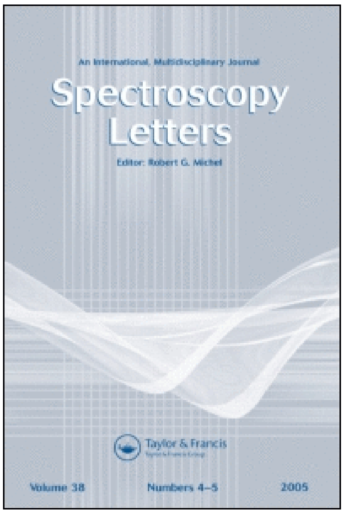

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# Experimental and Theoretical Study of "Anomalous" Intensity Variations in the Resonance Raman Excitation Profiles of the Fundamental and its Overtones for Totally Symmetric Raman Stretching Vibration (Mo-Mo) of Quadruple Molybdenum-Molybdenum Bonds

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# EXPERIMENTAL AND THEORETICAL STUDY OF "ANOMALOUS" INTENSITY VARIATIONS IN THE RESONANCE RAMAN EXCITATION PROFILES OF THE FUNDAMENTAL AND ITS OVERTONES FOR TOTALLY SYMMETRIC RAMAN STRETCHING VIBRATION $\tilde{v}$(Mo-Mo) OF QUADRUPLE MOLYBDENUM-MOLYBDENUM BONDS

***Key words***: Electronic and Raman spectra; Raman intensity variations; Hexahalo-di(aqua) molybdate (II) anions, containing quadruple metal-metal bonds.

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## *ABSTRACT*

The electronic (800-400 nm), and Raman (2750-20cm$^{-1}$) spectra of several hexahalo-di (aqua) dimolybdate (II) anions, $MO_2X_6(H_2O)_2^{2-}$ with X=Cl, Cl/Br, Br and I, containing quadruple metal-metal bonds were investigated.

The electronic spectra of the solid compounds at 300 K show intense broad bands in the visible region (510-582nm) assigned to the expected $\delta\rightarrow\delta^*$ transitions. More interestingly, the transmission electronic spectra of these anions at low temperatures (25-100K) display vibronic structures which are particularly well-resolved for the $Mo_2I_6(H_2O)_2^{2-}$anion.

The resonance Raman spectra exhibit an overtone progression $v\tilde{v}_1$, where $\tilde{v}_1$ is the metal-metal stretching vibration. At low temperature (25K) for the iodo anion, the experimental and the theoretical Raman excitation profiles of the fundamental ($I\tilde{v}_1$) and its overtones ($Iv\tilde{v}_1$) were compared in order to investigate the "anomalous" intensity variations.

Roman intensity variations depend strongly on the displacement parameters ($\beta_{1e}$ or $\delta_{1e}$) and the damping factors ( $\Gamma_i$ ).

Since the $\beta_{1e}$ or $\delta_{1e}$ values are stable while $\Gamma_i$ values vary with temperature, at the low temperature (25-100K),when $\Gamma_i$ values are decreased below the 100cm$^{-1}$ therefore the "anomalous" intensity variations are occurred.

## *INTRODUCTION*

To date, the "anomalous" intensity variations heve been observed in the resonance Raman spectra of $MnO_4^-$ (2) and $Cu_3PS_4$ (3, 4) compounds under particular resonance conditions.

Raman intensity variations depend strongly on the displacement parameters ($\beta_{1e}$ or $\delta_{1e}$) and the damping factors ( $\Gamma_i$ ). The damping factors ( $\Gamma_i$ ) vary as a function of temperature (1, 2, 5):

- At the ambient temperature (300K), $\Gamma_i$ are large, then the interference phenomena (1, 5) will be effective within vibronic excited levels.
- At the low temperature (25-100K), $\Gamma_i$ values are diminished. When Raman intensities vary with $\Gamma_i$ values; therefore, the "anomalous" intensity variations occur for the small ( $\Gamma_i$ <100cm$^{-1}$ ) values of $\Gamma_i$, in the resonance Raman spectra. This work focuses on the experimental and theoretical study of "anomalous" intensity variations in the resonance Raman excitation profiles of the fundamental $\tilde{\nu}_1$ and its overtones $v\tilde{\nu}_1$ within Franck-Condon type scattering mechanism for a pyridinium complex $(PyH)_2Mo_2I_6(H_2O)_2$.

Since the $\beta_{1e}$ or $\delta_{1e}$ values are stabilized (1,5) while $\Gamma_i$ values vary with temperature, when only one mode $\tilde{\nu}_{1g}$(Mo-Mo) effective, and the interference effects within vibronic excited levels were considered (6).

Therefore, the experimentally determined values (1, 5) of the best fit parameters ($\beta_{1e}$ , the dimensionless displacement parameter of the equilibrium position; $\tilde{\nu}_{0.0}$ , the wavenumber of the transition 0→0; $\tilde{\nu}_{1g}$, the ground state wavenumber and $\tilde{\nu}_{1e}$, the excited state wavenumber) were used while the $\Gamma_i$ values were altered.

## *EXPERIMENTAL*

### Preparative details

A gift from J.V.Brencic, the morpholinium salts $(mpH)_2Mo_2Cl_6(H_2O)_2$(I), $(mpH)_2Mo_2Cl_xBr_{6-x}(H_2O)_2$(II), $(mpH)_2Mo_2Br_6(H_2O)_2$(III) and the pyridinium complex $(PyH)_2Mo_2I_6(H_2O)_2$(IV) were prapered by the methods given in the literature (7, 8).

All compounds except II were recrystallized from 1:1 mixtures of halide acids and of the appropriate morpholinium or pyridinium salt. The recrystallizations of II from a 1:1 HBr gave III.

### Instrumental details

Electronic spectra were recorded using a Cary 17 spectrometer either in the diffuse reflectance mode (at 300K) or in the transmission mode with potassium or cesium halide pressed discs at various temperatures (25-300K).

The low-temperature spectra were obtained using a liquid nitrogen cryostat or a Cryodine Model 21 closed-cycle helium refrigerator.

Raman spectra were recorded with either a Coderg T800 or a Dilor RT130 triple monochromator instrument using nine emission lines of Model 164 Spectra-Physics $Kr^{+}$ and $Ar^{+}$ lasers ($\lambda_0$ from 676.4 to 457.9 nm). Dedection was by conventional d.c. techniques using a cooled RCA C31034 photomultiplier tube.

Repeat scan measurements were carried out with a Mostek Z80 microprocessor and all data could also be transferred to a PDP 11 computer. Spectra from samples held at room temperature were obtained by use of a sample holder rotating at ca 1600 rev $min^{-1}$ (9, 10) and those from samples held at ca 25-80K were obtained from $K_2SO_4$ or $KClO_4$ sample discs in conjunction with a glass block rotating at ca 1500 rev $min^{-1}$; the latter refracts the incident laser beam across the surface of the sample in order to minimize any local heating effects. Excitation profiles were measured with respect to some bands of $SO_4^{2-}$ or $ClO_4^{-}$ used as internal standards and integrated Raman band intensities were always considered. Finally, the spectra were calibrated by reference to either the emission lines of a neon lamp or the plasma laser lines.

## *RESULTS*

### Electronic spectra

The electronic spectra of I, II, III, and IV at 300K in the transmission or diffuse reflectance mode exhibit intense broad bands at about 515, 520, 534 and 582 nm, respectively.

These bands are confidently assigned to the $^1Ag \rightarrow {}^1Au$ or $\delta(a_g) \rightarrow \delta^*(a_u)$ (in the $C_{2h}$ symmetry group) axially polarized and dipole allowed transitions by analogy with the corresponding transitions in similar $Mo_2X_8^{4-}$, $Mo_2(SO_4)_4^{4-}$ or $Mo_2X_4L_4$ systems with quadruple Mo-Mo bonds (11).

The transmission electronic spectra of these anions at low-temperatures (25-100K) display vibronic structures which are particularly well resolved for the iodo anions IV. The experimentally measured wavenumbers of the vibronic lines and their energy spacings are reported (1). Assuming Lorentzian shapes and similar half-widths for all the vibronic lines, the electronic spectra, corrected from a baseline background, were deconvoluted in order to find the electronic origins, the wavenumbers, half-widths and relative intensities of all the vibronic levels.

We paid particular attention to the possible occurrence of several progressions and to the variation of the half-widths as a function of the temperature.

Typical results of such fits were shown, experimental and computed electronic spectra were composed;the corresponding best-fit parameters($\tilde{v}_{0.0}$,$\tilde{v}_{1e}$ and $\Gamma_i$) obtained at 300, 90 and 25K were reported (1,5). The large increases of half-width of vironic lines over the 25-300K temperature range can explain the loss of vibronic structures at room temperature. Such a temperature dependence of the spectra were illustrated (1, 5) for the iodo anion (IV), where the half-band widths increase from 160 $cm^{-1}$ (at 25K) to about 200$cm^{-1}$ (at 90K).

The values of these parameters will be extremely helpful later in the analysis of the resonance Raman excitation profiles.

## Resonance Raman spectra

Resonance Raman experiments were investigated only in solid state because the complexes were not stable in the solvents.

Irradiations within the contours of the electronic Laporte allowed $\delta(a_g) \rightarrow \delta^*(a_u)$ transitions were carried out using mainly the 488.0, 501.7, 514.5 and 568.2 nm laser lines.

Experimental and theoretical Raman excitation profiles were compared in order to determine reasonable estimates of the displacement parameters $\beta_{1e}$.

The resonance Raman spectra of these compounds exhibit an overtone progression $v\tilde{v}_1$, where $\tilde{v}_1$ is metal-metal stretching vibration, for all values of v up to and including v=7 or v=4 for the morpholinium and pyridinium complexes respectively. The numbers of $v\tilde{v}_1$ progressions display characteristic features of the resonance effect with a continuos increase in half-band widths and a decrease in intensities when increasing the vibrotional quantum number v.

## Experimental and theoretical Raman excitation profiles

The experimental and theoretical Raman excitation profiles for the $\tilde{v}_1$(Mo-Mo) fundamental and its overtone $v\tilde{v}_1$ were studied thoroughly in order to observe the "anomalous" intensity variations at the low-temperatures (25-100K), especially for the well-resolved pyridinium complex.

Since the displacement parameter $\beta_{1e}$ of the metal-metal bond in the excited state and the parameters $\tilde{v}_{0.0}$ , $\tilde{v}_{1g}$ , $\tilde{v}_{1e}$ and $\Gamma_i$ were determined (1, 5), therefore theoretical excitation profiles can be calculated using A term scattering intensity expression as proposed by Clark and Steward (6):

$$I_{vv1g} \,\alpha\, (\tilde{v}_0 - v\tilde{v}_{1g})^4 \Big\{ \sum_{v'} \frac{|\langle 0|v'\rangle\langle v'|v\rangle|^2}{(\tilde{v}_{0.0}-\tilde{v}_0+v'\,\tilde{v}_{1e})^2+\Gamma_v^2} + 2\sum_{v'<v''}\sum \langle 0|v'\rangle\langle v'|v\rangle\langle 0|v''\rangle\langle v''|v\rangle$$

$$x[(\tilde{v}_{0.0}-\tilde{v}_0+v'\,\tilde{v}_{1e})(\tilde{v}_{0.0}-\tilde{v}_0+v''\,\tilde{v}_{1e})+\Gamma_{v'}\Gamma_{v''}] x [|(\tilde{v}_{0.0}-\tilde{v}_0+v'\,\tilde{v}_{1e})^2+\Gamma_{v'}^2| x |(\tilde{v}_{0.0}-\tilde{v}_0+v''\,\tilde{v}_{1e})^2+\Gamma_{v''}^2|]^{-1} \Big\}$$

Where $\tilde{\nu}_o$ is the exciting radiation wavenumber, $v'$ and $v''$ are vibrotional quantum numbers in the excited state (e), $\Gamma_{v'}$and $\Gamma_{v''}$are the damping factors (all assumed equal) and $< 0|v' >$, $< 0|v'' >$...are the Franck-Condon overlap matrices of vibrational wavefunctions which, in the multi-mode approach must be written as products of normal mode functions, so that $< v''|v > = \pi_{i\ \text{modes}} < v_{ei}''|\ v_{gi} >$. Here, only the metal-metal stretching mode will be considered, so that these vibrational overlap integrals can be readily expressed in terms of shifts in vibrational equilibrium position $\Delta Q_i$ and in vibrational wavenumber ($\tilde{\nu}_{1e}$-$\tilde{\nu}_{1g}$ ) through the dimensionless parameters (22, 23).

$$\beta_{1e}=[2\tilde{\nu}_{1g}\,\tilde{\nu}_{1e}/(\tilde{\nu}_{1g}+\tilde{\nu}_{1e})]^{\frac{1}{2}}\,\Delta Q_1$$

$$\delta_{1e}= \beta_{1e}\,[(\tilde{\nu}_{1e}+ \tilde{\nu}_{1g}) / 2\,\tilde{\nu}_{1g}]^{\frac{1}{2}} = (\tilde{\nu}_{1e})^{\frac{1}{2}}\,\Delta Q_1$$

$$\text{and } \xi_{1e}= (\tilde{\nu}_{1e}-\tilde{\nu}_{1g}) / (\tilde{\nu}_{1e}+\tilde{\nu}_{1g})$$

Franck-Condon factors are then calculated according to the recurrence formula proposed by Manneback (12) and the shape of the electronic absorption band, composed of Lorentzian sub-bands is also obtained through the expression:

$$I_{abs}\ \alpha\ \sum_{v'}\frac{|<0\,|\,v'>|^2}{[(\tilde{\nu}_{o.o}-\tilde{\nu}_0-v\tilde{\nu}_{1e})/\,\Gamma_{v'}]^2+1}$$

Hence, the experimental, the theoretical excitation profiles and the absorption spectra were compared at various temperatures (25, 100 and 300K) in order to determine an accurate value of the $\beta_{1e}$ ( or $\delta_{1e}$ ) parameter.

## *DISCUSSION*

We were concentrated particularly the well-resolved pyridinium complex $(PyH)_2Mo_2I_6(H_2O)_2$ to investigate the "anomalous" intensing variations which have already been observed in the Raman spectra of $MnO_4$ (2) and $Cu_3PS_4$ (3, 4) compounds under resonance conditions.

The electronic spectra of pyridinium complex, in the transmissions mode exhibit intense broad band at about 582 nm. At low-temperature (25-90K), the transmission electronic spectra of this anion display particularly well-resolved vibronic structures. In this condition, the parameters: $\beta_{1e}$=2.78±0.01, $\Gamma_i$=160±5cm$^{-1}$, $\tilde{\nu}_{0.0}$ = 16300±10cm$^{-1}$ , $\tilde{\nu}_{1g}$=339.5cm $^{-1}$ and $\tilde{\nu}_{1e}$=320±0.20cm$^{-1}$ were obtained (1, 5). In the exciting wavenumbers range 15625-19600 cm$^{-1}$, the experimental Raman excitation profiles were investigated in order to observe the "anomalous" intensity variations.The case, this complex $(PyH)_2Mo_2I_6(H_2O)_2$ is a black coloured,at low-temperature (25K), after first scanning, the signal was disappeared.

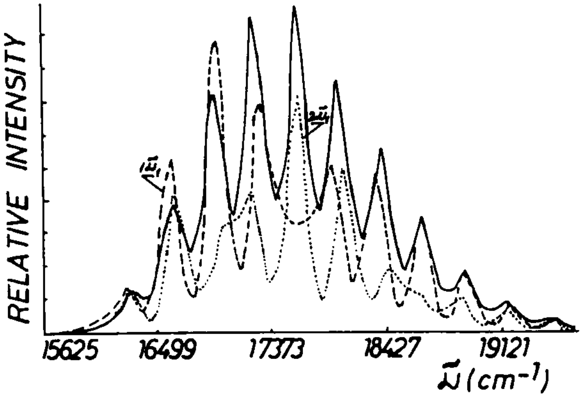

Fig. 1 Theoretical Raman excitation profiles and the electronic absorption spectrum of the iodo complex $(PyH)_2Mo_2I_6(H_2O)_2$ at 25K, the intensity of the fundamental $I\tilde{\nu}_1$(- - -) and its first overtones $I_2\tilde{\nu}_1$( . . . ) were compared.

This black colored sample could be decomposed, because of the absorption of the radiation. The several attempts were made to detect the "anomalous" intensity variation, but, it has never been observed for the systems under study at the first scanning as well. After we have decided to study the theoretical "anomalous" insensity variations in order to understand the phenomena.

In the exciting wavenumbers range 15625-19600cm$^{-1}$, at 25K, using the values of the parameters previously determined ($\beta_{1e}$=2.78±0.01, $\tilde{\nu}_{o.o}$ =16300±10cm$^{-1}$ $\tilde{\nu}_{1g}$=339.5cm$^{-1}$ ,$\tilde{\nu}_{1e}$=320±0.20cm$^{-1}$), the Raman excitation profiles and the electronic spectra were calculated at various $\Gamma_i$ values (160, 140, 120, 100 and 80 cm$^{-1}$).

For the $\Gamma_i$=80 cm$^{-1}$, the calculated results are illustrated in Fig. 1 where the electronic absorption spectrum of the pyridinium complex $(PyH)_2Mo_2I_6(H_2O)_2$ at 25K, with the theoretical Raman excitation profiles for the fundamental ( $I\tilde{\nu}_1$ ) and its first overtone ($I_2\tilde{\nu}_1$) were compared as a function of the exciting wavenumbers ($\tilde{\nu}_{oi}$)

From Fig. 1 the exciting wavenumber $\tilde{\nu}_o$=17575cm$^{-1}$, the resonance Raman intensity ratio $I_2\tilde{\nu}_1$/ $I\tilde{\nu}_1$ =2.5, which means that the intensity of first overtone ($I_2\tilde{\nu}_1$) is 2.5 times more intense than the intensity of the fundamental ($I\tilde{\nu}_1$) and at the exciting wavenumber $\tilde{\nu}_o$=17920cm$^{-1}$, the intensity of first overtone ($I_2\tilde{\nu}_1$) is greater than the intensity of the fundamental ($I\tilde{\nu}_1$) as well. Also, from the calculations the Raman intensity of the 3rd and 4 th overtones are greater than those of the first overtone and the fundamental.

In conclusion, in these complexes, the $\Gamma_i$ values were too large (1, 5), at 25K, the smallest $\Gamma_i$ values were 160cm$^{-1}$ (all assumed equal) for the iodo anion.

The theoretical results confirm that when $\Gamma_i$ values below the $100cm^{-1}$, in this case, the "anomalous" intensity variations were occurred.

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