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# Laser Spectroscopy of Open-shell Sandwich Complexes

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**Abstract**

Emission and excitation spectra of the metallocenes, $Cp_2M$ (M = Re, Mo, W) and $Cp^*_2Re$ ($Cp = \eta^5\text{-}C_5H_5$, $Cp^* = \eta^5\text{-}C_5Me_5$) isolated in $N_2$ and Ar matrices at 12 K have been excited by low-power irradiation with a tunable pulsed laser into their lowest LMCT bands. This method generates vibrationally resolved spectra which are much sharper than their absorption counterparts because the laser selects individual conformers or matrix trapping sites of the guest molecule. Emission lifetimes of 72 and 3.6 ns have been measured for $Cp_2Re$ and $Cp^*_2Re$ respectively. The arene sandwich complexes, $V(\eta^6\text{-}C_6H_6)_2$ and $V(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2$, respond differently to laser irradiation yielding resonance Raman spectra with long vibrational progressions.

## 1. INTRODUCTION

The metallocenes of molybdenum, tungsten and rhenium are highly reactive open-shell molecules which act as short-lived intermediates in solution chemistry. They may be generated in low temperature matrices by the photolysis of the corresponding hydride complexes, $Cp_2MH_n$ ($Cp = \eta^5\text{-}C_5H_5$) [1]. In contrast, decamethylrhenocene, $Cp^*_2Re$ ($Cp^* = \eta^5\text{-}C_5Me_5$) is an isolable compound [2]. We have shown previously that these metallocenes have vacancies in their $e_{2g}$ ($d_{xy,\ x^2-y^2}$) orbitals giving rise to $^3E_{2g}$ ground states for the $d^4$, 16 electron complexes, $Cp_2Mo$ and $Cp_2W$, and $^2E_{2g}$ ground states for the $d^5$, 17 electron complexes, $Cp_2Re$ and $Cp^*_2Re$ (figure 1). They all exhibit absorption bands in the visible or near UV corresponding to LMCT transitions [1].

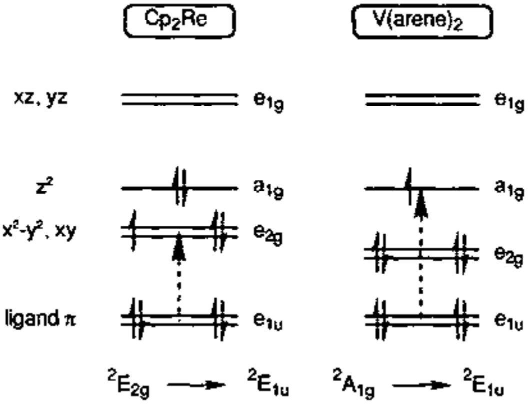

Figure 1. Ground configuration and electronic state of left $d^5$ metallocenes and right $d^5$ $M(\eta^6\text{-arene})_2$ complexes. The $^2E_{2g}$ ground state of the $d^5$ metallocenes is subject to strong spin-orbit coupling yielding a $E_{5/2g}$ ground spin orbit state. The LMCT transition is shown by the arrow. (Centrosymmetric point groups $D_{5d}$ and $D_{6h}$ are assumed).

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The $d^5$ arene sandwich complexes M($\eta^6$-arene)$_2$ (M = V, Nb, Ta) are isolable and have $^2A_{1g}$ ground states with a vacancy in the $d_{z^2}$ orbital (figure 1). They, too, have low lying LMCT bands [3].

In this review, we summarise experiments in which we probe the lowest LMCT bands with laser radiation in order to excite fluorescence or resonance Raman (RR) scattering. The resulting spectra yield information about the totally symmetric vibrations of the ground electronic state. The corresponding excitation spectra enable vibrational changes in the excited state to be monitored precisely. The laser-induced fluorescence (LIF) measurements also offer the opportunity to record the decay kinetics of the excited state. Details of the RR spectra of V($\eta^6$-arene)$_2$ and preliminary results on the metallocenes have been published [3,4].

## 2. EXPERIMENTAL PRINCIPLES

The LIF spectra of the metallocenes were excited by an excimer-pumped dye laser. The fluorescence is dispersed by a triple spectrometer and detected on an intensified diode array which is gated by a delay generator. Care is taken to record the laser energy (< 0.1 mJ per pulse) during each run. The excitation spectra are obtained point-by-point by monitoring the intensity or area of a single emission band as a function of excitation wavelength. The lifetime of the excited state of $Cp_2Re$ was measured on this apparatus, moving the gate stepwise out of synchronisation with the laser. The lifetime of $Cp^*{}_2Re$ is too short for this technique and was measured with apparatus for single photon counting [5], in which the sample is irradiated by a train of laser pulses at a repetition rate of 4 MHz with and instrument response function of about 300 ps in width. A single emission band is selected by an interference filter for detection.

The RR spectra of V($\eta^6$-arene)$_2$ were excited by a cw $Ar^+$ laser and recorded on a standard Raman spectrometer [3]. No excitation spectra were recorded.

## 3. LIF SPECTRA OF THE METALLOCENES

### 3.1. Unsubstituted metallocenes

The principal features of the LIF spectra of the unsubstituted metallocenes $Cp_2Re$, $Cp_2Mo$ and $Cp_2W$, are summarised below (see figures 2,3).

(i) Each molecule exhibits emission from the same electronic state as that probed by the laser beam. The (0,0) bands in absorption and emission are coincident. Thus, we are observing prompt or resonance fluorescence from the LMCT excited state.

(ii) Emission spectra show well-resolved progressions in $\nu_4 = \nu_{sym}$(Cp-M-Cp) with additional features arising from $\nu_3 + n\nu_4$ (n = 0,1,2...) where $\nu_3$ is the symmetric breathing mode of the Cp rings.

(iii) The emission lifetimes are 72 ns for $Cp_2Re$, but < 10 ns for $Cp_2Mo$ and $Cp_2W$.

(iv) The emission spectra are usually much sharper than the absorption spectra because the laser selects conformers or matrix trapping sites of the guest. With judicious choice of laser wavelength, a single conformer/site may be selected.

(v) The corresponding fluorescence excitation spectra are also conformer/site selective providing us with an experimental method of deconvoluting the absorption spectra.

(vi) The absorption spectra are demonstrated to be the sum of overlapping contributions of several conformers/sites.

(vii) The changes in $\nu_4$ in the excited state ($\nu_{excited}$- $\nu_{ground}$) are +17 cm$^{-1}$ ($Cp_2Re$), +7cm$^{-1}$ ($Cp_2Mo$), -4 cm$^{-1}$ ($Cp_2W$) (range -1% to +5%). The changes in $\nu_3$ are much

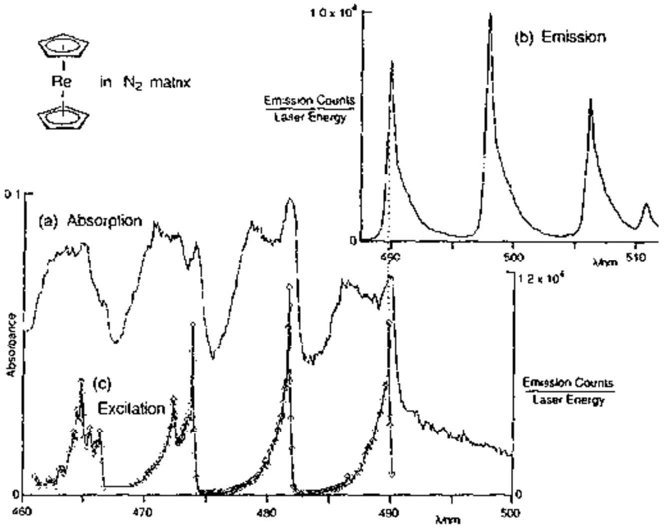

Figure 2. Spectra of $Cp_2Re$ generated by UV photolysis of $Cp_2ReH$ isolated in a $N_2$ matrix at 12 K. (a) Absorption spectrum, (b) emission spectrum (sharp site), (c) excitation spectrum corresponding to the emission spectrum corrected for laser energy.

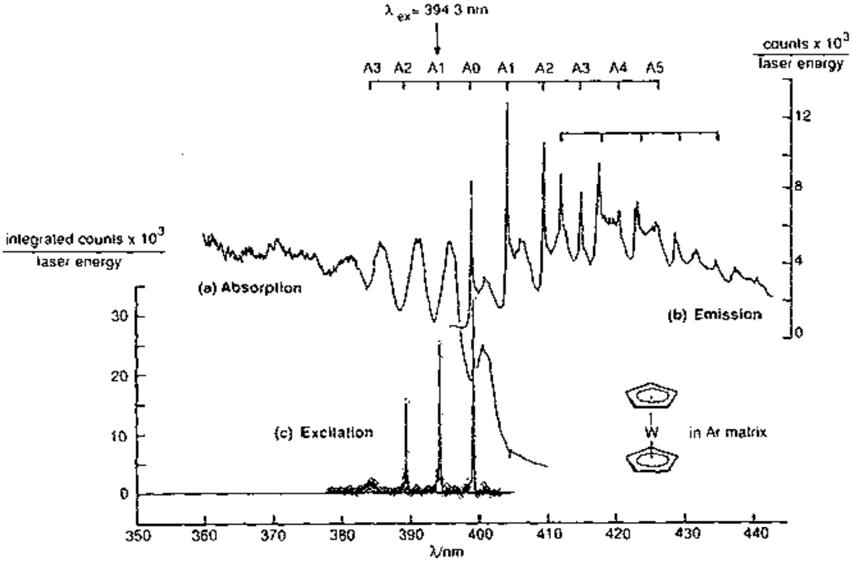

Figure 3. Spectra of $Cp_2W$ generated by UV photolysis of $Cp_2WH_2$ isolated in an argon matrix at 12 K. (a) Absorption spectrum, (b) emission spectrum, (c) corresponding excitation spectrum. The emission and excitation spectrum are shown for one site only.

larger: -77 cm$^{-1}$ (Cp$_2$Re), -60 cm$^{-1}$ (Cp$_2$Mo) (9% and 7% respectively). Thus the excited states of Cp$_2$Re and Cp$_2$Mo conform to the simple picture of a delocalised state with enhanced metal ring bonding and reduced π-bond character in the ring.

(viii) There is some unrelaxed fluorescence from Cp$_2$Mo on probing higher vibrational levels of the upper electronic state.

### 3.2. Decamethylrhenocene

The absorption spectra of Cp$^*{}_2$Re present a somewhat different picture from those of the unsubstituted metallocenes since the vibrational progressions are already fully resolved (figure 4a).

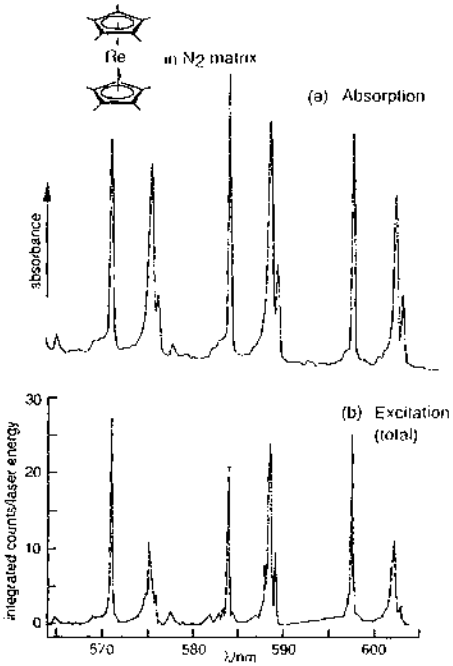

Figure 4. (a) Absorption spectrum of Cp$^*{}_2$Re isolated at high dilution in a N$_2$ matrix at 12 K. (b) Total excitation spectrum formed by summing all the components in figure 5.

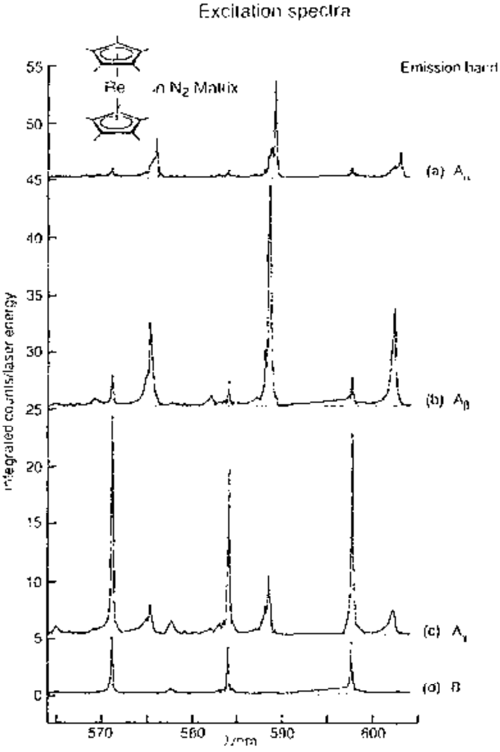

Figure 5. Excitation spectra of Cp$^*{}_2$Re in N$_2$ matrix for individual sites/conformers: (a) site Aα, (b) site Aβ, (c) site Aγ, (d) site B. Notice that emission from Aγ sites is excited by absorption in B sites. Since Aα, Aβ and Aγ are very close together, there is some overlap between them.

As for the unsubstituted metallocenes, the electronic origin of the emission spectrum is identical to that of the absorption spectrum. The spectra again result from a fully allowed LMCT transition. The emission lifetime is reduced compared to rhenocene by a factor of ca. 20 ($Cp_2Re$ 72 ns, $Cp^*_2Re$ 3.6 ns), is site independent and fits a single exponential. The principal vibrational progression is *increased* compared to $Cp_2Re$ by about 50 $cm^{-1}$ in both ground and excited states.

In nitrogen matrices, there are two principal sets of progressions in absorption (A and B), separated by ca. 130 $cm^{-1}$ which belong to two conformers/sites of the guest. The A set shows further structure which is examined more effectively by studying the emission and excitation spectra. Emission spectra show that the A progression is split into 3 components $A\alpha$, $A\beta$ and $A\gamma$ which may be excited selectively. The $A\alpha$ and $A\beta$ series are excited by the corresponding components of the emission spectra, as is the B emission (figure 5a, b, d). Surprisingly however, the $A\gamma$ emission progression is excited by absorption in the B series (figure 5c). This result indicates that electronic energy transfer occurs between the B and $A\gamma$ conformer/sites within the emission lifetime. The total excitation spectrum is compared to the absorption spectrum in Figure 4. The effect of the matrix splittings proves even more complex in argon than in nitrogen matrices.

## 4. RESONANCE RAMAN SPECTRA OF V($\eta^6$-ARENE)$_2$

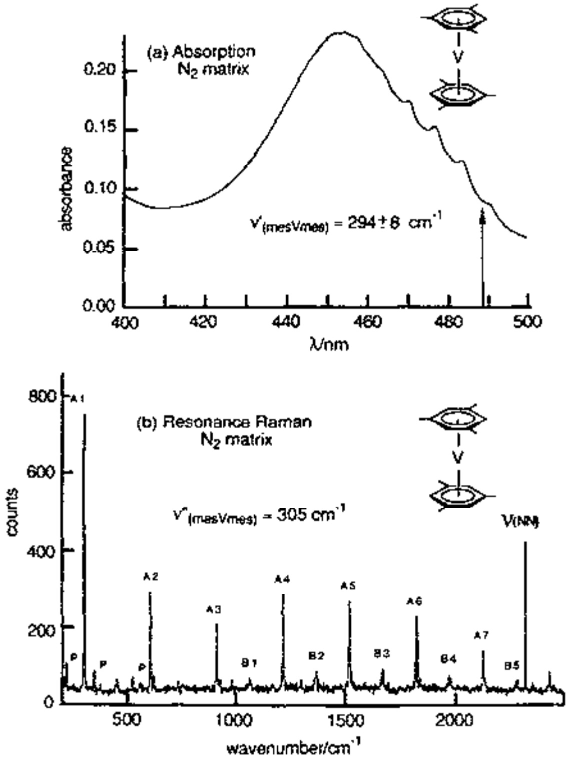

Figure 6. (a) Absorption spectrum of V($\eta^6$-1, 3, 5-$C_6H_3Me_3$)$_2$ isolated in $N_2$ matrix at 12 K. Notice the weak vibrational progression. (b) Resonance Raman spectrum obtained by excitation at 488 nm (arrow in upper spectrum). The band marked ν(NN) is due to scattering from the $N_2$ matrix. P = plasma line. The two progressions are marked A1, A2,... and B1, B2,....

The arene sandwich complexes, V($\eta^6$-$C_6H_6$)$_2$ and V($\eta^6$-1, 3, 5-$C_6H_3Me_3$)$_2$, isolated in $N_2$ matrices, have broader absorption than their metallocene counterparts with poorly resolved vibrational fine structure. Irradiation into the lowest energy LMCT band ($^2A_{1g}$ —> $^2E_{1u}$, see figure 1) does not induce any detectable fluorescence, but a long resonance Raman progression is observed extending out to the eighth overtone of the Ring-V-Ring symmetric stretching mode. Further progressions in the same mode begin at higher frequency (figure 6). Other notable features are listed below [3]
(i) The progression-carrying mode increases in frequency with the more massive arene. We postulate that the increase arises because of mixing with the symmetric combination of the out-of-plane methyl deformation mode which lies to low frequency. The same mechanism will apply to the vibrations of $Cp^*_2Re$.
(ii) The progression frequency decreases in the excited state.
(iii) The RR spectra are polarised, but the experimental value of $\rho$ exceeds the theoretical value.
(iv) The RR progression does not decrease in intensity monotonically (figure 6).

## 5. CONCLUSIONS

The open-shell sandwich complexes exhibit low lying LMCT bands. When the metallocenes are probed by a laser, intense fluorescence ensues, whereas the analogous experiment on V($\eta^6$-arene)$_2$ generates RR spectra. The emission, excitation and RR spectra are extraordinarily well resolved, providing detailed information about the totally symmetric vibrations in the ground and excited states. The move from LIF to RR reflects a decrease in the rate of vibrational relaxation in the upper electronic state which is not yet understood. The transition from prompt fluorescence to RR scattering is a continuous one, suggesting that these processes are aspects of the same phenomenon.

## 6. ACKNOWLEDGEMENTS

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