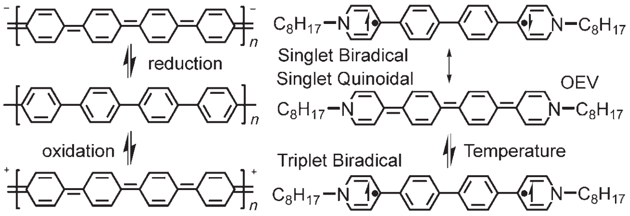
DOI: 10.1002/anie.200704398

Raman Detection of Biradicals

Raman Detection of “Ambiguous” Conjugated Biradicals: Rapid Thermal Singlet-to-Triplet Intersystem Crossing in an Extended Viologen**

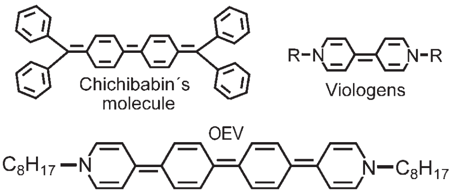
Juan Casado, Serguei Patchkovskii,* Marek Z. Zgierski, Laura Hermosilla, Carlos Sieiro, María Moreno Oliva, and Juan T. López Navarrete**

Raman spectroscopy has proven to be an indispensable tool for the analysis of the electronic, molecular, and solid-state structures of polyconjugated organic molecules.[1] In π-electron delocalized systems, the intensity of Raman scattering is amplified by electron–phonon coupling within the conjugated chromophore, where modifications in the electronic structure simultaneously drive structural (that is, skeletal) changes; for instance, pristine (nonconductive) conjugated polymers and oligomers based on aromatic and heteroaromatic units (such as polyparaphenylene (PPP), polypyrrol, polythiophene, etc.) evolve into quinoid ring structures upon doping in the conducting state (see the redox processes in Scheme 1). The aromatic↔quinoidal structural transformation upon electron or hole injection has been elegantly followed by means of Raman spectroscopy.[2] Comparable skeletal modifications may be expected upon spin-state changes in organic biradicals, which would take place in strongly spin-correlated or ferromagnetic systems (that is, low-bandgap conjugated molecules). Our goal is to follow spin-state evolution in an organic biradical by using Raman techniques. The ability to unambiguously detect the spin-driven skeletal dynamics has important implications for understanding both electron transport and magnetic activity of the sample.



Scheme 1. Left: Structural changes upon doping of PPP. Right: closed- and open-shell resonant forms and triplet species of the extended viologen (OEV).

Magnetic activity is unusual for a neutral, even-electron molecule with a formal closed-shell electronic structure. Both organic and inorganic examples are known,[3] the first and best-known one being the Chichibabin hydrocarbon (see Scheme 2).[4] In the last few years, other conjugated biradicals in which the biradicaloid nature is promoted by aromatic stabilization have been characterized.[5] Among them, a closely related Chichibabin hydrocarbon—or extended viologen (OEV, see Schemes 1 and 2)—was recently reported,[6] in which the open–closed shell electronic-spin transition is accompanied by a drastic change in the C=C/C−C conjugation pattern (Scheme 1). Thus, this extended viologen molecule represents a perfect model for following spin transformations with Raman spectroscopy.



Scheme 2. Structures of Chichibabin’s molecule, the viologens, and OEV.

The OEV presents an enigmatic electronic structure, which is caused by a strong configuration mixing within the low-bandgap π-conjugated system.[6] Conventional magnetic and electron paramagnetic resonance (EPR) techniques yield ambiguous results for this molecule and the prototypical Chichibabin hydrocarbon.[4,6] In contrast, we show that

---

[*] Dr. J. Casado, M. Moreno Oliva, Prof. J. T. López Navarrete
Department of Physical Chemistry, University of Málaga
Campus de Teatinos s/n, 29071 Málaga (Spain)
Fax: (+34) 952-132-000
E-mail: casado@uma.es
teodomiro@uma.es

Dr. S. Patchkovskii, Dr. M. Z. Zgierski
Steacie Institute for Molecular Sciences
National Research Council of Canada
K1A 0R6, Ottawa (Canada)
E-mail: serguei.patchkovskii@nrc-cnrc.gc.ca

L. Hermosilla, Prof. C. Sieiro
Department of Physical Chemistry
Universidad Autónoma de Madrid
Cantoblanco, 28049 Madrid (Spain)

[**] J.C. thanks the Ministerio de Educación y Ciencia of Spain for an I3 research position and for funding his stay at the National Research Council of Canada (PR2006-0253, Programa Nacional de Ayudas a la Movilidad de Profesores e Investigadores en el Extranjero, and project CTQ2006-14987). We also thank the Junta de Andalucía for supporting our FQM-0159 group as well as Dr. William W. Porter III and Prof. Thomas P. Vaid at the Department of Chemistry, Washington University in St. Louis, Missouri (USA) for kindly providing the extended viologen samples.

Supporting information for this article (additional theoretical and experimental data) is available on the WWW under http://www.angewandte.org or from the author.

Raman spectroscopy can discriminate between spin states of OEV, thus yielding spectra of the individual spin species. We propose that on the timescale of molecular vibrational motion, the singlet ground electronic state of OEV is in thermal equilibrium with a triplet biradical state, with both states being populated at ambient conditions (see Scheme 1). We provide temperature-dependent vibrational Raman data which support this hypothesis. The experimental results are compared with ab initio complete active space self-consistent field (CASSCF) and multireference second-order Møller–Plesset (MP2) calculations (see the Supporting Information for additional details).

Besides the valuable interest of applying spectroscopic tools to complement the magnetic measurements, the study of variable spin systems has itself a profound relevance. Interesting properties are often associated with molecules that have two or more frontier orbitals that are similar in energy, because they may exhibit properties such as, high- or low-spin ground states, unique reactivities, significant sensitivity to condensed-phase effects. Furthermore, modeling such specific molecular architectures poses unique challenges to the electronic-structure methodologies. We think that the analysis of OEV proposed herein represents such an example.

The experimental Raman spectrum of OEV is shown in Figure 1. Although the calculated spectra of the singlet or triplet species alone do not match the experimental results, superposition of the two curves accounts for the full set of experimental bands and their relative intensities. The supposition that the Raman spectrum of OEV arises from two distinct species is further supported by calculated relative energies of the singlet and triplet states of OEV (see Figure 2). Both the S_0 and T_1 states are very close in energy and, at planar geometries, the singlet state is slightly preferred. Thus, at ambient conditions, both states can be populated and will contribute to the Raman response.

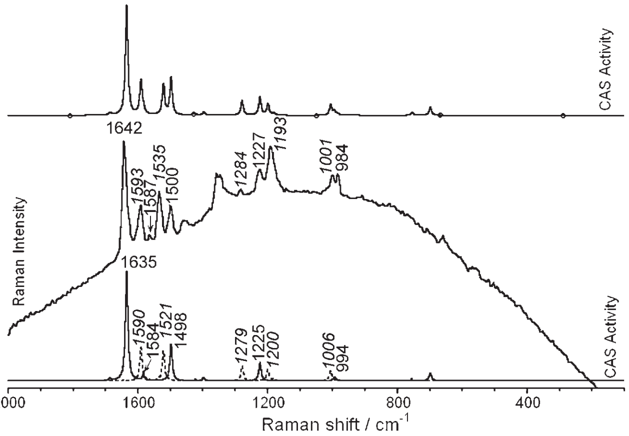


Figure 1. Bottom: CAS(4,4) Raman spectra of the singlet planar (——) and planar triplet (-----) species. Middle: solid-state FT-Raman spectrum of OEV (1064 nm). Top: sum of the equally weighted theoretical S_0 and T_1 spectra. The broad band at 1350 cm^{-1} emerges from the octyl side groups.

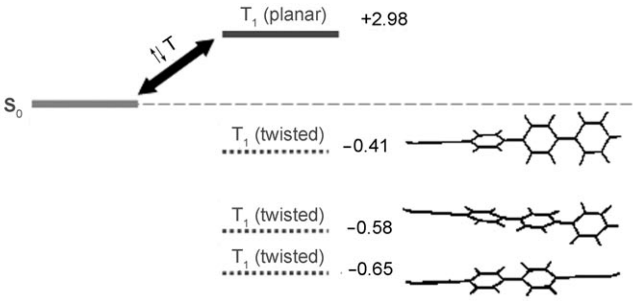


Figure 2. MRMP2//CAS(10,10) energies (in kcal mol^{-1}) for the OEV conformers.

The presence of biradical states can be additionally explored by examining the electronic structure of the molecule. Calculated CAS(10,10) frontier natural orbitals for the singlet state (see Figure 3) show that the highest occupied natural orbital (HONO) is populated by 1.85 electrons (see Table 1) and is of the expected quinoidal character (Scheme 1). Interestingly, the biradical-like lowest unoccupied natural orbital (LUNO) hosts 0.15 electrons, and hence, gives a significant singlet biradical proaromatic contribution to the ground electronic state (see Figure 3 and Figure S1 of the Supporting Information).

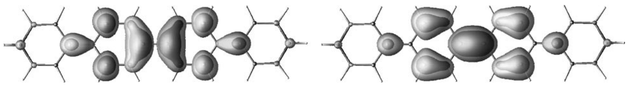
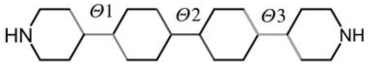


Figure 3. Lowest unoccupied (left) and highest occupied (right) CAS-(10,10) natural orbitals for the model singlet viologen (R = H). The corresponding occupation numbers are 1.85 (HONO) and 0.15 (LUNO).

Two species in thermal equilibrium are expected to exhibit temperature-dependent Raman spectra. We measured the spectra in a reasonably broad temperature range (namely, between −150 and 120 °C, see Figure 4). Upon cooling to −150 °C, the spectrum simplifies considerably, and nearly coincides with the calculated CAS(4,4) S_0 result. The experimental spectrum obtained at 120 °C is very similar to the CAS result for the planar T_1 species. This result is consistent with both species being in thermal equilibrium, as would be necessary to account for the magnetic activity of the solid, neutral OEV.[6] Adopting the gas-phase $\Delta E(S_0–T_1) = +2.98$ kcal mol^{-1} (Figure 2) and Maxwell–Boltzmann populations, 1.75 % of the sample is expected to be in the biradical triplet state at 20 °C, this amount decreasing to 1.36×10^{-3} % at −150 °C and increasing to 6.39 % at 120 °C. The actual S_0–T_1 splitting in the solid state is likely to be lower as a result of solid packing forces, environment polarization, etc. Indeed, taking the calculated Raman intensities at the face value, a 1:1 weighting of the spectra at 20 °C would result in an energy difference of 0.6 kcal mol^{-1}, which in turn would imply a triplet population of 20 % at −150 °C and 60 % at 120 °C.

The experimental results reported so far were obtained in the solid state, where the conjugated core of OEV is planar, which justifies the use of calculated spectra for the planar

Table 1: CASSCF theoretical data obtained for OEV (R = H).



	Energy[a,b] (4,4)/(10,10)	Dihedral angles (4,4)/(10,10)			Neese's index [%] (4,4)/(10,10)	Natural orbital occupation (4,4) (10,10)
		Θ1	Θ2	Θ3		
S_0-planar	0.00/0.00	0/0	0/0	0/0	21/33	1.94 1.93 0.07 0.06 1.95 1.93 1.92 1.91 1.85 0.15 0.09 0.08 0.07 0.04
T_1-planar	+2.99/+2.98	0/0	0/0	0/0	91/88	1.96 1.37 0.62 0.04 1.95 1.93 1.93 1.92 1.28 0.72 0.08 0.07 0.07 0.05
T_1-twisted	−1.54/−0.41	+23/+16	+43/+44	+17/+16		
T_1-twisted	−1.67/−0.58	−17/−16	+42/+43	+24/+16		
T_1-twisted	−1.73/−0.65	−23/−16	+42/+43	−18/−16		

[a] Energies are given in kcal mol^{-1}, with the S_0 level as the reference (0.00 kcal mol^{-1}). [b] Nitrogen atoms were allowed to pyramidalize in the planar T_1 structure (see the Supporting Information).

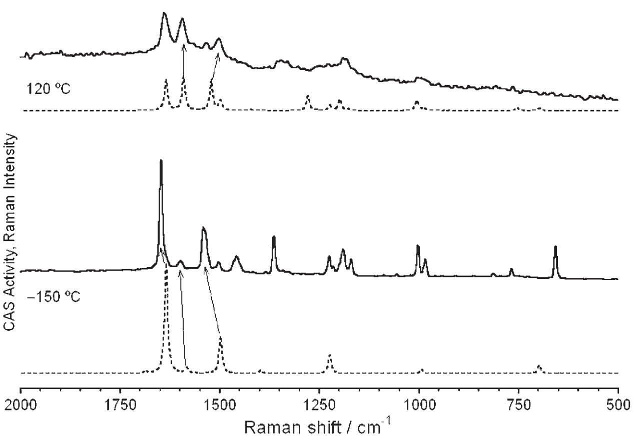


Figure 4. Comparison of the CAS(4,4) theoretical spectra (-----) of the Maxwell–Boltzmann-weighted planar singlet and triplet species [$\Delta E(S_0–T_1) = 2.98$ kcal mol^{-1}] with the FT-Raman spectra (——) recorded at low (bottom) and high (top) temperatures for OEV in the solid state.

species. Theory, however, predicts stabilization of the helical conformers of the triplet, formed by rotation around the inter-ring single C–C bonds (see the inserts in Figure 2). Raman spectra recorded in a tetrahydrofuran (THF) solution—compared with the CAS theoretical Raman spectra of the triplet distorted species (see Figures S2 and S3 of the Supporting Information)—appear to corroborate the presence of helical conformers of the triplet OEV species.

To summarize our findings, we established that in a crystalline environment, the extended viologen possesses a singlet S_0 ground state, which is stabilized by resonance between the closed-shell quinoidal and the open-shell aromatic or biradical electronic configurations. The electronically excited biradical triplet T_1 state is thermally accessible and lies less than 3 kcal mol^{-1} above the singlet state at planar geometries. Both experiment and theory suggest that twisting the inter-ring C–C bonds may stabilize the T_1 state.

The "classical" approach for the detection of stable triplet species is based on directly measuring their magnetic properties (namely, magnetic susceptibility or EPR). Such measurements are often inconclusive for triplet species.[4,6,7] In contrast, we show that Raman spectroscopy is quite successful for this purpose. A likely explanation is that at short timescales, such as those associated with vibrational motion, the dynamics of OEV proceed on an electronic-energy surface with a well-defined electron spin (singlet or triplet). As a result, the individual singlet and triplet vibrational modes can be resolved in the Raman spectra. At longer timescales, associated with EPR transitions, the system undergoes repeated $S_0 \leftrightarrow T_1$ intersystem crossings, which prevents observation of the excessively broadened magnetic transitions. We show that Raman spectroscopy can still succeed in observing the T_1 state, as well as its singlet biradical in fast equilibrium.

In conclusion, we present a new approach—inspired by the classical Raman studies of the doping of conducting polymers—which provides molecular spectra associated with different spin states of organic biradicals. To do so, we take advantage of two main features of Raman spectroscopy of polyconjugated molecules, namely, its selectivity to conjugated chromophores and its high sensibility to changes in the electron delocalization patterns. From a modeling point of view, the good estimation of experimental data provides new guidelines for the prediction of accurate spectroscopic results on challenging biradical molecules.

Received: September 24, 2007

Keywords: conjugated systems · Raman spectroscopy · singlet biradicals · theoretical chemistry · viologens

---

[1] G. Zerbi, M. Gussoni, C. Castiglioni in *Conjugated Polymers* (Eds.: J. L. Bredas, R. Silbey), Kluwer, Dordrecht, **1991**; M. Gussoni, C. Castiglioni, G. Zerbi in *Spectroscopy of Advanced Materials, Vol. 1* (Eds.: J. H. Clark, R. E. Hester), Wiley, New York, **1991**; H. Kuzmany in *Infrared and Raman Spectroscopy* (Ed.: B. Schrader), VCH, Weinheim, **1995**, p. 372; *Electronic Properties of Conjugated Polymers* (Eds.: H. Kuzmany, M. Mehring, S. Roth), Springer, Berlin, **1987**; Z. Vardeny, E. Ehrenfreund, O. Brafman, B. Horovitz, *Phys. Rev. Lett.* **1985**, *54*, 75.

[2] Y. Furukawa, S. Tazawa, Y. Fujii, I. Harada, *Synth. Met.* **1988**, *24*, 329; J. Mikat, I. Orgzall, H. D. Hochheimer, *Phys. Rev. B* **2002**, *65*, 174202; Y. Furukawa, *J. Phys. Chem.* **1996**, *100*, 15644; G. Louarn, J. P. Buisson, S. Lefrant, D. Fichou, *J. Phys. Chem.* **1995**, *99*, 11399;

J. T. López Navarrete, G. Zerbi, *J. Chem. Phys.* **1991**, *94*, 965; G. Zannoni, G. Zerbi, *J. Chem. Phys.* **1985**, *82*, 31.

[3] F. Breher, *Coord. Chem. Rev.* **2007**, *251*, 1007; A. Rebmann, J. Zhou, P. Schuler, H. B. Stegmann, A. Rieker, *J. Chem. Res. Synop.* **1996**, 318; A. Rebmann, J. Zhou, P. Schuler, A. Rieker, H. B. Stegmann, *J. Chem. Soc. Perkin Trans. 2* **1997**, 1615.

[4] A. E. Tschitschibabin, *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 1810; L. K. Montgomery, J. C. Huffman, E. A. Jurczak, M. P. Gredze, *J. Am. Chem. Soc.* **1986**, *108*, 6004, and references therein.

[5] a) T. Kubo, A. Shimizu, M. Sakamoto, M. Uruichi, K. Yakushi, M. Nakano, D. Shiomi, K. Sato, T. Takui, Y. Morita, K. Nakasuji, *Angew. Chem.* **2005**, *117*, 6722; *Angew. Chem. Int. Ed.* **2005**, *44*, 6564; b) T. Kubo, M. Sakamoto, K. Nakasuji, *Polyhedron* **2005**, *24*, 2522; c) T. Kubo, A. Shimizu, M. Uruichi, K. Yakushi, M. Nakano, D. Shiomi, K. Sato, T. Takui, Y. Morita, K. Nakasuji, *Org. Lett.* **2007**, *9*, 81.

[6] W. W. Porter III, T. P. Vaid, A. L. Rheingold, *J. Am. Chem. Soc.* **2005**, *127*, 16559.

[7] W. T. Borden, *Diradicals*, Wiley, New York, **1982**.