sup>-1</sup> to 1500 cm<sup>-1</sup> region.<sup>[1,2]</sup> This comparison illustrates common characteristics and slight shifts in ligand frequencies for compounds of the f-block compared to d-block metals.



Figure 16. Raman spectra of different clusters. Top  $Ln_5$  ([Ln(III)<sub>5</sub>(dbm)<sub>10</sub>( $\mu_3$ -OH)<sub>4</sub> ( $\mu_4$ -OH)]), middle  $Ln_8$  ([Ln(III)<sub>8</sub>(thd)<sub>10</sub>( $\mu_4$ -O)<sub>1</sub>( $\mu_3$ -OH)<sub>12</sub>]), bottom  $Ln_9$  ([Ln(III)<sub>9</sub>(acac)<sub>16</sub> ( $\mu_3$ -OH)<sub>8</sub>( $\mu_4$ -O)<sub>1</sub>( $\mu_4$ -OH)] · H<sub>2</sub>O). Ligand abbreviation: Hdbm = dibenzoylmethane, Hthd = 2,2,6,6-tetramethylheptane-3,5-dione and Hacac = acetylacetone.

Clusters of different sizes are compared in Figure 16. Each cluster size has its distinct spectrum, with frequencies showing very small changes for different lanthanide centers. The comparison of spectra allows us to efficiently categorize and identify different cluster types, of importance in the synthesis of mixed-metal or doped clusters.<sup>[79]</sup> The comparisons in Figures 15 and 16 show that compounds beyond the simple complexes used to illustrate effects of temperature and pressure can be easily characterized by Raman spectroscopy.

The examples discussed in this Comment are intended to demonstrate that Raman spectroscopy is a useful technique for the characterization of a wide variety of transition metal complexes. There are a number of additional techniques not presented in this overview, such as polarized Raman spectroscopy, electronic Raman spectroscopy, of particular interest for complexes with near-degenerate electronic ground states,<sup>[83]</sup> and time-resolved pump-probe measurements. Surface-enhanced (SERS) Raman spectroscopy and the use of nanoparticles to enhance Raman scattering are highly promising, modern options for applications to inorganic chemistry.<sup>[14]</sup>

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