

**Table VII.** Ab Initio  $\tau$  Coefficients, Exchange Integrals (in hartree) and Energy Differences between the  ${}^2A_1$  and  ${}^2B_1$  Components of  ${}^2E_g$  Origin (in  $\text{cm}^{-1}$ ) for the *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub><sup>+</sup> and the *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>F<sub>2</sub><sup>+</sup> complexes<sup>a</sup>

	<i>trans</i> -Cr(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> <sup>+</sup>	<i>trans</i> -Cr(NH <sub>3</sub> ) <sub>4</sub> F <sub>2</sub> <sup>+</sup>
$\tau_{b_2}$	0.996	0.996
$\tau_e$	0.985	0.986
$K_{b_2e}$	0.031 919	0.032 231
$K_{ee}$	0.031 614	0.032 235
$E({}^2B_1) - E({}^2A_1)$	134	-2

<sup>a</sup> The  $\tau$  coefficients are defined in eqs 13 and 14;  $E({}^2B_1) - E({}^2A_1)$  is given in eq 16. The  $b_2$  orbital is of dominant  $d_{xy}$  character; the orbitals of  $e$  symmetry are of dominant  $d_{xz}$  and  $d_{yz}$  characters.

At the ab initio level, the  $\tau$  coefficients and the relevant  $K$  integrals can be evaluated explicitly. The results for the two *trans* complexes are shown in Table VII. In agreement with the ligand field model, the ab initio method identifies the lowest  ${}^2E_g$  component of the *trans* dichloro compound as the  ${}^2A_1$  state. Moreover, Table VII shows that the  $e$  orbitals are indeed more covalent than the  $b_2$  orbital. More specifically, for the  $\tau$  coefficients we have  $\tau_e = 0.985 < \tau_{b_2} = 0.996$  and for the  $K$  integrals  $K_{b_2e} = 0.0319$  hartree  $> K_{ee} = 0.0316$  hartree. A somewhat different situation appears from the *trans*-difluoro compound. Although the  $\tau$  coefficients are virtually identical with those of the *trans*-dichloro complex, the two  $K$  integrals are hardly different in this case. As a consequence, in the absence of CI effects, the  ${}^2A_1$  state is calculated to have almost the same energy as the  ${}^2B_1$  component. Clearly, the relative magnitude of the  $K$  integrals does not only depend on the  $\tau$  coefficients, and the size of the mixing ligand orbitals is certainly an additional element that has to be taken into account. Indeed, the F orbitals are more compact than the Cl or the NH<sub>3</sub> orbitals; moreover, the CrF bond length is shorter than the CrN or CrCl bonds. As a consequence of these two factors, decreasing  $\tau$  will have a smaller effect on the  $K$  integrals for F ligands than for Cl or NH<sub>3</sub> ligands. In the rationalization of Schmidtke et al., both factors were neglected.

When CI is taken into account, the  ${}^2E_g$  splittings of Table V are obtained. Apparently, CI causes a greater stabilization for the  ${}^2B_1$  than for the  ${}^2A_1$  component: for the *trans*-dichloro compound, the  ${}^2E_g$  splitting becomes smaller ( $134 \text{ cm}^{-1} \rightarrow 104 \text{ cm}^{-1}$ ), for the *trans*-difluoro complex, CI leads to a larger  ${}^2A_1$ - ${}^2B_1$  separation ( $-2 \text{ cm}^{-1} \rightarrow -314 \text{ cm}^{-1}$ ). Although the LFT splittings

are systematically too small, it is worth mentioning that they always have the same sign as the ab initio splittings: for the *trans*-dichloro complex and the *cis* compound, the resulting  $E({}^2B_1) - E({}^2A_1)$  (Table V) is positive; for Cr(NH<sub>3</sub>)<sub>5</sub>F<sub>2</sub><sup>+</sup> and the *trans*-difluoro compound, this energy difference is negative.

#### IV. Conclusions

A Mulliken population analysis of the  $Av(d^3)$  orbitals confirms the ligand field assumption that  $\pi_{\text{NH}_3} = 0$ . Yet, such an analysis does not support the idea that each metal ligand bond is a completely independent entity: it reveals that the donation of a particular ligand is influenced to some extent by the other ligands in the complex. However, it appears that these donation differences hardly affect the additivity and transferability postulate at the state level: the ab initio spectra for all complexes under consideration can be described quite reasonably with only one set of ligand field parameters. These parameters agree with the semiempirical values in classifying the Cl<sup>-</sup> ion as the weakest  $\sigma$  donor, the weakest ligand field, and a weaker  $\pi$  donor than F<sup>-</sup>; F<sup>-</sup> is identified as the strongest  $\sigma$  donor, having a smaller spectrochemical strength than the NH<sub>3</sub> molecule. These conclusions also follow from the relative order of the orbital energies in the  $Av(d^3)$  state.

From a quantitative point of view, the quartet-quartet transition energies agree reasonably well with experiment. On the other hand, the quartet-doublet excitation energies are calculated much too large at the ab initio ligand field CI level. A better description of the spin-forbidden transitions requires an extensive treatment of electron correlation. It is gratifying though that already at the ligand field CI level, the ab initio results are in agreement with experiment in identifying the *trans*-difluoro compound as a  ${}^2T_1$  emitter and the other substituted complexes as  ${}^2E$  emitters. Moreover, these results lead to a deeper understanding of the origin of the  ${}^2E_g$  splitting in tetragonal chromium(III) compounds. Apparently, this splitting does depend not only on the delocalization coefficients but also on the metal ligand bond lengths and the shape of the interacting ligand orbitals. Also, it is strongly affected by a complete ligand field CI within the  $d^3$  manifold.

The nephelauxetic reduction in the different complexes has been analyzed by means of the average (d,d) repulsion. This led to the conclusion that NH<sub>3</sub> is a more covalent ligand than F<sup>-</sup> but a less covalent ligand than the Cl<sup>-</sup> or CN<sup>-</sup> ions. This conclusion is perfectly in line with the nephelauxetic series.

Contribution from the School of Chemistry,  
Queen's University of Belfast, Belfast BT9 5AG, Northern Ireland

## Time-Resolved Resonance Raman Spectroscopy of [Cu(dmp)<sub>2</sub>]<sup>+</sup> in Solution

Keith C. Gordon and John J. McGarvey\*

Received July 10, 1990

Pulsed and CW-laser-excited resonance Raman (RR) spectra are reported at a number of excitation wavelengths for the ground state and lowest energy metal-to-ligand charge-transfer (MLCT) excited state of [Cu(dmp)<sub>2</sub>]<sup>+</sup> (1) (dmp = bis(2,9-dimethyl-1,10-phenanthroline)). From analysis of the ground-state RR spectra, evidence has been obtained that three distinct transitions contribute to the MLCT absorption profile over the wavelength range 340–550 nm. The conclusions are in agreement with a recent independent analysis of the low-temperature UV-visible absorption spectrum of 1. The time-resolved RR spectra which are reported provide convincing evidence that the lowest MLCT excited state is localized, [(L)Cu<sup>II</sup>(L<sup>-</sup>)]<sup>+</sup>, corroborating earlier, less extensive RR spectral data. The consequence of this assignment, that the effective symmetry of the thermally equilibrated MLCT excited state is  $C_{2v}$  or possibly  $C_2$ , is considered in relation to a recent spectroscopic analysis of the MLCT excited states of related Cu(I) complexes.

### Introduction

In recent papers, we have reported<sup>1,2</sup> the resonance Raman spectra of the ground states and metal-ligand charge-transfer

(MLCT) excited states of copper(I) complexes with 2,9-disubstituted 1,10-phenanthroline ligands. The evidence supported a localized formulation, (L)Cu<sup>II</sup>(L<sup>-</sup>) for the MLCT states. In the case where L = 2,9-diphenyl-1,10-phenanthroline (dpp), bands attributable to both neutral ligand L and radical anion L<sup>-</sup> were observed, but for the 2,9-dimethyl-substituted analogue (dmp) at the probe wavelength (532 nm) used in the two color experiments carried out, depletion of the ground-state bands was ob-

(1) McGarvey, J. J.; Bell, S. E. J.; Bechara, J. N. *Inorg. Chem.* **1986**, *25*, 4325–4327.

(2) McGarvey, J. J.; Bell, S. E. J.; Gordon, K. C. *Inorg. Chem.* **1988**, *27*, 4003–4006.

served but no features attributable to the MLCT excited state were detected. To account for this absence of excited-state scattering it was proposed<sup>2</sup> that the MLCT state initially populated by the 354.7-nm pump pulse was sequentially pumped by the probe pulse at 532 nm into a relatively long-lived ( $\tau \geq$  the laser pulse duration) upper excited state with a small scattering cross section at 532 nm. Investigations at other laser excitation wavelengths resonant with transitions of  $L^{\bullet-}$  are reported here, and more complete evidence in support of the localized formulation for the lowest MLCT excited state has been obtained.

### Experimental Section

The Q-switched Nd/YAG laser and stimulated Raman wavelength-shifting cell used for both single- and two-color TR<sup>3</sup> work has been described in detail previously.<sup>2</sup> A two-element quartz lens system was used to telescope the laser beam. The energy flux was controlled by neutral density filters. Raman spectra were recorded in a backscattering geometry by using a two-stage triple spectrometer assembled<sup>3</sup> in the School of Chemistry and an optical multichannel analyzer (EG&G Model 1463 OMA III system). The diode array detector (EG&G Model 1420B) was normally run at a temperature of  $-24^\circ\text{C}$ . This enabled spectra to be integrated on the detector for periods of up to 400 s. The filter stage of the spectrometer was fitted with 1200 groove/mm gratings and the spectrograph stage with either a ruled 1200 groove/mm element or an 1800 groove holographic grating.

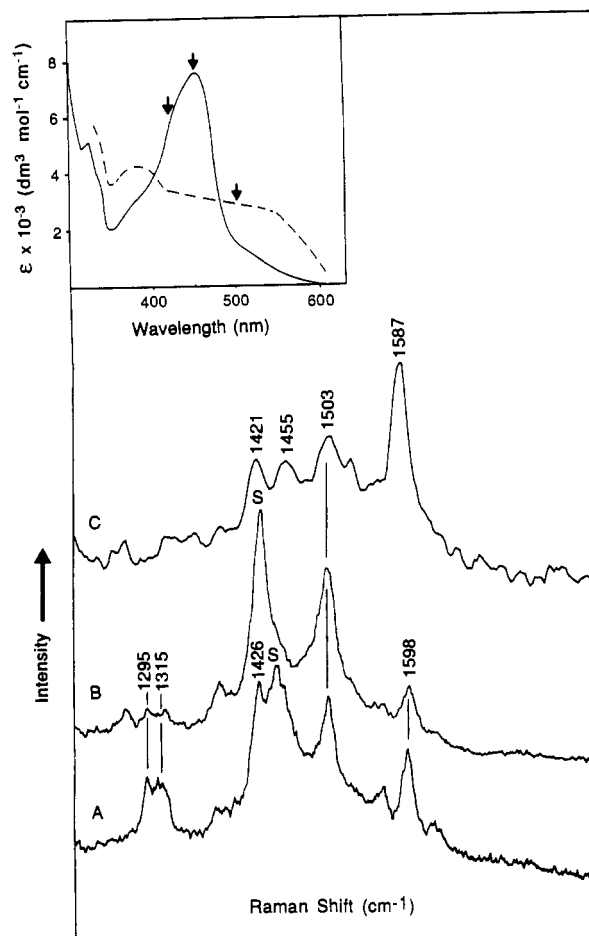
Spectra under CW excitation conditions were recorded either at the Laser Support Facility (LSF) of the Science and Engineering Research Council, Rutherford Appleton Laboratory, by using an Ar<sup>+</sup> laser (Coherent Innova 90-4) or at QUB by means of a Spectra-Physics Model 2025-03 Ar<sup>+</sup> system. In the former case a 90° scattering geometry was used whereas for the majority of the QUB-based studies a backscattering arrangement was employed.

The excited-state absorption (ESA) spectra of the complexes, essential to guide the selection of pump and probe wavelengths for the Raman studies, were investigated and recorded by means of conventional laser flash photolysis techniques as described in detail elsewhere.<sup>4</sup>

The complexes used were prepared by established literature methods<sup>5</sup> and argon-purged solutions (Aldrich Gold Seal solvents) flowed from a syringe through 1-mm-i.d. quartz capillaries at a rate which ensured that each laser pulse in the 10-Hz train from the YAG encountered a fresh volume element of sample.

### Results

Figure 1 shows resonance Raman spectra of  $[\text{Cu}(\text{dmp})_2]^+\text{BF}_4^-$  ( $1\text{BF}_4$ ) generated by using pulsed excitation at 416 nm in two different solvents. In MeOH (trace a), in which the MLCT excited state lifetime is shorter than the laser pulse duration, the spectrum recorded is attributable to the ground electronic state and shows bands at 1598, 1503, and 1426  $\text{cm}^{-1}$  and a pair of features at 1295 and 1315  $\text{cm}^{-1}$ . The spectrum in trace b, recorded in  $\text{CH}_2\text{Cl}_2$  as solvent, where the MLCT excited state lifetime is at least an order of magnitude longer, is assigned to scattering from that state. The main differences compared to the spectrum in MeOH are the increased intensity of a band at 1503  $\text{cm}^{-1}$  and, more significantly (vide infra), a marked reduction in intensity (though not complete disappearance) of the pair of features near 1300  $\text{cm}^{-1}$ . The excited-state resonance Raman spectrum of  $[(\text{PPh}_3)_2\text{Cu}(\text{dmp})]^+$  is shown in Figure 1c. The scattering observed in this spectrum is characteristic<sup>1,14</sup> of  $\text{dmp}^{\bullet-}$ , resonant



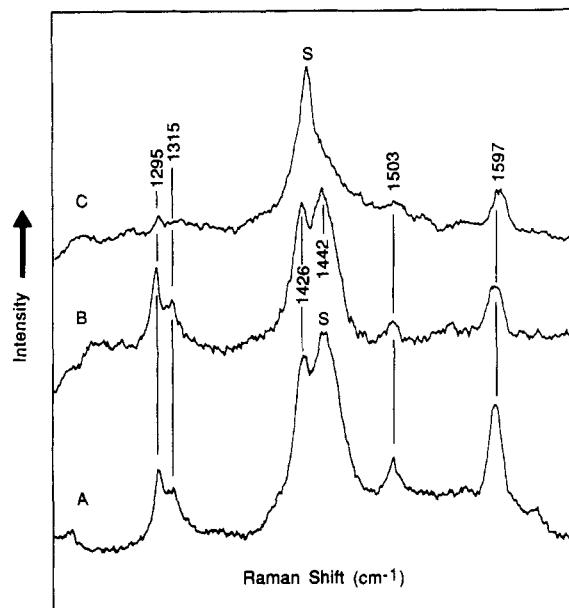
**Figure 1.** Resonance Raman spectra of argon-purged solutions (ca.  $10^{-3}$  mol  $\text{dm}^{-3}$ ) of  $[\text{Cu}(\text{dmp})_2]^+$  excited at 416 nm (first Stokes Raman line from  $\text{H}_2$  excited at 354.7 nm) in MeOH (trace a) and  $\text{CH}_2\text{Cl}_2$  (trace b) and of  $[(\text{Ph}_3\text{P})_2\text{Cu}(\text{dmp})]^+$  in MeOH (trace c) excited at 354.7 nm. Pulse energy and laser spot size were 2 mJ and 0.7 mm, respectively, for traces a and b and 3 mJ and 0.8 mm for trace c. Inset: Ground state (—) and MLCT excited state (---) absorption spectra of  $[\text{Cu}(\text{dmp})_2]^+$  in  $\text{CH}_2\text{Cl}_2$  (from ref 2). Arrows show laser excitation wavelengths used for ground-state resonance Raman and TR<sup>3</sup> studies; see other figure captions.

through a  $\pi \rightarrow \pi^*$  transition; it shows bands at 1587, 1503, 1455, and 1421  $\text{cm}^{-1}$  but differs from the ground-state resonance Raman spectrum of the mixed-ligand complex in that features at 1300  $\text{cm}^{-1}$  do not turn up in the excited state spectrum. The disappearance of these bands provides a convenient indicator<sup>1,2</sup> of the presence of  $\text{dmp}^{\bullet-}$  radical anion. Since the spectrum of the latter includes a band at 1503  $\text{cm}^{-1}$ , it might be concluded that the increased intensity of the 1503- $\text{cm}^{-1}$  band noted above in the spectrum of the excited state of 1 is due to resonance with a ( $\text{dmp}^{\bullet-}$ )-centered transition. However, the intensity relative to other features is rather different in the two spectra. That, coupled with the fact that the 1300- $\text{cm}^{-1}$  bands have not totally disappeared in trace b, suggests that the latter spectrum is not entirely due to resonance with the radical anion transition.

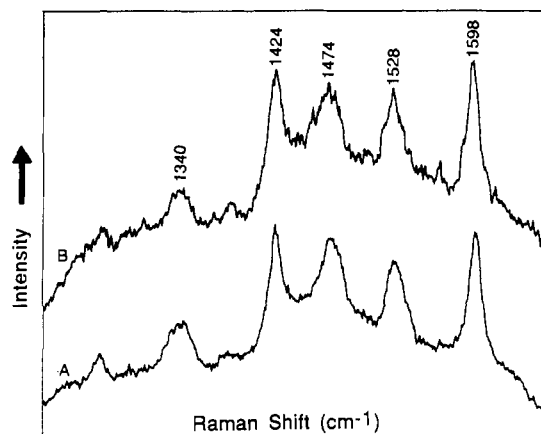
When the excitation wavelength is moved further to the red, an important change takes place, as shown by the spectra in Figure

- (3) Bell, S. E. J.; Gordon, K. C.; McGarvey, J. J. *J. Raman Spectrosc.* **1989**, *20*, 105–109.
- (4) Bell, S. E. J.; McGarvey, J. J. *Chem. Phys. Lett.* **1984**, *124*, 336–340.
- (5) Berger, R. M.; McMillin, D. R.; Dallinger, R. F. *Inorg. Chem.* **1987**, *26*, 3802–3805.
- (6) Ichinaga, A. K.; Kirchoff, J. R.; McMillin, D. R.; Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J.-P. *Inorg. Chem.* **1987**, *26*, 4290–4292.
- (7) Johnson, C. R.; Ludwig, M.; Asher, S. A. *J. Am. Chem. Soc.* **1986**, *108*, 905–912.
- (8) De Vito, V. L.; Asher, S. A. *J. Am. Chem. Soc.* **1989**, *111*, 9143–9152.
- (9) Buntinx, G.; Poizat, O. *J. Chem. Phys.* **1989**, *91*, 2153–2162.
- (10) Gordon, K. C.; McGarvey, J. J. *Chem. Phys. Lett.* **1989**, *162*, 117–122.
- (11) Parker, W. L.; Crosby, G. A. *J. Phys. Chem.* **1989**, *93*, 5692–5696.
- (12) Ceulemans, A.; Vanquickenborne, L. G. *Struct. Bonding* **1989**, *71*, 126–159.
- (13) Carroll, P. J.; Brus, L. E. *J. Am. Chem. Soc.* **1987**, *109*, 7613–7616.

- (14) Attempts to prepare  $\text{dmp}^{\bullet-}$  by Na film reduction of  $\text{dmp}$  ligand in THF were unsuccessful. The alternative strategy adopted here of generating the radical anion through population of the lowest MLCT excited state of the mixed ligand complex  $[(\text{Ph}_3\text{P})_2\text{Cu}(\text{dmp})]^+$ , in which the "transferred" electron is localized on the unique  $\text{dmp}$  ligand, is an established one (see refs 1, 10, 15, and 16). In the present instance it has the advantage over the chemical preparation of  $\text{dmp}^{\bullet-}$  that the radical anion is bound to a (formal)  $\text{Cu}^{\text{II}}$  center, rather than being "isolated" in solution.
- (15) Caspar, J. V.; Westmoreland, D.; Allen, G. H.; Bradley, P. G.; Meyer, T. J.; Woodruff, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 3492.
- (16) Smothers, W. K.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1067.



**Figure 2.** Resonance Raman spectra of argon-purged solutions ( $10^{-3}$  mol  $\text{dm}^{-3}$ ) of  $[\text{Cu}(\text{dmp})_2]^+$ . Trace a: spectrum excited at 447.2 nm (second Stokes line from  $\text{CH}_4$  excited at 354.7 nm) in MeOH solution; pulse energy, 1.5 mJ; spot size, 0.8 mm. Trace b: spectrum excited at 457.9 nm ( $\text{Ar}^+$ , 200 mW, 0.8 mm spot size) in  $\text{CHCl}_3$  solution. Trace c: spectrum excited at 447.2 nm in  $\text{CH}_2\text{Cl}_2$  solution; pulse energy, 1.5 mJ; spot size, 0.8 mm.



**Figure 3.** Resonance Raman spectra of argon-purged solutions ( $10^{-3}$  mol  $\text{dm}^{-3}$ ) of  $[\text{Cu}(\text{dmp})_2]^+$  excited at 503 nm (second Stokes line from  $\text{H}_2$  excited at 354.7 nm) in MeOH (trace a) and  $\text{CH}_2\text{Cl}_2$  (trace b). Pulse energy was 1.5 mJ; spot size was 0.8 mm.

2 of **1** in MeOH and in  $\text{CH}_2\text{Cl}_2$  generated by using pulsed excitation at 447.2 nm. The spectrum taken in methanol (trace a) is due to the ground state, as evidenced by the similarity to the spectrum recorded under CW excitation conditions at 457.9 nm (trace b). The bands observed have the same frequencies as those measured at 416 nm, but the intensities are different. However the excited-state spectrum generated in  $\text{CH}_2\text{Cl}_2$  at 447.2 nm (trace c), shows no features in the 1300- $\text{cm}^{-1}$  region. The disposition and relative intensities of the bands that turn up in the excited-state resonance Raman spectrum bear a strong resemblance to those for the excited state of the mixed-ligand complex, Figure 1c, indicating that it arises from resonant scattering via a radical anion-centered transition. This is strong evidence that the lowest MLCT state of **1** is localized on the time scale of these experiments.

Figure 3 shows resonance Raman spectra of the complex generated by pulsed excitation at 503 nm in MeOH and  $\text{CH}_2\text{Cl}_2$  as solvents. In this case, the two spectra are essentially identical, with no evidence of excited-state scattering in the  $\text{CH}_2\text{Cl}_2$  solution. Thus a striking change in the scattering pattern accompanies the change in excitation wavelength from 447.2 to 503 nm.

**Table I.** Raman Frequencies ( $\text{cm}^{-1}$ ) Observed for  $[\text{Cu}(\text{dmp})_2]^+$  in Methanol Using Pulsed Laser Excitation at an Excitation Wavelength  $\lambda$  (nm)

$\lambda = 355^a$	$\lambda = 416$	$\lambda = 447$	$\lambda = 503$	$\lambda = 532^a$
	1295	1295		
1317	1315	1315		
1426	1426	1426	1340	1340
1467			1424	1426
			1474	1478
1503	1503	1503		
1596	1598	1597	1528	1533
1615			1598	1600

<sup>a</sup> Reference 2.

## Discussion

Before considering the excited-state RR spectra that are the primary concern of this paper, it is useful first to look at the ground-state RR spectra, which exhibit distinct changes in the pattern of ground-state Raman scattering frequencies as the excitation wavelengths are tuned across the absorption profile. Table I summarizes the prominent vibrational features as a function of excitation wavelength. Because of the varying conditions of excitation and scattering geometry used in the different cases no attempt has been made to construct excitation profiles. Nevertheless, it is clear that the patterns of vibrational mode enhancement vary with excitation wavelength in a way which suggests that more than one vibronic transition contributes to the visible absorption of the complex over the range 350–550 nm. The low-temperature UV-visible spectra of **1** and related systems have recently been analyzed.<sup>6</sup> In the case of **1**, three bands labeled I, II, and III have been discerned at 510 (shoulder), 450, and 390 nm, respectively. Bands II and III are assigned respectively under assumed  $D_{2d}$  symmetry to the d-orbital  $\rightarrow$  ligand LUMO transitions  $e(xz,yz) \rightarrow e(\psi^*)$  and  $b_1(x^2 - y^2) \rightarrow a_2(\chi^*)$ . In the ground-state resonance Raman spectrum<sup>2</sup> of **1** generated at 355 nm, the enhancement may be assigned primarily to resonance with band III. (A reviewer has suggested that since 355 nm is close to the onset of intraligand  $\pi \rightarrow \pi^*$  absorption, preresonance with this transition might also contribute to the Raman scattering here.) The distinct pattern of modes generated at 447.2 and 416 nm suggests enhancement via a different transition, band II. Of course, since bands II and III terminate on ligand LUMOs of different symmetry, some differences at least in the modes enhanced is to be expected. In actual fact, the two spectra are similar in several respects, possibly indicating that  $\psi^*$  and  $\chi^*$  may not exist as pure states, in line with what has already been pointed out in the earlier analysis.<sup>6</sup> Band I appears as a shoulder and has not been definitely assigned.<sup>6</sup> However, the ground electronic state Raman spectra generated in the present work at 503 and 532 nm (Table I) show additional modes, not seen at the other excitation wavelengths, and this is strongly indicative of a distinct allowed transition being involved in this spectral region.

In a previous paper, the evidence that the lowest MLCT excited state of **1** was asymmetric,  $[(\text{L})\text{Cu}^{\text{II}}(\text{L}^-)]^+$ , with the electron localized on one of the ligands, rested on the observation of neutral ligand vibrational modes only. No radical anion modes enhanced through a  $\pi \rightarrow \pi^*$  ( $\text{L}^-$ )-centered transition were observed even at a probe wavelength of 532 nm where, as the ESA spectrum in Figure 1 suggests, the absorption intensity due to  $\text{L}^-$  should be significant. The present single-color TR<sup>3</sup> experiments at 447.2 nm (Figure 2) now provide strong evidence for the presence of  $\text{L}^-$  and consequently a sound basis for the localized formulation of the lowest MLCT excited state.

As pointed out above, resonance enhancement at 416 nm of the ground electronic state scattering of **1** can reasonably be attributed to the MLCT transition identified<sup>6</sup> as band II, in which the  $\psi^*$  LUMO of the dmp ligand is populated. In the excited state, there is an interesting interplay between two transitions. The intensity gained by the 1503- $\text{cm}^{-1}$  band is due to resonance via a LMCT transition.<sup>4</sup> The oscillator strength of the latter is

a maximum in the near-UV region (ca. 390 nm), but it is still significant at 416 nm. On the other hand, the intensities of the pair of features at 1295 and 1315  $\text{cm}^{-1}$  are lower than would be expected if scattering at this wavelength were enhanced exclusively by an LMCT transition. This indicates that at 416 nm a radical anion-centered transition must also have appreciable intensity. Hence at this wavelength it seems that both the radical anion and neutral ligand moieties of the MLCT excited state are probed in the  $\text{TR}^3$  experiment. When one moves to an excitation wavelength of 447.2 nm, the striking observation is the total disappearance of the pair of bands near 1300  $\text{cm}^{-1}$ . Discussion of this observation is taken up again below. For the present however, the key inference is that at this wavelength the excited-state absorption must be predominantly due to a radical anion-centered transition in the MLCT excited state.

In view of this conclusion it is something of a surprise at first sight that the spectra generated a little further to the red, at 503 nm, show only ground-state features. The spectrum recorded in  $\text{CH}_2\text{Cl}_2$  solution looks identical with that in MeOH. The situation is similar to that previously observed<sup>2</sup> in experiments using a 532-nm probe wavelength. In that case, bands due to the ground state decreased with increasing pulse energy, but no new features grew in. In the scheme proposed to account for the phenomenon, the initially populated MLCT excited state absorbs a second photon, creating a relatively long-lived upper state with a low absorption and hence a low resonance Raman scattering cross section at 532 nm. The present findings at 503 nm can be accommodated within the same scheme, and indeed the observation of the same phenomenon as in the earlier 532-nm-based study gives us some confidence that the proposal is well-founded.

One might wonder how this stands in relation to the findings from the experiments at 416 nm and 447.2 nm in both of which resonant scattering through a  $(\text{dmp}^{\cdot-})$ -centered  $\pi \rightarrow \pi^*$  transition is observed. In considering that point, it is necessary to realize that in order to populate the higher, relatively long-lived state it is not only the lifetimes of the states relative to the laser pulse duration which are significant but also the extinction coefficients of the transitions involved. In the single-color  $\text{TR}^3$  experiments at 416 and 447.2 nm, population of the lowest MLCT state is readily achieved because the extinction coefficient of the ground state of **1** is large at these wavelengths. In these circumstances, the probing edge of the laser pulse encounters a sample that is >90% in the MLCT state.

The striking disappearance of some vibrational modes in the RR spectrum of  $\text{dmp}^{\cdot-}$  deserves some comment. The finding bears comparison with recent work<sup>9</sup> on the RR spectroscopy of biphenyl where it has been shown that deuteration of the triplet state of biphenyl results in a dramatic change in the mode enhancement pattern for the species. Drastically altered force fields upon deuteration have been invoked<sup>9</sup> as a means of explaining the effect. In the present instance, the comparison is between two rather different entities, neutral and radical anion ligands coordinated to a metal center. The difference is even more accentuated by the fact that the resonance enhancement of the Raman scattering arises through quite distinct transitions in the two instances. The

neutral modes are enhanced via ground electronic state MLCT transitions (vide supra) whereas the radical anion mode enhancement arises through an  $(\text{L}^{\cdot-})$ -centered  $\pi \rightarrow \pi^*$  transition. In such circumstances, it is not too surprising that a particular vibrational feature should exhibit such a striking change in intensity. The differences between L and  $\text{L}^{\cdot-}$  modes are well illustrated by the case of  $\text{Cu}(\text{biq})_2^+$ , which we have reported on elsewhere.<sup>10</sup>

The phenomena we have observed in the earlier work<sup>2</sup> at 532 nm and now at 503 nm are similar to the saturation effects reported by Asher et al.<sup>7</sup> in the course of UV and resonance Raman studies, where increases in laser flux at the sample were accompanied by a depopulation of the ground state. In more recent work<sup>8</sup> on heme systems where the excited-state lifetimes are extremely short relative to the laser pulse duration, no saturation effects were observed. This apparent link between the degree of saturation and the shortness of excited-state lifetimes is consistent with our earlier proposal.<sup>2</sup>

While the lowest MLCT excited state of  $[\text{Cu}(\text{dmp})_2]^+$  is not a strong Raman scatterer, it has nevertheless been possible to obtain convincing evidence that the transferred electron is localized on one of the dmp ligands. This conclusion has a bearing on a recent group theoretical analysis<sup>11</sup> of the temperature dependence of the emission spectra and lifetimes of the thermally equilibrated (thexi) charge-transfer excited states of some  $[\text{Cu}(\text{NN})_2]^+$  complexes (where NN = substituted 2,2'-bipyridyl or 1,10-phenanthroline ligands). To account for the findings Parker and Crosby<sup>11</sup> invoked a lowering of the thexi state symmetry from  $D_{2d}$  to  $D_2$ . While Jahn-Teller distortions associated with the open-shell configuration ( $e^3_{xz,yz}, e_L^1$ ) of the MLCT excited state could lower the symmetry to  $D_2$ , this is not the only possibility, an alternative being  $C_{2v}$  symmetry. Indeed the latter may be favored since<sup>12</sup>  $C_{2v}$  is a stable solution of the Jahn-Teller effect in the parent  $t_2$  shell, while  $D_2$  is not (we are grateful to Dr. A. Ceulemans for pointing this out). Our resonance Raman results bear directly on this point since they show that the electron is localized on one ligand in the thexi states and hence that the symmetry will be no higher than  $C_{2v}$  or possibly  $C_2$ . Of course, the resonance Raman data refer to the systems in fluid solvents whereas the assignments of Parker and Crosby<sup>11</sup> concern luminescence in rigid media. However, by analogy with the findings of Carroll and Brus<sup>13</sup> for the lowest MLCT excited state of  $[\text{Ru}(\text{bpy})_3]^{2+}$ , which show that the triplet MLCT state is localized in both fluid and glassy media, the localization of charge observed in the fluid phase for  $[\text{Cu}(\text{dmp})_2]^+$  might be expected to persist in a rigid medium.

**Acknowledgment.** We thank the Science and Engineering Research Council for support of this work [Grant Nos. GR/E 01928 and GR/F 42980] and for the award of a postdoctoral research assistantship (to K.C.G.). We wish to thank the staff at the Laser Support Facility, Rutherford Appleton Laboratory, for assistance with some of the CW resonance Raman studies. We also gratefully acknowledge comments communicated by Dr. A. Ceulemans concerning Jahn-Teller effects in the open shell of these Cu(I) complexes and for calling ref 12 to our attention.