

Communication: Manipulating the singlet-triplet equilibrium in organic biradical materials

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David von Seggern
(vonseg@seismo.unr.edu) University of Nevada
July 2012, page 10
DIGITAL OBJECT IDENTIFIER
<http://dx.doi.org/10.1063/PT.3.1619>
The article by Thorne Lay and Hiroo Kanamori is an interesting one. It discusses the energy released by the 2011 Tohoku earthquake. While that of a 100-megaton nuclear explosion is approximately five times as much energy as a 50-megaton atmospheric explosion, the 2011 Chilean earthquake had still more energy by a factor of about 3 or 4 than the nuclear device. I believe the authors used the relation for seismic energy release rather than total strain energy release. The seismic energy underestimates the total strain energy release by a variable that depends on friction on the fault plane. Accounting for total strain energy release would increase the earthquake energy number by orders of magnitude. Despite the catastrophic damage potential of nuclear bombs, the forces of nature occasionally unleash much larger energy releases. Although the nuclear bombs are under our control, earthquakes, volcanic eruptions, and extreme weather events are not. However, by judicious preparation and avoidance measures, humans can significantly diminish the damage of natural events.

Comment on this article
By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck team. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon later becomes released in a new event. Perhaps calculations of one added that in while another's calculations did not. E.M.C.
Written by Edgar McCarvill, 14 July 2012 19:59

Communication: Manipulating the singlet-triplet equilibrium in organic biradical materials

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We investigated the tunability of the singlet-triplet equilibrium population in the organic biradical 1,4-phenylenedinitrene via magneto-optical spectroscopy. A rich magnetochromic response occurs because applied field increases the concentration of the triplet state species, which has a unique optical signature by comparison with the singlet biradical and the precursor molecule. A Curie-like analysis of the magneto-optical properties allows us to extract the spin gap, which is smaller than previously supposed. These measurements establish the value of local-probe photophysical techniques for magnetic property determination in open-shell systems such as biradicals where a traditional electron paramagnetic resonance Curie law analysis has intrinsic limitations. © 2011 American Institute of Physics. [doi:10.1063/1.3672101]

The photophysics of small organic molecules is of foundational importance to the field of physical organic chemistry. One very useful aspect of small molecule photochemistry is the ability to create and stabilize trapped spin states via low temperature photolysis.¹⁻³ Open-shell molecules created in this way display unique electronic structure and magnetic exchange interactions that allow investigation of the interplay between charge, structure, and magnetism.⁴⁻⁹ When a ground or thermally accessible, paramagnetic state is generated, they also provide close insight into the behavior that is very promising for light harvesting, controllable reactivity, and spin valve applications.¹⁰⁻¹² 1,4-Diazidobenzene attracted our attention in this regard. Like several other aromatic azides, it undergoes a photochemical reaction to yield 1,4-phenylenedinitrene (Fig. 1). The latter is a persistent biradical (in rigid matrices at $T \leq 90$ K) with a magnetic energy diagram that includes a ground state singlet plus triplet and (high lying) quintet excited states.^{13,14} The singlet-triplet gap Δ_0 estimated by electron paramagnetic resonance (EPR) is 288 K, small enough to allow population changes with temperature^{13,15} and potentially support tuning by magnetic field.

To extend our understanding of coupling across different energy scales and test whether a magnetic field can manipulate singlet-triplet equilibrium populations while creating optical contrast, we measured the optical properties of the organic precursor 1,4-diazidobenzene and its biradical photoproduct 1,4-phenylenedinitrene. We find strong color changes upon photolysis that are well-described by our complementary electronic structure calculations, with broad evidence for vibronic coupling, and a rich magnetochromic response that derives from the dissimilarity of the singlet and

triplet state spectra and magnetoelectric coupling. Ordinarily, one does not expect a low energy tuning parameter such as magnetic field to impact high energy properties such as electronic structure. Things are different here because a small spin gap allows an applied field to manipulate the population and (at high enough fields) drive the system into the fully polarized triplet state. In 1,4-phenylenedinitrene, a Curie-like analysis reveals that the magneto-optical properties are sensitive to magnetic energy scales. This presents an advantageous method for spin gap determination that side steps major challenges to commonly used electron paramagnetic resonance-based Curie law methods for determining reactive biradical spin state energy gaps, particularly that the presence of magnetically silent singlet states can only be deduced, and that temperature ranges needed for accurate energy gap determination are often circumscribed by the softening temperatures of frozen matrices. Use of magnetic field rather than temperature as the external stimuli by which we modify population introduces a broadly useful, rigid,¹⁶ and multi-wavelength (with optical spectroscopy) method for extracting reliable spin gap values in open shell systems (Fig. 2).

Thin films were prepared by suspending 1,4-diazidobenzene in an inert polymethylmethacrylate matrix, and the low temperature (≤ 90 K) photochemical reaction (Fig. 1) employed a pyrex-filtered xenon source or the 325 nm

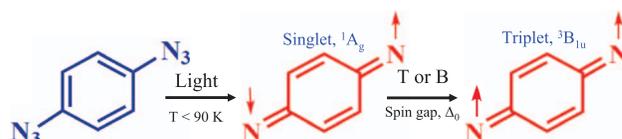


FIG. 1. Chemical structure of the 1,4-diazidobenzene precursor (blue), and the dinitrene biradical 1,4-phenylenedinitrene (red) after photochemical reaction. Temperature or applied magnetic field drives the singlet-triplet equilibrium.

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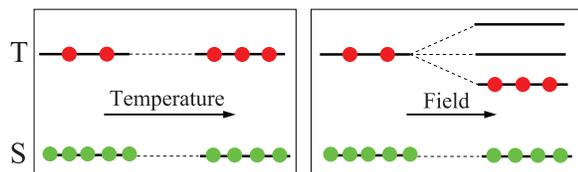


FIG. 2. Schematic view of how temperature and magnetic field act to populate the triplet state in the biradical.

line of a HeCd laser. Transmittance was measured using a Perkin Elmer λ -900 grating spectrometer (3000–190 nm; 1 nm resolution; 4–300 K), and absorption was calculated as $\alpha(\lambda) = (-1/(hd)) \ln T(\lambda)$, where h is loading, d is thickness, and $T(\lambda)$ is transmittance. To emphasize temperature-induced changes, we calculated the absorption difference spectra as $\alpha(T) - \alpha(5 \text{ K})$. The absolute value of this quantity was employed in the population analysis. Magneto-optic experiments were carried out at the National High Magnetic Field Laboratory using a 35 T resistive magnet. To extract field-induced changes in the optical response, we calculated the absorption difference spectra $\alpha(B) - \alpha(0 \text{ T})$. The absolute value was used in our population analysis.

First principles electronic structure calculations were carried out using NWChem (Ref. 17) on relaxed structures of the target materials using time-dependent density functional theory (TDDFT, B3LYP functional,¹⁸ 6-311+g* basis), and also with configuration interaction (CI) energy-selected with a threshold of 0.0001 E_h (Ref. 19) (eight frozen core orbitals, 6-31g* basis using orbitals from complete active space self-consistent field with an active space of ten electrons in ten orbitals). For both methods, the lowest 40 states were computed. Although it provides the preferred single determinant triplet wavefunction, the TDDFT is not expected to yield a good description of the biradical singlet spectrum since it does not treat near-degeneracy of the b_{2g} and b_{3u} orbitals; indeed, TDDFT predicts the $b_{2g} \rightarrow b_{3u}$ transition to be at 1750 nm while the most intense feature in the singlet CI spectrum is at

251 nm. On the other hand, since the limited CI expansion recovers only a fraction of the correlation energy, the CI transitions are expected to be too high in energy. Nevertheless, the basic trends are apparent (Fig. 3). The dipole-allowed spectrum of the triplet species is less intense and at higher energy than that of the singlet, the features in common between the singlet and triplet spectra are primarily $\pi \rightarrow \pi^*$, and many of the lower energy features are either of low intensity or dipole forbidden.

Figure 4 displays the low temperature absorption spectrum of 1,4-diazidobenzene. We employed a symmetry analysis, comparison with model compounds, and first principles calculations to assign the transitions. In addition to the strong dipole-allowed $\pi \rightarrow \pi^*$ transitions at $\lambda < 300$, 308, and 345 nm,²¹ several weak features are observed between 400 and 450 nm that we assign as forbidden $\pi \rightarrow \pi^*$ excitations activated by vibronic coupling, analogous to the situation in C_{60} .²² Temperature effects on the unphotolyzed organic precursor are best seen by following changes in the absolute value of the absorption difference (left inset, Fig. 4). They are consistent with changes in ring planarity and azide group conformations, which can be syn- or anti- to one another, or be within a continuum of rotamers about the phenyl- N_3 bonds.^{21,23}

Figure 4 also displays the post-photolysis absorption spectrum assigned to 1,4-phenylenedinitrene. The photolyzed biradical displays dramatically different color properties compared to its organic precursor with an overall increase in absorption along with some new electronic excitations, several of which were originally reported by Reiser *et al.*^{21,24} From Fig. 3, we see that the singlet and triplet state spectra of 1,4-phenylenedinitrene are predicted to be quite different. The selected-CI results indicate that in the singlet spectrum $\pi \rightarrow \pi^*$ excitations acquire significant intensity through simultaneous excitation of $b_{2g} \rightarrow b_{3u}$, whereas the triplet spectrum is dominated by single excitations. At the lowest temperature, the excitations are essentially those assigned to

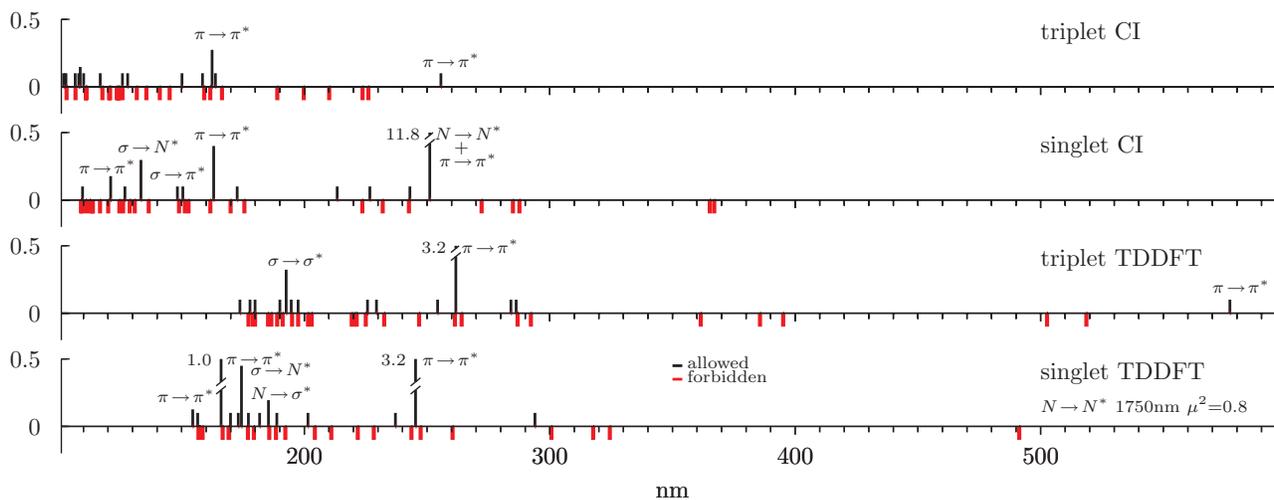


FIG. 3. TDDFT and selected CI spectra (square of the transition dipole, μ^2 , in atomic units) of 1,4-phenylenedinitrene. For clarity, dipole-allowed transitions are indicated in black. Dipole-forbidden transitions are indicated in red as negative -0.1 , weak allowed transitions are increased to 0.1, and intense transitions truncated to 0.5. The most intense feature in the singlet CI spectrum at 251 nm (predominantly $N \rightarrow N^*$ single excitation, with lesser $\pi \rightarrow \pi^*$ single excitation) has $\mu^2 = 12$ and does not appear in the triplet spectrum that has its most intense feature with $\mu^2 = 0.3$ at 162 nm. The spurious low energy features in the singlet TDDFT spectrum are omitted. N and N^* indicate the b_{2g} and b_{3u} orbitals, respectively.

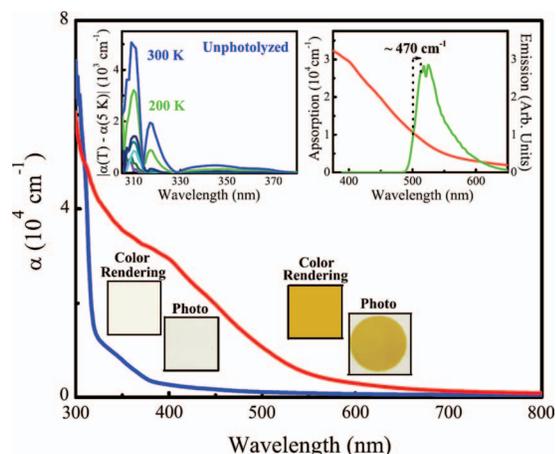


FIG. 4. Absorption spectra of pristine 1,4-diazidobenzene and the biradical photo-product 1,4-phenylenedinitrene at 5 K. Color-rendering calculations²⁰ and photos are in good agreement. Left: Absolute value of the absorption difference, $|\Delta\alpha| = |\alpha(T) - \alpha(T = 5 \text{ K})|$, vs. wavelength for the unphotolyzed film at 300, 200, 100, 80, 60, 40, and 20 K. Right: Emission vs. wavelength for the photolyzed film from which the Stokes shift was extracted.

the singlet ground state, with weaker features of triplet origin growing at higher temperatures (Fig. 5). Defining n_S as the fraction of molecules in the singlet state with absorption $\alpha(\lambda)_S$ and n_T as the fraction of molecules in the triplet state with absorption $\alpha(\lambda)_T$, optical property changes will be given by $(1 - n_S)[\alpha(\lambda)_T - \alpha(\lambda)_S] = n_T[\alpha(\lambda)_T - \alpha(\lambda)_S]$. Clearly, the number of molecules in the triplet state depends upon temperature as is expected by the Boltzmann distribution.

A Curie-like analysis of the absolute value of the absorption difference data at different wavelengths (Fig. 5) allows us

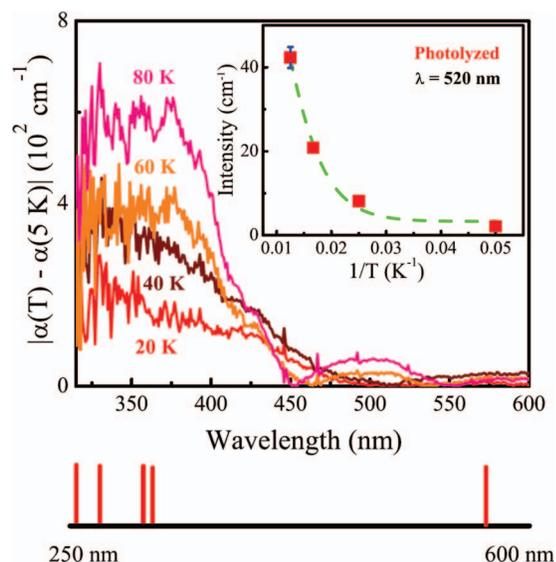


FIG. 5. Absolute value of the absorption difference, $|\Delta\alpha| = |\alpha(T) - \alpha(T = 5 \text{ K})|$, vs. wavelength for the photolyzed biradical film at 80, 60, 40, and 20 K. Inset: Example Curie fit at 520 nm. These data allow a direct comparison of electron paramagnetic resonance and optical methods of spin gap determination. We find $\Delta_0 = 230 \pm 22 \text{ K}$, which compares well with that from electron spin resonance (288 K). A schematic view of the calculated triplet state excitations using the TDDFT method (shown at the bottom) in reasonable agreement with the $|\Delta\alpha|$ data in the main panel. The fine structure in the absorption difference spectrum is discussed in the supplementary material.²⁶

to identify the electronic excitations associated with the thermally populated triplet state, compare the electron spin resonance and optics methods, and extract the value of the singlet-triplet gap in the biradical using the optics technique. We find that the spectral variation with temperature, detectable due to the modern methodology, is consistent with previous electron paramagnetic resonance determinations of a singlet ground state for this system, but ascertained under conditions where both the singlet and the triplet spectra are seen (unlike EPR). Here is how it works. Following the approach developed for electron spin resonance,^{13,25} triplet state intensity is given as $I = (C_1/T)[3 \exp(-\Delta_0/T)/[1 + 3 \exp(-\Delta_0/T)]] + C_2$, where Δ_0 is the singlet-triplet spin gap at zero magnetic field, T is the temperature, and C_1 and C_2 are the fitting constants. Employing a spin Hamiltonian of $\sum J_{ij} S_i \cdot S_j$, Δ_0 is equal to the exchange constant J for a simple spin dimer. We fit the absolute value of the absorption difference, $|\Delta\alpha|$, vs. inverse temperature at several different wavelengths to extract the spin gap, Δ_0 . An example fit is shown in the inset of Fig. 5. This analysis allows us to (1) extract an independent estimate of $\Delta_0 = 230 \pm 22 \text{ K}$ which agrees well with the aforementioned electron spin resonance estimate of 288 K,¹³ and (ii) experimentally assign features that correspond to the triplet state: 333, 350, 380, 403, and 490–550 nm. The latter are supported by our electronic structure calculations. Moreover, the quality of the fit to our optical data reveals that we have a viable and sensitive technique for following spin population changes in the biradical.

Because the spin gap is small, we decided to test the ability of a strong magnetic field to manipulate the singlet-triplet equilibrium. Figure 6 displays the 4.2 K magneto-optical response of 1,4-phenylenedinitrene. A field-induced color change is clearly observed. This color change occurs because the applied field increases the triplet biradical concentration, which has a unique optical signature by comparison with the singlet biradical and precursor molecule. We can monitor this interconversion and the associated spectral

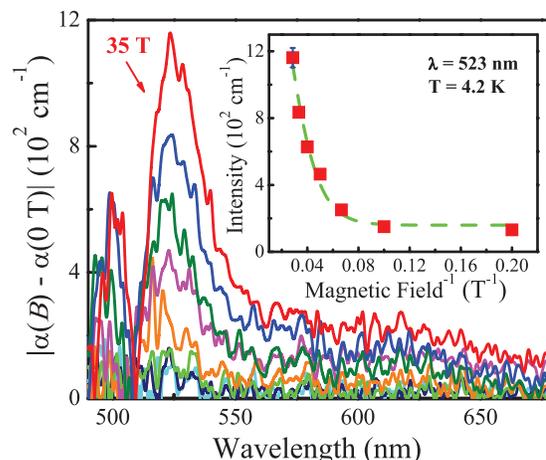


FIG. 6. Absolute value of the absorption difference spectrum, $|\alpha(B) - \alpha(0 \text{ T})|$, of the biradical photo-product vs. wavelength at 4.2 K, from which we extracted data for the Curie-like analysis. Data shown for $B = 0, 5, 10, 15, 20, 25, 30,$ and 35 T . Inset: Example fit at 523 nm. These data allow us to probe the spin gap with field rather than with an analysis of relative thermal populations. We find $\Delta_0 = 128 \pm 18 \text{ K}$.

changes as $n_T[\alpha(\lambda)_T - \alpha(\lambda)_S]$, the triplet state population times the absorption difference between the two states. The absorption difference spectrum therefore reveals how the optical signature of the triplet state differs from that of the singlet state, which in the wavelength range of Fig. 6, emphasizes change in vibronically activated $\pi \rightarrow \pi^*$ excitations.

A Curie-like analysis of the magneto-optical data was carried out as $I = (C_3/B)[\exp(-\Delta_0/B)/[1 + \exp(-\Delta_0/B)]] + C_4$. Here, Δ_0 is the zero field spin gap, B is the magnetic field, and C_3 and C_4 are the fitting constants. Note that we have exchanged T for B compared to the previous fitting formula. This change of thermodynamic variables is justified because T and B are related by a Maxwell relation,²⁷ a result that is equivalent to explicit inclusion of Zeeman splitting. We fit the absolute value of the absorption difference, $|\Delta\alpha|$, vs. B^{-1} at several different wavelengths to extract Δ_0 (inset, Fig. 6). This is essentially a Curie analysis of the magneto-optical response carried out at different wavelengths, justified because closing singlet-triplet gaps with magnetic field is similar to temperature-induced population changes. Averaging our results at different wavelengths, we find $\Delta_0 \approx 128 \pm 18$ K.

The value of the zero-field spin gap extracted from our analysis of the magneto-optical spectra of 1,4-phenylenedinitrene (128 K) is smaller than that obtained from the variable temperature optical response (230 K) and the electron spin resonance data (288 K). That all estimates are a similar order of magnitude indicates that the magneto-optical approach provides fundamental information on magnetic energy scales in open shell molecules (such as the singlet-triplet spin gap). The difference is, however, even more interesting and reveals important physics. Traditionally, variable temperature EPR Curie analysis experiments are carried out between 20 and 80 K, the latter being determined by sample degradation issues. This is a very limited temperature range from which to extrapolate a spin gap, a constraint that is well-recognized in the literature.^{28,29} Using magnetic field to close the gap is a much cleaner alternative. It obviates the weakness associated with temperature extrapolation in the biradicals, offers a general technique to rigidly¹⁶ increase the triplet state population, and in the case of 1,4-phenylenedinitrene suggests that the true value of the spin gap is significantly lower than the previously supposed.^{30,31} While our magneto-optical Curie analysis side-steps the well-known temperature range limitation, it does have challenges of its own. The chief restriction is the size of the available field, although in sufficiently high magnetic fields or in the limit of small spin gaps, the analysis can be carried out with great accuracy. In fact, the magnetic method is likely to be better and more precise in many cases.

Summarizing, we investigated the photophysical properties of 1,4-diazidobenzene and its biradical photo-product 1,4-phenylenedinitrene and compared the results with complementary first principles electronic structure calculations. We directly observed the effects of manipulating the singlet-triplet equilibrium with temperature and magnetic field, with color property changes in both cases. These effects arise from the dissimilarity of the singlet and triplet state spectra. A

Curie-like analysis of the optical response allows us to extract magnetic properties, in this case the spin gap. We find that the singlet-triplet gap is 128 ± 18 K, significantly lower than previously supposed. This work demonstrates the power and breadth of magneto-optical spectroscopy, positioning it to advance magnetic property determination in organic solids with unusual trapped spin states such as biradicals. Similar themes are of interest in complex oxides.³²

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