

Two Photon Excitation Spectrum of a Twisted Quadruple Bond Metal–Metal Complex

Daniel S. Engebretson,[†] Evan M. Graj, George E. Leroi,[†] and Daniel G. Nocera*

Department of Chemistry, 6-335
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
LASER Laboratory

Michigan State University, East Lansing, Michigan 48824

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The overlap of two orbitals, each containing an electron, defines the most significant chemical interaction between atoms. The electron population of the resulting bonding and antibonding orbitals gives rise to four electronic states: a singlet ground state, one-electron triplet and singlet excited states, and a two-electron, singlet excited state. Although recognized at the inception of valence¹ and molecular orbital² bonding theories, these four states are difficult to spectroscopically characterize for an isolated two-electron bond of a molecular species. The challenge comes in the identification of the highest energy singlet state, which amounts to the promotion of two electrons into an antibonding orbital. For a σ bond, this state is dissociative, and for a π bond, the state is energetically unstable with respect to rotation.^{3,4} Conversely, overlap of the d_{xy} orbitals on the metal centers of a bimetallic core presents a stable two-electron δ bond, which is ideally adapted for spectroscopic investigation when incorporated within the sterically constrained coordination environment of quadruple metal–metal bonded species.⁵ In this case, the four states resulting from electron occupation of the δ HOMO and the δ^* LUMO are $^1\delta\delta$, $^3\delta\delta^*$, $^1\delta\delta^*$, and $^1\delta^*\delta^*$, each of which has been independently characterized. The dipole-allowedness of the $^1\delta\delta \rightarrow ^1\delta\delta^*$ transition led to the identification of the $^1\delta\delta$ ground and $^1\delta\delta^*$ excited states early in the study of the electronic absorption spectroscopy of these compounds.^{5,6} The espial of the $^3\delta\delta^*$ state has come in quadruple-bond complexes featuring bridging phosphines that induce rotation about the metal–metal bond. In these complexes, the δ bond is sufficiently weakened that the $^3\delta\delta^*$ state is lowered in energy and can be populated at reasonable temperatures, thus allowing its energy to be determined from temperature-dependent measurements of the magnetic susceptibility⁷ and of ligand $^3\text{P}\{\text{H}\}$ NMR signals.⁸ Most recently, we have demonstrated that the $^1\delta^*\delta^*$ excited state, which is forbidden by the selection rules of conventional optical spectroscopy, may be located by two-photon spectroscopy of quadruple-bond metal–metal complexes possessing eclipsed ligand geometries.⁹

Although the methods for detection of the individual states that define the δ bond have been assembled, a complete spectroscopic description of the two-electron bond in a single complex has not

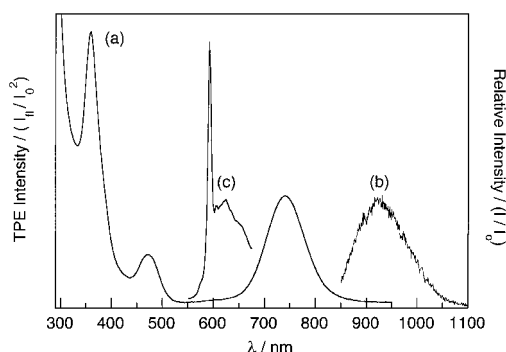


Figure 1. (a) One-photon absorption (295 K) and (b) emission ($\lambda_{\text{exc}} = 740$ nm, 60 K) spectra of $\beta\text{-Mo}_2\text{Cl}_4(\text{S,S-dppb})_2$ in 3-methylpentane. (c) The two-photon excitation of fluorescence spectrum in the same solvent at 60 K. Spectrum (a) is described by the right ordinate axis and spectrum (c) by the left ordinate axis. The emission spectrum is normalized to that of the absorption profile and was not corrected for the detector response function. The sharp feature in trace (c) results from the 1184-nm overtone absorption band of 3-methylpentane (see text).

yet been achieved owing to the spectroscopic incompatibility of the magnetic and electronic measurements. Significant population of the $^3\delta\delta^*$ state requires weakening of the bond to such an extent that the electronic excitation and detection wavelengths required for the two-photon experiment occur in the spectrally troublesome near-infrared region. With advances in our spectroscopic instrumentation, we now report the successful detection of the $^1\delta^*\delta^*$ excited state of the twisted $\beta\text{-Mo}_2\text{Cl}_4(\text{S,S-dppb})_2$ complex (S,S-dppb = S,S-bis(diphenylphosphino)butane, $\chi = 24.7^\circ$). This result, together with Cotton's previous measurements of the $^3\delta\delta^*$ and $^1\delta\delta^*$ excited states for this complex,^{8,10} provides a complete description of the four states that characterize a two-electron bond in a discrete molecular species.

The $^1\delta\delta \rightarrow ^1\delta\delta^*$ transition of $\beta\text{-Mo}_2\text{Cl}_4(\text{S,S-dppb})_2$ in 3-methylpentane appears at $\lambda_{\text{abs,max}} = 741$ nm (Figure 1a).¹⁰ On the basis of this low-energy absorption, corresponding luminescence is expected to occur, if at all, in the near-infrared spectral region where the response function of conventional detectors is compromised. We addressed this issue by rebuilding the detection system of a previously described emission instrument so that the pertinent spectral region could be accessed.¹¹ 3-Methylpentane glasses of $\beta\text{-Mo}_2\text{Cl}_4(\text{S,S-dppb})_2$, excited with 740-nm light, produce the luminescence profile shown in Figure 1b. As is the case for the $^1\delta\delta^*$ excited state of many quadruple bond metal–metal complexes, the emission spectrum ($\lambda_{\text{em,max}} = 921$ nm) is nearly a mirror image of the absorption spectrum and a Stokes shift of ~ 2500 cm^{-1} is observed.

The detection of this near-infrared emission allows us to investigate the two-photon spectroscopy of the complex. In this experiment, the $^1\delta^*\delta^*$ state is pumped by two near-infrared photons, followed by internal conversion to the emissive $^1\delta\delta^*$ excited state. The $^1\delta^*\delta^*$ excitation profile is constructed by monitoring the intensity of the $^1\delta\delta^*$ luminescence as the infrared excitation wavelength (normalized in intensity) is scanned in to and out of resonance with the $^1\delta^*\delta^*$ state. Consistent with this experimental scheme, excitation of the 3-methylpentane glass (60 K) of $\beta\text{-Mo}_2\text{Cl}_4(\text{S,S-dppb})_2$ over the spectral range 1100 to 1350

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[†] Department of Chemistry, Michigan State University.

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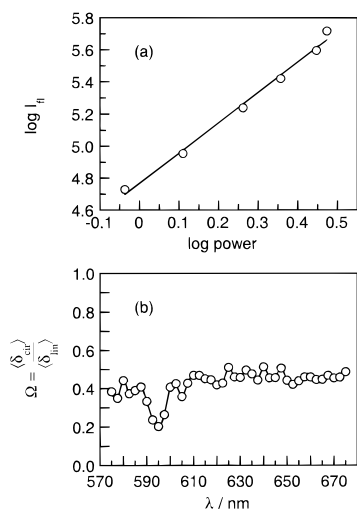


Figure 2. (a) The two-photon excited fluorescence intensity versus the incident dye laser intensity. These data were collected for $\lambda_{\text{exc}} = 1250$ nm in linear polarization; the slope is 2.02. (b) The polarization ratio, $\Omega (= \langle I_{\text{cir}} \rangle / \langle I_{\text{lin}} \rangle)$, plotted versus half the wavelength of the incident dye laser radiation.

nm^{12} produces ${}^1\delta\delta^*$ luminescence, even though detailed spectroscopic investigation reveals no discernible absorption features to the red of the ${}^1\delta\delta \rightarrow {}^1\delta\delta^*$ transition. Figure 1c shows the two-photon excitation (TPE) of fluorescence spectrum of $\beta\text{-Mo}_2\text{Cl}_4\text{(S,S-dppb)}_2$ (plotted as $\lambda_{\text{exc}}/2$), obtained under linear polarization of the incident laser radiation. Imposed on a broad two-photon absorption with maximum at $\lambda = 625$ nm is a sharp feature, which is energetically coincident with the frequency of an overtone absorption of 3-methylpentane ($\lambda_{\text{max}} = 1184$ nm; another peak due to solvent overtone absorption at 1405 nm in the TPE spectrum is not shown). Inasmuch as the TPE signal is constructed by dividing the fluorescence intensity by the square of the transmitted laser energy, solvent absorption will be manifested in an attenuated power, thus leading to artificially large features in the TPE spectrum as we observe here. Of pertinence to the $\beta\text{-Mo}_2\text{Cl}_4\text{(S,S-dppb)}_2$ complex, the band at 625 nm is consistent with two-photon absorption by the ${}^1\delta^*\delta^*$ excited state. The fluorescence intensity varies with the square of the incident laser intensity (logarithmic slope = 2.02, see Figure 2a), as expected for a two-photon excitation process.¹³ Moreover, the ratio of the fluorescence intensity for excitation under circular vs linear polarized radiation ($\Omega = \langle I_{\text{cir}} \rangle / \langle I_{\text{lin}} \rangle$) is constant and < 1.0 across the observed band; Figure 2b reproduces Ω plotted vs the incident $2h\nu$ laser wavelength. In D_2 symmetry, such a polarization ratio occurs for transitions to a two-photon state of identical symmetry to the ground state.^{14,15} The two-photon excited state of $\beta\text{-Mo}_2\text{Cl}_4\text{(S,S-dppb)}_2$ is therefore of A_1 symmetry. Excluding the energetically remote ${}^1\sigma^*\sigma^*$ excited state, the only spin-allowed, metal-localized excited state of such symmetry is ${}^1\delta^*\delta^*$. If one assumes similar Franck–Condon factors for the ${}^1\delta\delta \rightarrow {}^1\delta\delta^*$ and ${}^1\delta\delta \rightarrow {}^1\delta^*\delta^*$ transitions, a ${}^1\delta\delta^* - {}^1\delta^*\delta^*$ energy gap of 2505 cm^{-1} is calculated, which compares well to Cotton's measurement⁸ of 2240 cm^{-1} for the energy difference between the ${}^1\delta\delta$ and ${}^3\delta\delta^*$ states.¹⁶

The similarity of the ${}^1\delta\delta^* - {}^1\delta^*\delta^*$ and ${}^1\delta\delta - {}^3\delta\delta^*$ energy gaps is consistent with two-electron bonding models. Scheme 1

(12) The requirement of intense, tunable near-infrared photons was satisfied with the output of an OPO (Type I XPO operated in the idler mode) pumped by the third harmonic (3.5 ns pulse width, 100 Hz, and 170 mJ/pulse) of a Coherent Infinity 40–100 Nd:YAG laser (Coherent Laser Group, Santa Clara, CA). The details of the experimental apparatus, which has been significantly altered from a previous instrument so that the near-infrared spectral region could be accessed, will be reported in a future publication.

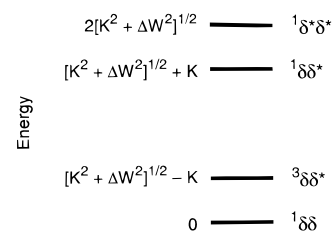
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Scheme 1



summarizes the state ordering of the δ manifold in terms of the one-electron energy $\Delta W (= W_{\delta^*} - W_{\delta})$, the difference between the energies of an electron in a singly occupied δ and δ^* orbital) and two-electron energy K (i.e., the exchange integral).^{17–20} For both sets of states, the energy gaps are predicted to be identical, $(\sqrt{K^2 + \Delta W^2} - K)$,¹⁸ a result that is now experimentally confirmed. Moreover, the determination of the ${}^1\delta\delta^*$ and ${}^1\delta^*\delta^*$ state energies allows for the evaluation of the spectroscopic parameters that engender a complete electronic description of the two-electron, two-orbital bond. Values of $K = 5495$ and $\Delta W = 5814 \text{ cm}^{-1}$ are obtained upon substituting the experimentally determined energies in the relations for $E({}^1\delta\delta^*)$ and $E({}^1\delta^*\delta^*)$ provided in Scheme 1. The small one-electron energy is consistent with the weak overlap between d_{xy} orbitals, which results from their parallel disposition to one another.

The manifold of states that is shown in Scheme 1 holds a central place in bonding descriptions for two interacting electrons in weakly coupled orbitals. The ${}^1\delta\delta$ and ${}^3\delta\delta^*$ states arise from one electron in each orbital with spins opposed (singlet) and parallel (triplet). Because the ${}^3\delta\delta^*$ state arises from a simple spin–flip of an electron in a relatively isolated orbital, the triplet state lies close in energy to the ground state for orbitals that are weakly coupled. Conversely, the ${}^1\delta\delta^*$ and ${}^1\delta^*\delta^*$ singlet states are derived from antisymmetric and symmetric linear combinations where both electrons are paired in one orbital of either center. These states are energetically far removed from their diradical counterparts, owing to large two-electron energies that result from pairing electrons in the confined volume of atomic-like orbitals centered on individual metals (as opposed to a molecular orbital extensively delocalized over the bimetallic core). Such a diagram was first invoked by Heitler and London in their presentation of valence bond theory¹ and subsequently implemented by Mulliken and by Coulson and Fischer in their molecular orbital analysis of the bonding in “stretched hydrogen”^{2,21} and “twisted ethylene”.²² The results described herein support the validity of the simple models originally put forth to describe the two-electron bonds in these molecular constructs.

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(16) The comparison is not rigorous, since the measurement of the ${}^1\delta\delta^* - {}^1\delta^*\delta^*$ energy gap by two-photon spectroscopy corresponds to a vertical transition from a molecule in its ground-state geometry to an excited state in the same geometry, whereas the measurement of the ${}^1\delta\delta - {}^3\delta\delta^*$ energy gap in ref 8 is for a molecule in its equilibrium ground- and equilibrium excited-state geometries (i.e., more closely approximating the 0,0 transition between the two states). The difference of 265 cm^{-1} between the two energy gap measurements may, therefore, reflect the relaxation energy of the ${}^3\delta\delta^*$ state. However, it should be noted that errors associated with the determination of the ${}^1\delta\delta^*$ and ${}^1\delta^*\delta^*$ transition energies (2 and 5 nm, respectively) result in an error limit of $\pm 164 \text{ cm}^{-1}$ on the 265 cm^{-1} difference between the two energy gap measurements.

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