

Remote Intermolecular “Heavy-Atom Effect”: Spin–Orbit Coupling Across the Wall of a Hemicarcerand

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Quenching of excited states via the “heavy atom effect”, that is the acceleration of the spin-forbidden intersystem crossing (ISC) by interaction with atoms carrying large orbital angular momentum, is frequently viewed as a short-distance phenomenon requiring direct contact between the participating species. This belief persists in the literature even though it was shown already in the early 1970s that an internal heavy atom can exert a significant influence on the fluorescence and phosphorescence yields, even if it is separated from the chromophore by two carbon–carbon σ -bonds.¹ More recently, a detailed study of the remote heavy atom effect was performed by Kuki et al. on model peptides bearing chromophores and quenchers.^{2,3} A measurable effect was observed even if the chromophore and the heavy atom quencher were separated by three amino acid residues. Because of the inherent conformational flexibility, it is difficult to completely exclude the possibility of a direct contact between the chromophore and the quencher in peptide-based systems. This becomes a particularly important issue if the quenching rates are slow. In this communication we report the observation of efficient external spin–orbit (SO) coupling effects in systems in which the direct contact between the chromophore and the halogenated solvent is rigorously precluded by encapsulation of the chromophore inside a hemicarcerand cage (Figure 1).⁵

The T₁ lifetime of the incarcerated biacetyl was measured in several halogenated solvents which are known to accelerate the ISC in solute molecules.⁶ A significant, 7-fold decrease of the phosphorescence lifetime^{7,8} of biacetyl was observed as progressively heavier halogenated solvents were used. The trend becomes even more apparent if, instead of monitoring the overall change of the lifetime, one defines the specific external heavy atom

contribution to the ISC rate as $k_x = 1/\tau_T^{\text{solventX}} - 1/\tau_T^{\text{benzene}}$. With benzene serving as the reference solvent, the external heavy atom contribution to the overall decay rate is found to increase dramatically from 60 s⁻¹ in dichloromethane to 6500 s⁻¹ in CH₂I₂ (Table 1). This shows that there is a substantial coupling between the spin angular momentum of the trapped biacetyl T₁ state and the unquenched orbital angular momentum carried by the halogen atoms of the solvent.

It is important to stress that this and other groups have demonstrated in the past that the incarcerated guests cannot participate in chemical reactions with external reactants.^{9–12} Only electron and excitation transfer reactions, that is, processes that do not necessitate the motion of an atom across the cage boundary, can proceed with appreciable rates.¹³ In this study, to confirm that the quenching of biacetyl indeed occurs as a result of a physical interaction (SO coupling with the external heavy atoms), rather than a chemical process (H-abstraction from a solvent molecule) we used the well-known hydrogen donor, 2-propanol, as the test solvent.¹⁴ As it can be seen in Table 1, the measured values of the triplet lifetimes of incarcerated biacetyl in neat CH₂-Cl₂ and in the 1:1 methylene chloride/2-propanol mixture¹⁵ are well within the experimental error. This rules out hydrogen abstraction from the solvent as a factor contributing to the observed decrease of triplet lifetimes. The only other mechanism that could be potentially responsible for the observed quenching, and that does not require a direct contact between the solvent and the incarcerated biacetyl, is electron transfer. Both biacetyl ($I_p = 9.24$ eV, $E_a = 0.75$ eV) and haloalkanes are weak electron acceptors; however, we are not aware of any literature examples in which either of them behaves as an electron donor. Balzani et al. studied bimolecular ET from a variety of amines to biacetyl encapsulated within a hemicarcerand similar to the one discussed here.¹⁰ In the case of such potent electron donors as diphenylamine, $E_{ox} = 0.83$ eV, and DABCO, $E_{ox} = 0.57$ eV, very slow ET rates of 3.5×10^4 M⁻¹ s⁻¹ and 5×10^3 M⁻¹ s⁻¹ were measured. Since haloalkanes have ionization and oxidation potentials at least ~ 1.5 eV higher than these two amines, the corresponding electron transfer is endothermic, and its rates must be several orders of magnitude lower. Indeed, even benzene ($I_p = 9.2$ eV) should act as a stronger electron donor than CH₂I₂ ($I_p = 9.5$ eV), yet in all biacetyl-containing hemicarceplexes that we have studied the longest T₁ lifetimes were observed in benzene solutions. Consequently, intermolecular electron transfer cannot account for the effects reported in this communication.

The observed quenching rates in the series of Cl-, Br-, and I-containing solvents do not follow the simple trend that would

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(1) Kavarnos, G.; Cole, T.; Scribe, P.; Dalton, J. C.; Turro, N. J. *J. Am. Chem. Soc.* **1971**, *93*, 1032.

(2) Basu, G.; Kubasik, M.; Anglos, D.; Secor, B.; Kuki, A. *J. Am. Chem. Soc.* **1990**, *112*, 9410.

(3) Basu, G.; Kubasik, M.; Anglos, D.; Kuki, A. *J. Phys. Chem.* **1993**, *97*, 3956.

(4) For the synthesis and the hemicarceplex characterization see Z. S. Romanova, Ph.D. Dissertation, BGSU, 1999. The specific hemicarcerand was selected for this series of experiments primarily because of its availability. The presence of one *o*-xylyl linkage has only a minor influence on the degree of communication between the guest and the outside. The dependence of the electronic coupling between the guest and the surroundings on the structure of the cage will be reported shortly.

(5) NMR and MS results, as well as modeling, show that the hemicarcerand cage can be occupied only by one guest molecule. It cannot simultaneously contain the biacetyl and the solvent.

(6) (a) Kasha, M. *J. Chem. Phys.* **1952**, *20*, 71. (b) Christodonleas, N.; McGlynn, S. P. *J. Chem. Phys.* **1964**, *40*, 166; (c) Kearns, D. R.; Case, W. A. *J. Am. Chem. Soc.* **1966**, *88*, 5087; (d) Marchetti, A. P.; Kearns, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 768; (e) Cheng, T. H.; Hirota, N.; Mao, S. W. *Chem. Phys. Lett.* **1972**, *15*, 274.

(7) Degassed solutions of the hemicarceplex were excited at 450 nm using a nanosecond OPO pumped by the third harmonic of an Nd:YAG laser. Phosphorescence lifetimes were monitored using a gated ICCD camera. Single exponential decays were observed in all cases.

(8) It was pointed out by one of the reviewers that the $n\pi^*$ excited states of organic molecules are typically much less sensitive to the external heavy atom effects than the $\pi\pi^*$ states. Indeed, we did not observe any variation in the fluorescence lifetime of the incarcerated biacetyl, suggesting that the solvent has a small influence on the intrinsically fast S₁–T₁ ISC rate. However, the exceptionally long lifetime of the T₁ state of biacetyl ($\tau_{T_1} \approx 1 \times 10^{-3}$ s versus $\tau_{S_1} \approx 1 \times 10^{-8}$ s, both at room temperature), makes the slow T₁–S₀ ISC rate much more sensitive to even small external perturbations, resulting in much more pronounced external heavy atom effects.

(9) Cram, D. J.; Cram, J. M. *Container Molecules and their Guests in Monographs in Supra-molecular Chemistry*; Stoddart, J. F., Ed.; Royal Society of Chemistry, Cambridge, UK, 1994.

(10) Parola, J.; Pina, F. A.; Ferreira, E.; Maestri, M.; Balzani, V. *J. Am. Chem. Soc.* **1996**, *118*, 11610.

(11) Farrán, A.; Deshayes, K.; Matthews, C.; Balanescu, I. *J. Am. Chem. Soc.* **1995**, *117*, 9614.

(12) Farrán, A.; Deshayes, K. *J. Phys. Chem.* **1996**, *100*, 3305.

(13) For example, we have shown that the T₁ state of imprisoned biacetyl does not abstract the highly labile methylenic hydrogen from cycloheptatriene, Place, I.; Farran, A.; Deshayes, K.; Piotrowiak, P. *J. Am. Chem. Soc.* **1998**, *120*, 12626.

(14) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993.

(15) Neat 2-propanol could not be used because of the poor solubility of the hemicarcerand.

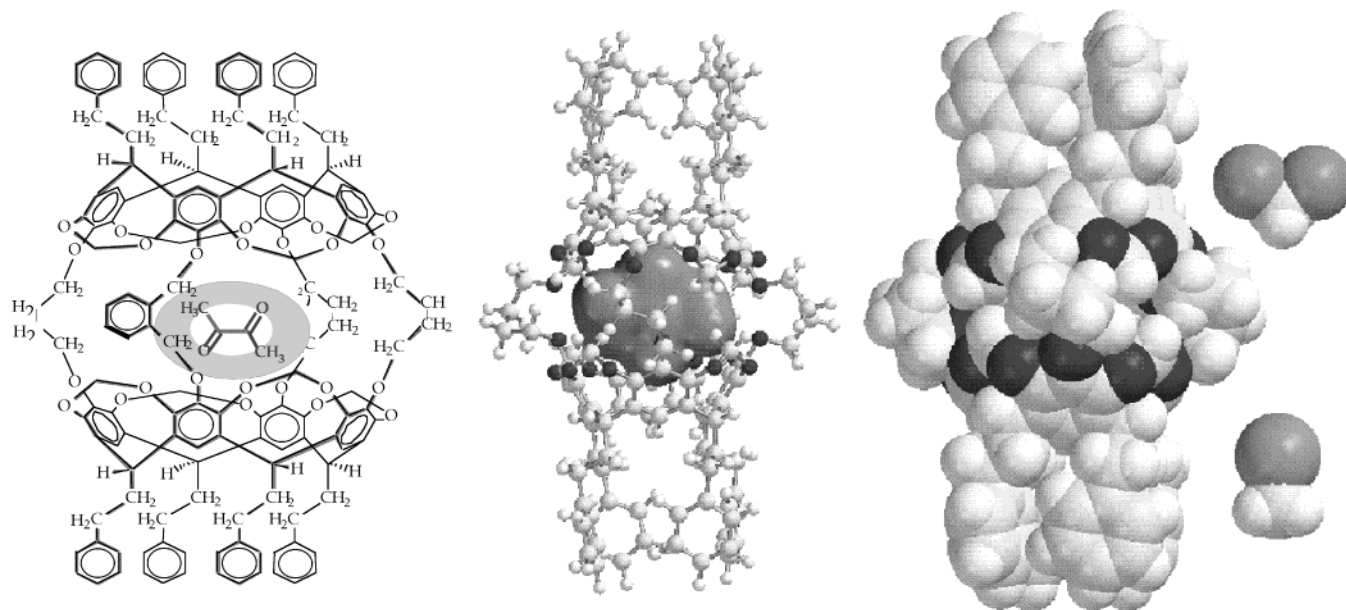


Figure 1. From the left: Structure of the investigated hemicarcerand indicating three butyl and one *o*-xylyl linkage;⁴ molecular mechanics (Sybyl)-optimized structure of the cage showing the electron density surface of the trapped biacetyl (AM1); space-filled model of the hemicarcerand with the molecules of dichloromethane and iodomethane shown for comparison.

Table 1. Triplet State Lifetimes of Incarcerated Biacetyl in Halogenated Solvents

| solvent | MW [g] | SO coupling in atom X [eV] | molarity of atom X [M] | $\tau_{T_1}^a$ [ms] | k_X [s^{-1}] |
|--|--------|----------------------------|------------------------|---------------------|--------------------|
| benzene | 78.11 | — | 0 | 1.01 | — |
| CH ₂ Cl ₂ | 84.93 | 0.055 ^b | 31.2 | 0.95 | 60 |
| <i>i</i> -PrOH/CH ₂ Cl ₂ | — | — | 15.6 | 0.95 | — |
| CHBr ₃ | 252.75 | 0.23 ^b | 34.3 | 0.83 | 220 |
| CH ₂ I ₂ | 267.84 | 0.65 ^b | 24.9 | 0.134 | 6500 |

^a The lifetimes carry a margin of error of $\pm 3\%$. ^b From ref 16.

be expected solely on the basis of the average spin-orbit coupling associated with the respective halogen atoms (Table 1).¹⁶ For example, upon transition from CHBr₃ to CH₂I₂ the component of the quenching rate induced by the external heavy atom, k_X , increases from 220 s⁻¹ to 6500 s⁻¹, that is, considerably more than the square of the ratio of the Br and I spin-orbit coupling

(16) Slichter, C. P. *Principles of Magnetic Resonance*; Harper & Row: New York, 1963 and Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito (adapted from McClure, D. S. *J. Phys. Chem.* **1949**, *17*, 905), 1991. It should be emphasized that the magnitude of the residual molecular orbit at angular momentum (always a small fraction of that of the corresponding free halogen atom X*) strongly depends on the details of the electronic structure of each molecule. The assumption that it scales in proportion to average atomic values is only a convenient but crude estimate.

(17) Petelenz, P.; Fuenfschilling, J. *Chem. Phys.* **1990**, *145*, 333.

(18) The crucial role of the resonance between the excited state of the chromophore with the virtual excited states of the heavy atom quencher was pointed out by G. W. Robinson, *J. Chem. Phys.* **1967**, *46*, 572. Consequently, eq 1 closely resembles the first-order perturbation theory equations used to describe electronic energy transfer, and indeed, the spin-orbit coupling with remote heavy atoms can be viewed as a virtual excitation transfer process. A strong dependence of energy transfer on the energy gap between the states of the donor and acceptor and the virtual states of the bridge was reported recently by B. Albinsson, and co-workers: Kilså, K.; Kajanus, J.; Mårtensson, J.; Albinsson, B. *J. Phys. Chem. B* **1999**, *104*, 7329 and Jensen, K. K.; van Berlekom, S. B.; Kajanus, J.; Mårtensson, J.; Albinsson, B. *J. Phys. Chem. A* **1997**, *101*, 2218.

(19) On the basis of the present data, it is not possible to resolve the direct and the cage-mediated contributions to the overall spin-orbit coupling between the guest and the solvent. In the case of the cage-mediated component, the relevant resonance is the one between the virtual states of the hemicarcerand and these of the halogenated solvents. Since the absorption edge of the empty cage is at ~ 300 nm, the mediated coupling should also be resonantly enhanced for CH₂I₂.

(20) D. R. Lide, *Handbook of Organic Solvents*; CRC Press: Boca Raton, 1995.

(21) Obtained from eq 1, using the SO parameters from Table 1 and the relevant energy gaps, $k_{ISC}^{CH_2I_2}/k_{ISC}^{CHBr_3} = (SO/SO_{Br})^2 (E_{S_1}^{CHBr_3} - E_{T_1}^{biacetyl})^2 / (E_{S_1}^{CH_2I_2} - E_{T_1}^{biacetyl})^2 = 24.1$.

constants, which grows only by a factor of 8. As discussed in detail by Petelenz¹⁷ and Kuki,³ the rate of intersystem crossing induced by the intermolecular SO coupling, like all perturbation phenomena, contains a resonance term which is inversely proportional to the square of the energy gap between the excited state of the chromophore and the open-shell virtual state (or states) of the quencher bearing the heavy atom.¹⁸

$$k_{ISC}^{solventX} \propto |\langle S_0^{biacetyl}, S_1^{solventX} | \hat{H} | T_1^{biacetyl}, S_0^{solventX} \rangle|^2 \times \frac{1}{(E_{S_1}^{solventX} - E_{T_1}^{biacetyl})^2} \quad (1)$$

The direct SO interaction between the T₁ state of the chromophore and the closed-shell S₀ state of the external quencher is extremely inefficient.¹⁹ The first term in the equation above contains both the direct and cage-mediated components of the matrix element, and is proportional to the square of the SO coupling carried by the halogenated solvent. The second term corresponds in our systems to the resonance between the T₁ state of biacetyl, $E_{T_1} = 2.5$ eV, and the relevant virtual state of the solvent. The lowest $n \rightarrow \sigma^*$ excitations of CH₂Cl₂, CHBr₃ and CH₂I₂ occur approximately at 210, 220, and 290 nm.²⁰ Thus, the corresponding energy gap drops from $\Delta E = 3.6$ eV for CH₂Cl₂, to 3.3 eV for CHBr₃, to 1.9 eV for CH₂I₂. As a consequence, with the resonance term included, a 24-fold increase in the externally induced ISC rate is predicted upon switching from CHBr₃ to CH₂I₂. This compares rather well with the experimentally observed ratio of 29.5.²¹

To summarize, we have demonstrated that the external “heavy atom effect” can propagate efficiently through the chemically impermeable walls of molecular cages, particularly if the resonant enhancement of the interaction is possible. Because of its close formal similarity to charge and electronic excitation transfer processes, the remote, or long-distance, spin-orbit coupling deserves to be studied in more detail.

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