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Single- and Two-Color Pulsed Laser Resonance Raman Spectroscopy of Excited States of Bis(2,9-dimethyl-1,10-phenanthroline)copper(I) in Solution

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Time-resolved Raman scattering studies are described for bis(2,9-dimethyl-1,10-phenanthroline)copper(I) ($[Cu(dmp)_2]^+$) in MeOH and CH_2Cl_2 as solvents, using a Q-switched Nd/YAG laser as the excitation source. Both single- and two-color pump and probe techniques have been employed, using for the latter the harmonic outputs from the single-laser source at 354.7 and 532 nm, optically delayed with respect to one another. At λ_{exc} = 354.7 nm the spectrum recorded for the complex in MeOH solution contains bands assigned to scattering from the ground electronic state of the complex in resonance with the metal-to-ligand charge-transfer (MLCT) absorption band. The spectrum generated at the same excitation wavelength but for the complex in CH_2Cl_2 solution contains bands assigned to the lowest energy MLCT excited state of the complex. The dominant feature here is scattering attributable to the neutral dmp ligand, resonantly enhanced via a ligand-to-metal charge-transfer transition. The findings are interpreted in terms of a localized formulation, $[(dmp)Cu^{II}(dmp^{•-})]^+$, for the excited state, on the time scale ($\sim$10 ns) of the Raman experiment. At λ_{exc} = 532 nm in CH_2Cl_2 solution with increasing laser beam power, features due to the ground state of the complex decrease relative to solvent Raman peaks, but no features attributable to the MLCT state appear. Likewise, in a two-color study using a 354.7-nm pulse as pump and a delayed 532-nm pulse as probe, the ground state is depleted and the solvent bands increase, but no bands due to resonant scattering from the excited state appear. To account for these results, it is suggested that the state populated by the blue pulse absorbs a second (532 nm) photon creating a relatively long-lived upper excited state with a small resonance Raman scattering cross section at 532 nm. The general implications of these findings in relation to the resonance Raman spectroscopy of transient species are briefly considered.

Introduction

Resonance Raman (RR) spectroscopy continues to be widely applied as a high-resolution structural probe in solutions of transient and excited-state species, especially metal-centered species,[1] including recently an example of resonantly enhanced Raman scattering from a photogenerated organometallic transient.[2] In an earlier communication we reported[3] the RR spectra of the copper(I) complex $[Cu(dpp)_2]^+$ (**1**) (dpp = 2,9-diphenyl-1,10-phenanthroline) and presented evidence that in the lowest energy metal-to-ligand charge-transfer (MLCT) excited state the transferred electron was localized on one of the dpp ligands, suggesting a wider incidence of the phenomenon first shown[4] for the lowest charge-transfer excited state of $[Ru(bpy)_3]^{2+}$. The work employed the well-established approach[4a] of populating the excited state and probing the Raman scattering from it by means of the leading and trailing edges, respectively, of a single laser pulse. We have now extended the study to the MLCT excited states of the complex $[Cu(dmp)_2]^+$ (**2**) (dmp = 2,9-dimethyl-1,10-phenanthroline) employing two-color pump and probe pulses from a single laser to supplement the single-color method. Use of a two-color arrangement in which one beam is a harmonic of or is generated by stimulated Raman λ-shifting from the other is necessary in situations where the ground- and excited-state absorption spectra do not overlap sufficiently for the single-color pulse technique to be applicable.

Experimental Section

A Q-switched Nd/YAG laser previously employed[5] to investigate the excited-state absorption spectroscopy of **1** and **2** was used as the excitation source for both the single- and two-color RR studies. In the majority of single-color experiments, the second or third harmonic output (532 or 354.7 nm, respectively) was used to both pump and probe the MLCT excited states, with additional wavelengths generated where necessary by means of a Raman λ-shifting cell filled with either H_2 or CH_4 at 10 MPa pressure. This cell also formed part of the setup for the two-color studies. A prism harmonic separator (Quanta-Ray PHS 1) was used to disperse the appropriate harmonics from the laser. One of these was taken directly to the sample and the other passed through the Raman cell, where after any necessary wavelength shifting it was returned along the original optical path. The Raman cell functioned not only as a wavelength-shifting device but also as an optical delay line, enabling the two beams to be temporally separated by up to 25 ns. Where the two harmonic outputs (532 and 354.7 nm) were being used as pump and probe, the Raman cell was evacuated. [The duration of a 532-nm pulse (9 ns) is $2^{1/2}$ times longer than that of the third harmonic at 354.7 nm (6.4 ns),

so that at "zero" delay between these pulses the sample has already been irradiated by an appreciable fraction of the 532-nm beam prior to the arrival of the 354.7-nm radiation. To avoid any possible complications in the two-color studies due to this, the minimum delay between the two pulses was set at 6 ns.] Raman scattered radiation (at 90° to the excitation laser beam) was dispersed through a two-stage triple spectrometer (1200 groove/mm gratings in both filter and spectrograph stages) assembled in this department[6] and detected by an intensified, gated diode array (PARC Model 1420) controlled by an EG&G Model 1463 OMA III system. Spectra were integrated on the detector for periods of up to 100 s. In practice it was necessary to sum several such integrated spectra (equivalent in effect to a total accumulation time of up to 16 min) to give spectra with a high signal:noise ratio. High-quality spectra were needed to allow meaningful solvent subtraction without the creation of artifacts. Laser pulse energies at the sample were measured by means of a Gentec joulemeter (Model ED 200).

Some single-color transient RR spectra were also recorded at the Laser Support Facility (LSF) of the Science and Engineering Research Council, Rutherford Appleton Laboratory, by using an excimer-pumped dye laser (Lambda-Physik FL 2002E) as described previously.[2,3,6a] Spectra of samples placed under CW excitation conditions at 363.8 nm were also recorded at the LSF by using an Ar^+ laser (Coherent Innova 90-4).

In all pulsed laser studies, solutions of complexes (ca. 10^{-3} mol dm^{-3}) were Ar-purged and flowed from a syringe through a quartz capillary (1-mm i.d.) at a rate sufficient to ensure that each laser pulse in the 10-Hz train encountered a fresh volume element of sample. Careful checks were carried out for evidence of sample decomposition, especially at an excitation wavelength of 354.7 nm, where bleaching of solutions of **2** in CH_2Cl_2 has recently been reported.[7] Under the conditions of the present studies (2-mJ maximum pulse energy irradiation with a beam focused to a minimum diameter of 0.25 mm), where the circulated solution of total volume 5–10 mL was irradiated for periods of up to 5 min, no measurable sample decomposition was found, as judged from UV-visible spectra. However, solutions of the mixed-ligand complex $[Cu(dmp)(Ph_3P)_2]^+$ (**3**) did undergo decomposition, in CH_2Cl_2 but not in MeOH. All complexes were prepared by literature methods.[7] Solvents were of Aldrich Gold Seal grade and were used without further purification.

(1) Caswell, D. S.; Spiro, T. G. *Inorg. Chem.* **1987**, *26*, 18–22.
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(4) (a) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391–4393. (b) Forster, M.; Hester, R. E. *Chem. Phys. Lett.* **1981**, *81*, 42–47.
(5) Bell, S. E. J.; McGarvey, J. J. *Chem. Phys. Lett.* **1986**, *124*, 336–340.
(6) (a) Bell, S. E. J.; Gordon, K. C.; McGarvey, J. J. *J. Am. Chem. Soc.* **1988**, *110*, 3107–3112. (b) *J. Raman Spectrosc.*, in press.
(7) Berger, R. M.; McMillin, D. R.; Dallinger, R. F. *Inorg. Chem.* **1987**, *26*, 3802–3805.

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Table I. Frequencies (cm^{-1}) of Bands Observed[a] in the 354.7-nm, Pulsed Laser-Excited RR Spectra of [Cu(dmp)$_2$]$^+$ and [Cu(dmp)(Ph$_3$P)$_2$]$^+$ in MeOH and CH$_2$Cl$_2$

[Cu(dmp)$_2$]$^+$ (MeOH)	[Cu(dmp)$_2$]$^+$ (CH$_2$Cl$_2$)	[Cu(dmp)(Ph$_3$P)$_2$]$^+$ (MeOH)
1026 w		1002 w
		1092 mw
1128 w	1133 mw	
	1151 w	
1208 w	1211 w	1202 mw
		1265 w
1317 m	1320 m	
1427 s	1425 s	1421 m
	1467 mw	1455 w
1509 mw	1500 mw	1503 m
		1531 w
1596 m	1596 m	1587 s
1615 mw		

[a] Peak positions are reproducible to ±1 pixel (≡2.5 cm^{-1}).

Results

Resonance Raman spectra of **2** obtained under pulsed excitation at 354.7 nm in MeOH and CH$_2$Cl$_2$ as solvents are shown in Figure 1, and the positions (cm^{-1}) of the principal features are listed in Table I. Although the spectra appear very similar, there are significant differences upon closer inspection. The spectrum recorded for the sample in MeOH solution shows a peak at 1615 cm^{-1}. This feature is absent from the spectrum recorded for the sample in CH$_2$Cl$_2$, where instead a new band appears at 1467 cm^{-1}. It should be stressed here that the absence of the 1615-cm^{-1} band and the presence of the one at 1467 cm^{-1} are features only of spectra obtained by using pulsed excitation of samples in CH$_2$Cl$_2$. Significantly, the CW spectrum of **2** in this solvent obtained with an Ar$^+$ laser (ca. 50-mW power) at 363.8 nm matches instead the 354.7-nm pulse-generated spectrum of **2** in MeOH, indicating that the latter is that of the ground state of **2**, rather than the MLCT excited state, which it is possible to populate[5,7] at 354.7 nm. This conclusion accords with the fact that luminescence from this state is not detectable in MeOH, and the excited-state lifetime in this case is expected[8] to be sufficiently short in comparison with the laser pulse length that the scattering is due to the ground electronic state.

By contrast, the MLCT state is luminescent[8] in CH$_2$Cl$_2$ and the lifetime[5,8] in this solvent is at least an order of magnitude longer than the laser pulse duration, making it readily possible to deplete the ground state and saturate the MLCT state. At the pulse energies typically used (2 mJ), there is a significant excess of photons over molecules in the irradiated volume (ca. 0.2 mm^3). Independent evidence that the ground state of the complex is indeed bleached under these conditions is provided by the results of some two-color pump and probe experiments, considered further below, where a 532-nm probe shows (see Figure 4a) that the ground state is depleted by a 354.7-nm pulse of energy similar to that used to produce the spectra in Figure 1. We thus assign the bands of the spectrum in Figure 1b to scattering from the MLCT excited state. As Table I shows, the majority of the bands occur at almost the same frequencies as those in the ground-state spectrum (Figure 1a), suggesting that they are due to neutral-ligand modes. Figure 1c shows the resonance Raman spectrum of the MLCT excited state of the mixed-ligand complex [Cu-(dmp)(Ph$_3$P)$_2$]$^+$ (**3**). The principal bands are also listed in Table I. No features appear around 1300 cm^{-1}. The absence of scattering in this region is a convenient spectroscopic marker[3] for the dmp$^{\bullet-}$ radical anion.
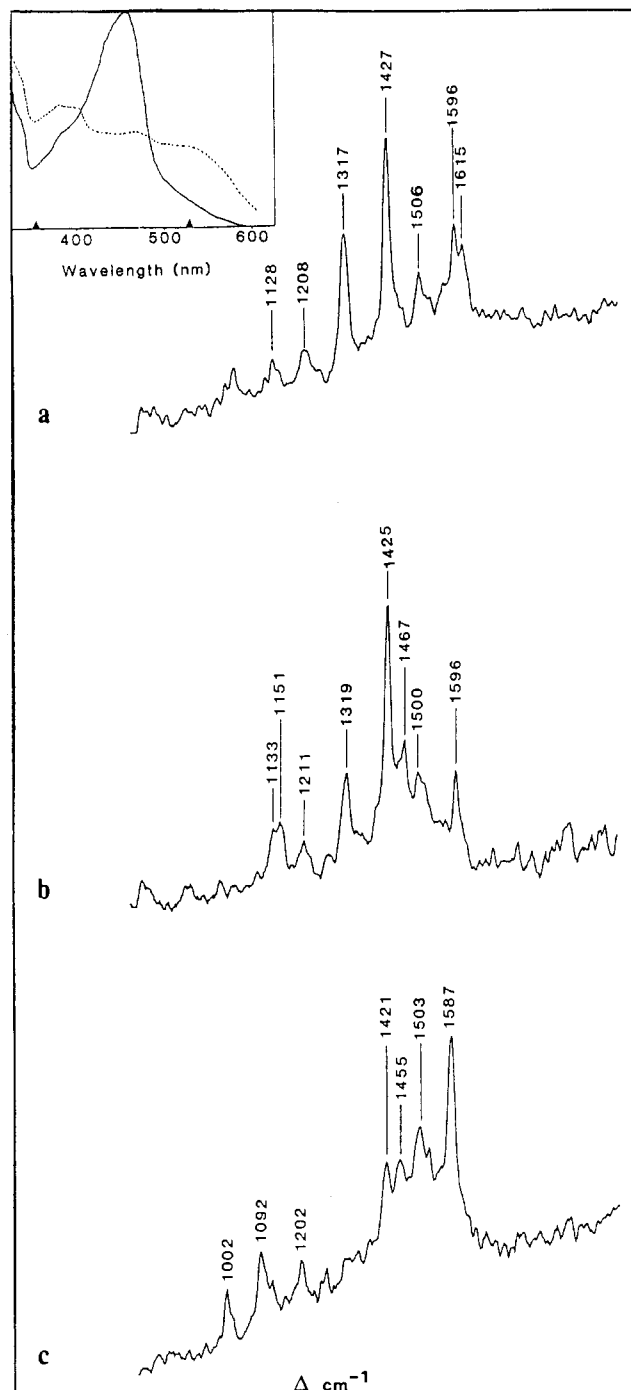
(8) Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J.-P.; Kirchoff, J. R.; McMillin, D. R. *J. Chem. Soc., Chem. Commun.* **1983**, 513–515.

(9) The resonance Raman spectrum of the MLCT excited state of **3** has been reported by us previously.[3] The very satisfactory performance of the two-stage spectrometer + OMA III system and the advantage gained by extensive signal integration on the detector are demonstrated by the good signal:noise ratio in the spectra reported here.

Figure 1. Resonance Raman spectra of argon-purged solutions (~10^{-3} mol dm^{-3}) of [Cu(dmp)$_2$]$^+$ in MeOH (trace a) and CH$_2$Cl$_2$ (trace b) and of [Cu(dmp)(Ph$_3$P)$_2$]$^+$ in MeOH (trace c). Spectra are of samples excited at 354.7 nm (Q-switched Nd/YAG). Solvent peaks were subtracted in each spectrum. Inset: Ground-state (—) and MLCT excited-state (---) spectra of [Cu(dmp)$_2$]$^+$ in CH$_2$Cl$_2$. Arrows indicate laser excitation wavelengths for Raman studies.

The RR spectrum recorded for **2** in MeOH but at an excitation wavelength of 532 nm is shown in Figure 2. As in the experiment in this solvent at λ_{exc} = 354.7 nm (Figure 1a), the spectrum contains bands attributable to scattering by the ground electronic state of **2**. The spectra in Figures 1a and 2 show distinct resonance enhancement patterns and several different frequencies, suggesting contributions from different resonant transitions at these two excitation wavelengths and the involvement of a significant number (~11) of ligand vibrational modes. At least 12 are possible[10] between 1650 and 1100 cm^{-1}.

(10) Clark, R. J. H.; Turtle, P. C.; Strommer, D. P.; Streusand, B.; Kincaid, J.; Nakamoto, K. *Inorg. Chem.* **1977**, *16*, 84–88.

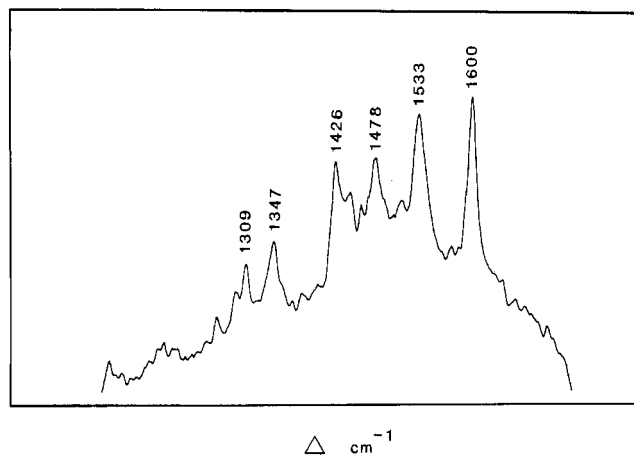**Figure 2.** Resonance Raman spectrum of an argon-purged solution (10^{-3} mol dm^{-3}) of [Cu(dmp)$_2$]$^+$ in MeOH, excited at 532 nm (Q-switched Nd/YAG). Solvent peaks were subtracted.

Figure 3 also shows the RR spectrum of **2** in CH$_2$Cl$_2$, recorded at 532 nm, but at two different laser power densities. Solvent bands in the upper (higher power) and lower spectra have been normalized. Comparison of the spectra shows that features due to the complex actually *decrease*, relative to the solvent scattering, with increasing laser-power density. Evidently, the 532-nm radiation is pumping the complex out of the ground state, but no new bands grow in, even at the narrowest beam diameter (0.25 mm) and hence highest laser power densities used.

The upper trace in Figure 4 shows the results of a two-color experiment in which the sample was pumped by a 354.7-nm pulse and then probed 6 ns later by a 532-nm pulse; for comparison, the spectrum obtained by using only the probe beam is shown in the lower trace. It is clear that the bands due to the ground electronic state of the complex virtually disappear when the 354.7-nm beam is turned on, implying that the ground state is being depopulated by the pulse, but no new features appear. The striking point however is that the absolute size of the signal due to Raman scattering by the solvent is greater in the two-color experiment than in the single-color case, even though the 532-nm energy has been kept the same in both experiments. We know that the virtual disappearance of the 532-nm-generated spectrum when the 354.7-nm beam was turned on is not simply the result of permanent bleaching of the sample, since reversing the order in which these experiments were done had no effect. Furthermore, solutions that had been subjected to numerous irradiation cycles in the course of multiple spectral accumulations gave the same RR spectra as freshly prepared samples.

Discussion

In earlier work we reported[5] the MLCT excited-state absorption spectrum of **2** and established on the basis of time-resolved absorbance differences (ΔA) and luminescence[8] measurements that the same state is populated by irradiation at either 354.7 or 532 nm. For convenience in the Discussion here, the spectrum is shown in Figure 1, where the probe wavelengths used for the present resonance Raman studies are also indicated. The appearance of neutral-ligand modes in the RR spectrum of the MLCT state of **2** (Figure 1b) generated by pulsed excitation in CH$_2$Cl$_2$ solution at 354.7 nm suggests that the state can be formulated as (L)-Cu^{II}(L$^{\bullet-}$) with the excited electron localized on one (dmp) ligand, the resonance enhancement arising through a ligand-to-metal charge-transfer (LMCT) transition from the neutral ligand to the (formal) Cu^{II} center. This parallels the conclusion we established[3] previously for the MLCT excited state of Cu(dpp)$_2$$^+$ (**1**), which has a very similar ESA spectrum.[5] The excited-state feature in Figure 1b at 1467 cm^{-1} could be due either to an additional mode of the neutral ligand coming into resonance via the LMCT transition or to a mode associated with the radical-anion moiety, L$^{\bullet-}$, of the localized MLCT state. However examination of the RR spectrum at this excitation wavelength of the MLCT state of the mixed-ligand complex **3** (Figure 1c and Table I) shows that

the strongest L$^{\bullet-}$ mode occurs at 1587 cm^{-1}. This would be expected to appear before any other L$^{\bullet-}$ feature in the RR spectrum of **2**, and since this is clearly not the case, we attribute the 1467-cm^{-1} band to a neutral-L mode in the MLCT state. The overall similarity between the pattern of mode enhancements in this spectrum and that in the RR spectrum of the ground electronic state of the complex is striking. It suggests that depopulation of the HOMO of the dmp ligand (via the LMCT transition) brings about distortions of the ligand skeleton similar to those brought about by the population of the Π* orbital in the resonant MLCT transition of the ground electronic state.

At an excitation wavelength of 532 nm it is more difficult to pump the ground state of **2** into the MLCT state on account of the lower extinction coefficient of the ground state at this wavelength. Nevertheless, as the results of the experiments (Figure 3) with increasing laser beam focus show, the complex can be successfully pumped out of the ground state by irradiation at 532 nm. The fact that no new Raman bands appear is puzzling however, since it suggests that the MLCT state that we would expect to be populated is not a strong scatterer in this region, despite the fact[5] (Figure 1) that its extinction coefficient at 532 nm is approximately twice as large as that of the ground state.

It was hoped that in the two-color experiments the complex could be pumped at a sufficiently high power level at 354.7 nm to ensure that the (delayed) 532-nm probe beam would encounter the MLCT excited state only. Examination of the pair of spectra in Figure 4, obtained by using the same 532-nm probe beam energy but with and without the 354.7-nm pump pulse, shows that while the ground-state scattering virtually disappears in the presence of the blue beam, the excited state that is ultimately populated cannot be the MLCT state. The latter is known to be more strongly absorbing at 532 nm than the ground state (Figure 1), so that if it were populated, the *absolute* size of the Raman signal from the solvent should decrease, whereas in fact a significant increase in the solvent scattering intensity is observed. This points to the population of a species that is less strongly absorbing in the excited state than the ground state. It should be emphasized here that this conclusion could only be established by a two-color experiment of the type described. In a single-color study, only changes in the *relative* heights of solvent and complex bands would be detectable.

It seems unlikely that the effects are due to an upper state produced by sequential absorption of a second 354.7-nm photon by the MLCT state. This would lead via a LMCT transition to a state (L$^{\bullet+}$)Cu^I(L$^{\bullet-}$), which must be short-lived (as shown by the 354.7-nm single-laser pump and probe experiments), whereas the results require that a significant proportion of the ground state must be pumped to a relatively long-lived upper state. This state must be relatively long-lived ($\geq$ the laser pulse duration, 9 ns), since if it decayed promptly, the absorbance of the solution at 532 nm would not change when the 354.7-nm beam is present.

The findings in Figure 3 resemble the line broadening reported recently by Carroll and Brus[11] in picosecond-pulsed Raman studies and attributed to nonlinear resonant scattering at high optical fields. However, the results of the two-color experiments shown in Figure 4 rule out such effects as the explanation of our observations. As Figure 4a shows, depletion of the ground state of **2** persists for more than 6 ns after the 354.7-nm pump pulse encounters the sample, by which time any high optical field conceivably associated with this pulse would have decayed. Without this two-color experiment, nonlinear scattering could not have been unequivocally eliminated as a possible explanation of the single-color results in Figure 3.

We now propose the scheme shown in Figure 5, in which it is envisaged that the localized MLCT state, (L)Cu^{II}(L$^{\bullet-}$) (hereafter referred to as state X), formed upon irradiation at 354.7 nm absorbs a 532-nm photon through a $\pi \rightarrow \pi^*$ transition of the L$^{\bullet-}$ moiety to create a second species, (L)Cu^{II}(L$^{\bullet-*}$) (state Y), which does not absorb appreciably at 532 nm, consistent with the fact shown in Figure 3a that no new Raman scattering appears in the

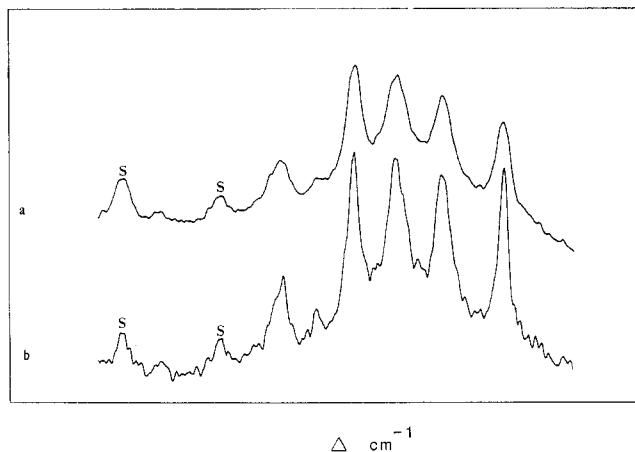(11) Carroll, P. J.; Brus, L. E. *J. Chem. Phys.* **1987**, *86*, 6584–6590.

Figure 3. Influence of excitation laser power density on resonance Raman spectra of argon-purged solutions (10^{-3} mol dm^{-3}) of [Cu(dmp)$_2$]$^+$ in CH$_2$Cl$_2$ (λ_{exc} = 532 nm, Q-switched Nd/YAG laser). The laser power density for recording trace a was increased by factor of 4 compared to that for trace b. (Normalized) peaks due to solvent scattering are denoted by S.
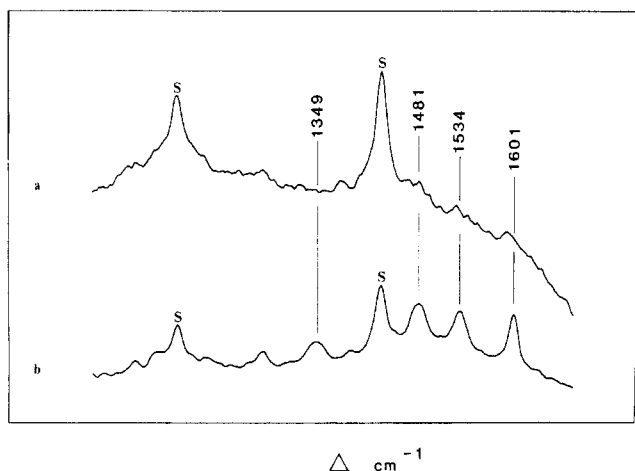

Figure 4. (a) Two-color pump and probe resonance Raman spectrum of [Cu(dmp)$_2$]$^+$ in CH$_2$Cl$_2$ (λ_{probe} = 532 nm; recorded 6 ns after 354.7-nm pump pulse (harmonic outputs from Q-switched Nd/YAG)). (b) Spectrum recorded at same 532-nm probe beam energy as for (a), in absence of 354.7-nm pulse. Samples for (a) and (b) were from the same batch of argon-purged solutions (ca. 10^{-3} mol dm^{-3}). Solvent peaks are denoted by S.

single color experiments at this wavelength.[12]   In state X the coordinated radical anion, L$^{•-}$, can be regarded as being in its ground electronic state. Absorption of the second (532 nm) photon leads to state Y, which is in effect the first excited state, L$^{•-*}$, of the radical anion. This remains populated during the 532-nm laser pulse. [In the 354.7-nm *single-color* experiments, absorption of a second photon is due to a LMCT transition rather than to a L$^{•-}$-centered $\pi \rightarrow \pi^*$ transition. The species produced in that case, (L$^{•+}$)Cu^I(L$^{•-}$) (vide supra), is sufficiently short-lived to prevent the buildup of a significant population during the laser pulse.] In our system, where the pulse duration is fixed (and apparently shorter than the lifetime of the upper state Y), the only way in principle to observe scattering from the lower state X is to do a "tickling" experiment in which the pulse energy is reduced to the point where there are far fewer photons than molecules in the irradiated volume so that state Y is no longer populated and scattering from X, resonant with the $\pi \rightarrow \pi^*$

(12) Preliminary single-color experiments at λ_{exc} = 447.2 nm (produced by second Stokes stimulated Raman λ-shifting from 354.7 nm in CH$_4$) show a relatively weak resonance Raman spectrum that we believe may be characteristic of L$^{•-}$ in the MLCT state X, on the grounds that it resembles our published[3] resonance Raman spectrum of dpp$^{•-}$ in the MLCT state of [Cu(dpp)$_2$]$^+$.

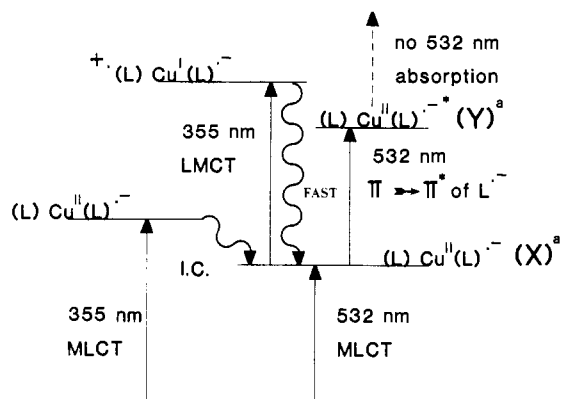**Figure 5.** Proposed qualitative energy level diagram and photophysical relaxation scheme for [Cu(dmp)$_2$]$^+$ (see text for details). The superscript a indicates labels used to refer to these MLCT states in the text.

transition of L$^{•-}$, should be observed. Unfortunately, in practice, at the photon energies needed to achieve this condition, the average power is too low to generate Raman scattering of sufficient intensity for our detector; a higher pulse repetition rate would be needed to maintain the necessary average power. Another complicating factor is that the 532-nm probe beam acts as a secondary pump source so that on reduction of the 532-nm energy (keeping the 354.7-nm energy constant), bands appear that are due to scattering from the ground electronic state rather than from the MLCT state X. An alternative strategy might be to experiment with other solvents[13] as a way of selectively decreasing the lifetime of state Y. However, the susceptibility[8] of state X itself to solvent quenching severly limits the range for investigation.

It is interesting to compare the present results with our earlier study[3] of [Cu(dpp)$_2$]$^+$, where it was possible to probe the Raman spectral bands of the species dpp$^{•-}$ at 540 nm that are resonant with the $\pi \rightarrow \pi^*$ transition. Assuming that a scheme similar to Figure 5 applies to this complex also, the result suggests that state Y is more short-lived in this case, indicating more efficient radiationless decay within the L$^{•-}$ manifold for *[Cu(dpp)$_2$]$^+$ than for *[Cu(dmp)$_2$]$^+$. A more extensive study of the CT excited-state resonance Raman spectroscopy of related complexes will be required to try to elucidate what structural features of ligand L may be important in controlling the lifetime of L$^{•-*}$.

The present investigation has drawn attention to a significant aspect of the resonance Raman spectroscopy of transient species, namely the interplay among the probe beam power density, the lifetimes of the upper and lower states involved in the resonant transition, and the oscillator strength of the latter at λ_{exc}. At the high peak powers required for generating Raman spectra from short pulses, relatively short-lived upper excited states may be populated and probed. Such species are less likely to be observed in time-resolved ΔA experiments[5] because of both the lower power normally used and the fact that in any case they would be significantly populated only during the laser pulse, thus requiring the use of deconvolution techniques. We are continuing our investigations of the RR spectroscopy of metal-centered species by two-color methods, which, as the work described here has shown, can uncover information about excited states that is not available from single-color studies alone.

Registry No. 2, 21710-12-3; [Cu(dmp)(Ph$_3$P)$_2$]$^+$, 78809-58-2.

(13) A reviewer's suggestion.