

TIME-DEPENDENT CALCULATION OF INTERSYSTEM CROSSING RATES OF SULFUR-SUBSTITUTED ADAMANTANE DERIVATIVES

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Introduction

- for *in vivo* bioimaging, sulfur derivatives of diamondoids may serve as alternative [1] to
 - conventional dye molecules (often toxic, less photostable)
 - quantum dots (too large, could disturb function of target)
- diamondoids: highly photostable, non-toxic, small size
- problem: optical gap of pristine diamondoids lies in UV region
 - replacing CH₂ with C=S ⇒ shift to vis (even IR) [1, 2]
 - but additional S-atoms enhance spin-orbit coupling ⇒ potentially detrimental for role as fluorescence marker

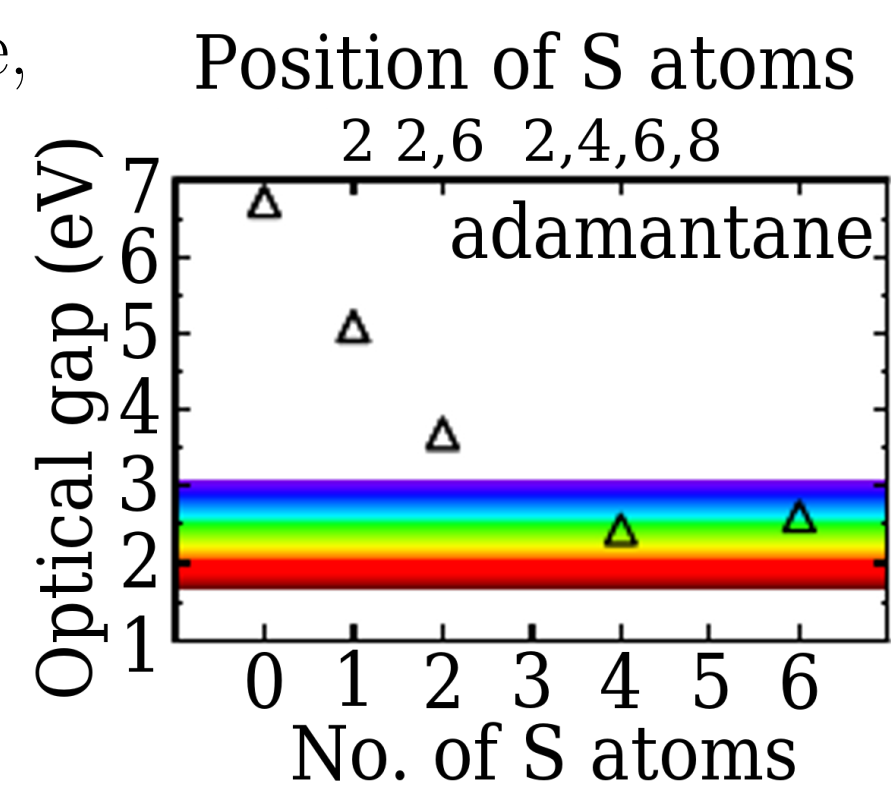


Fig. 1: Optical gap decrease with no. of C=S groups [1].

Investigated systems

- six thione derivatives of adamantane (smallest diamondoid):

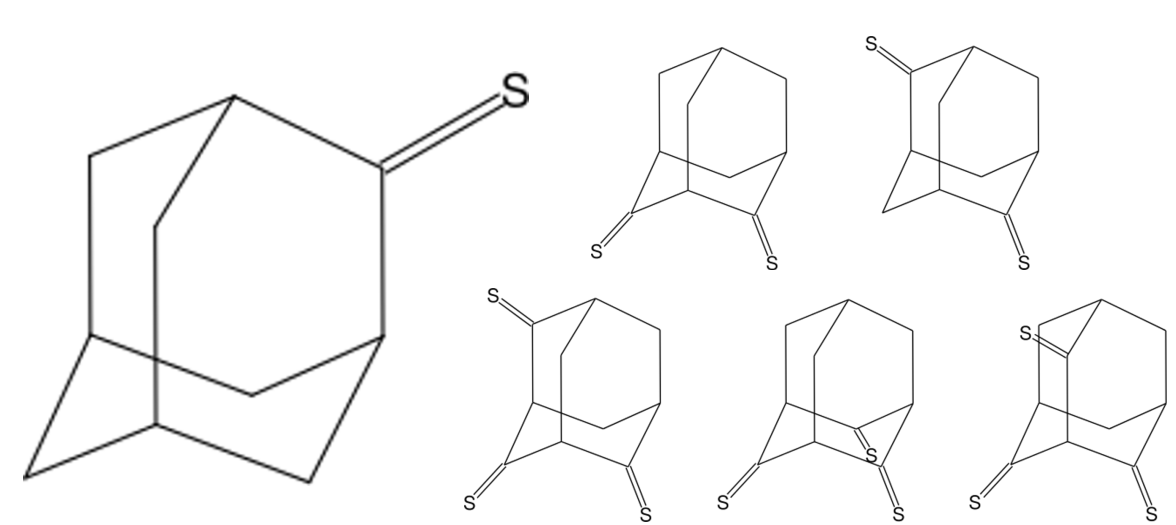


Fig. 2: Adamantane thione and the two di- and three trithiones.

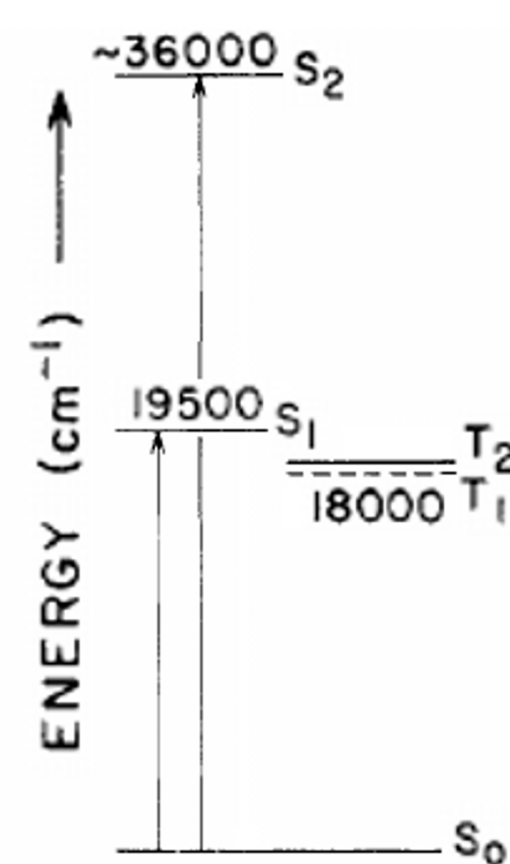


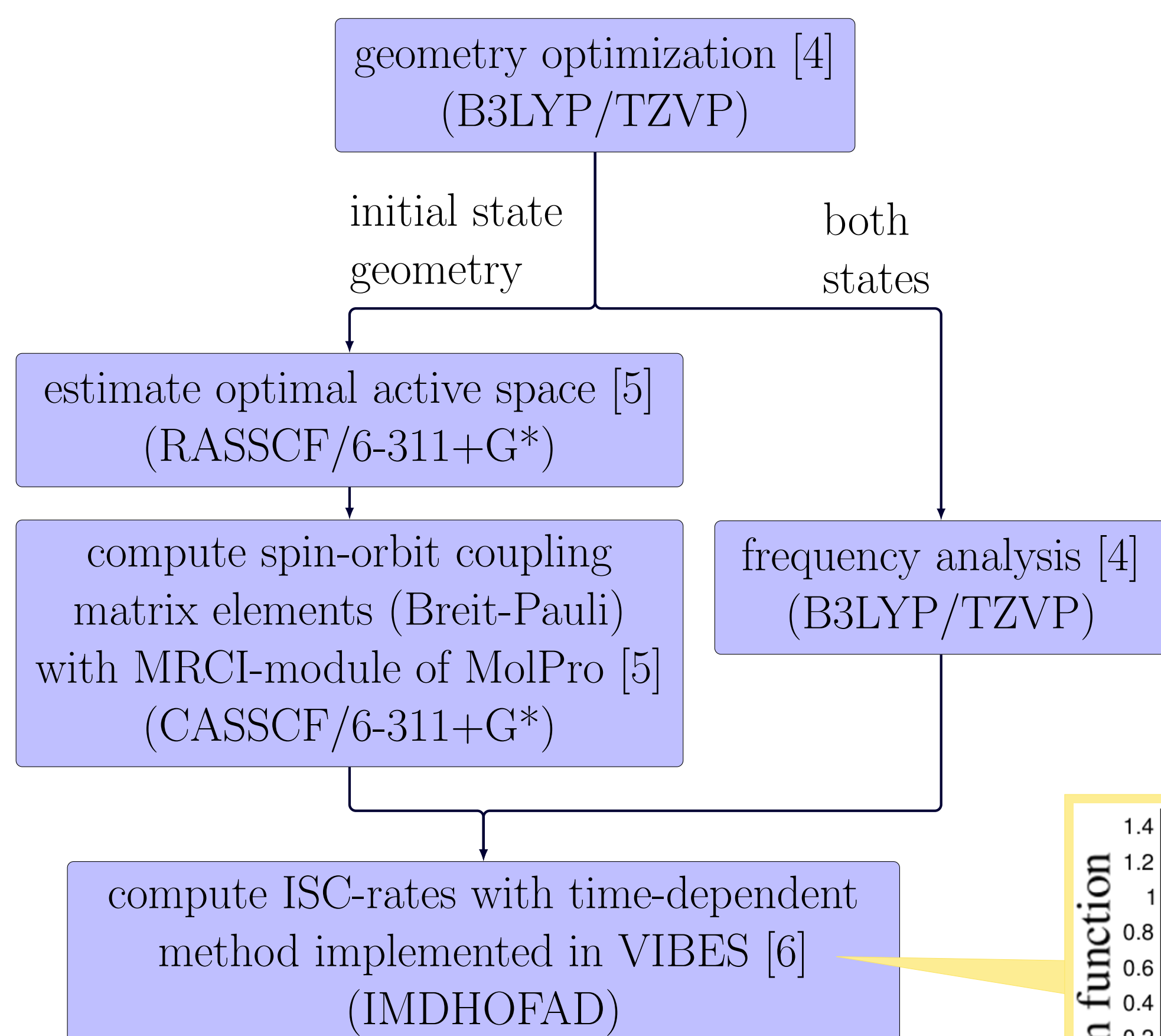
Fig. 3: Experimental excitation energies of adamantane thione [3].

- focus on intersystem crossing between S₁ / T₁ and T₁ / S₀
- adamantane thione also S₂ → T₁

Note, T₁ here always means ³(n → π*), but in exp. it is T₂, as ³(π → π*) is ≈ 500 cm⁻¹ lower, even in unpolar media [3].

Methodology

work flow for each transition:



- within golden rule framework and Condon approximation

$$k_{I \rightarrow F}^{\text{ISC}} = \frac{1}{\hbar} |\langle I | \mathcal{H}_{\text{SO}} | F \rangle|^2 \int_{-\infty}^{\infty} G(t) e^{\frac{i}{\hbar} (\Delta E_{IF}^0 + E_{I,\text{vib},0}) t} dt \quad (1)$$
- $G(t)$ -part of correlation fct. constructed via Mehler's formula
- implicit calculation of all Franck-Condon factors (via $G(t)$), unlike time-independent methods ⇒ much faster, especially for large molecules

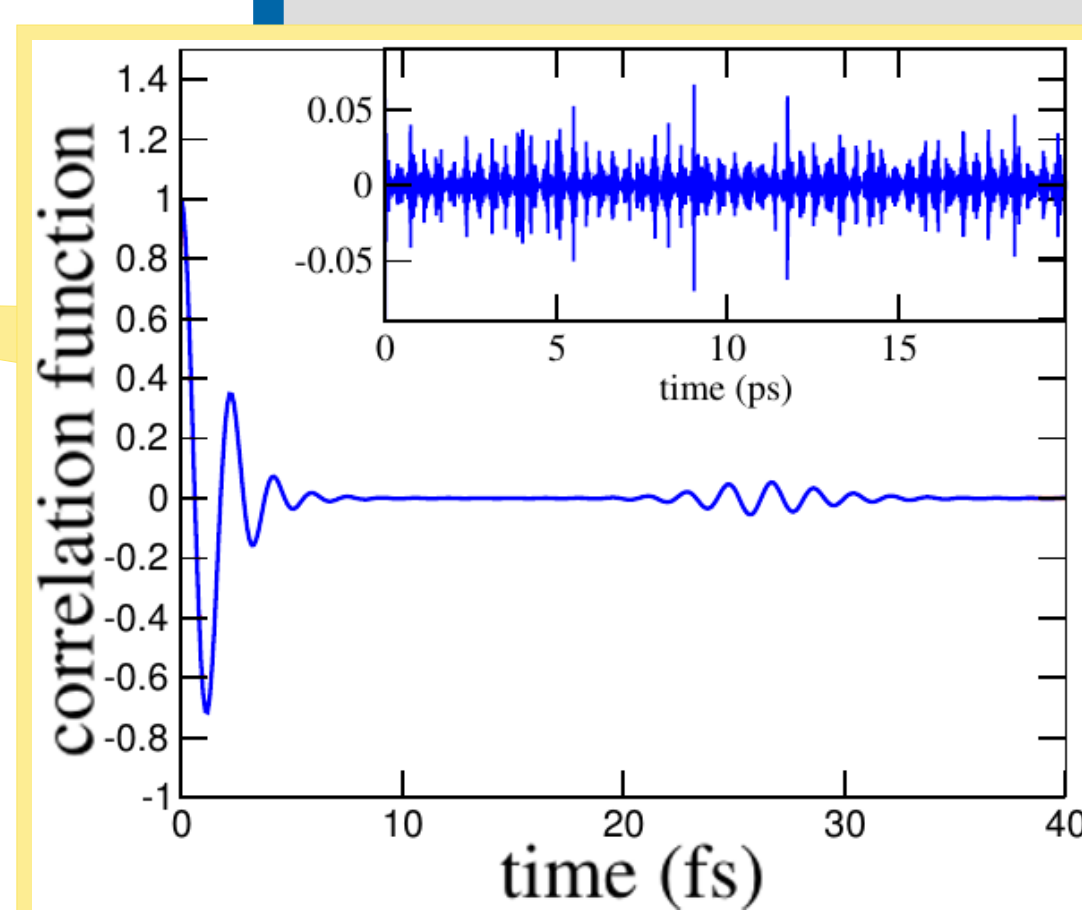


Fig. 4: Correlation function as produced by method [6].

References

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- [2] T. Stüker, Bachelor thesis, Universität Potsdam, (2013).
- [3] K. J. Falk and R. P. Steer *J. Phys. Chem.*, **94**, 5767 (1990).
- [4] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks *et al.*, Gaussian, Inc., Wallingford CT (2009).

Results

Geometries

Adamantane thione

- excited states: elongated C=S bond, tilted relative to ground state S₀.

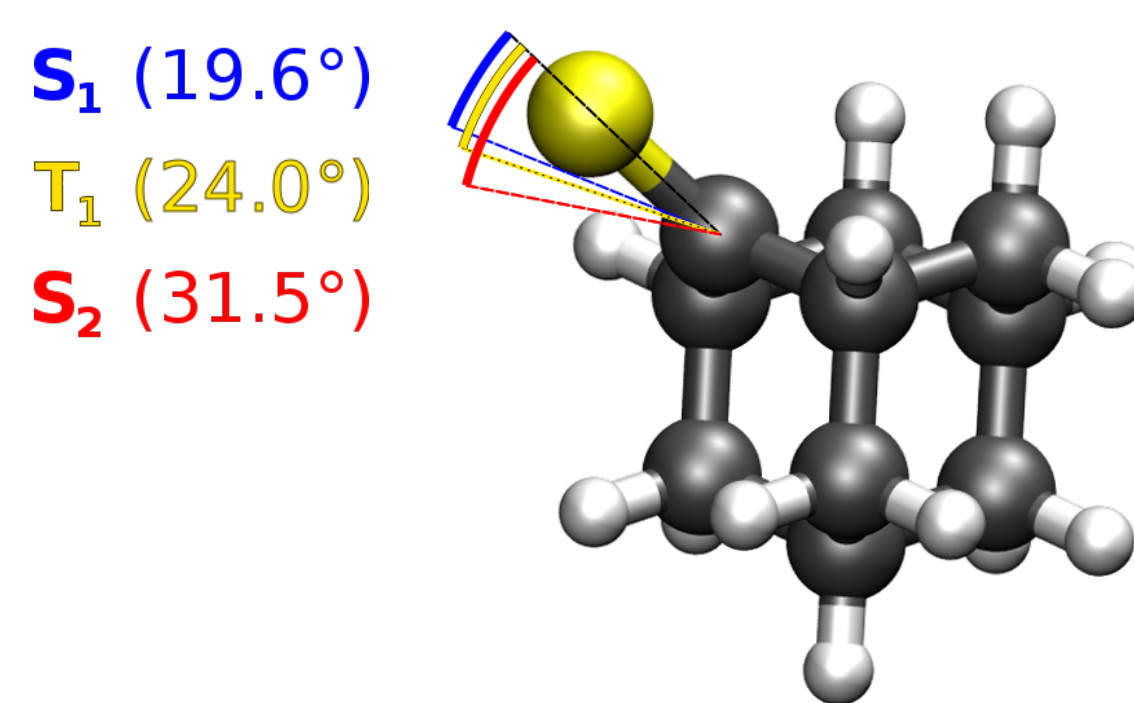


Fig. 5: S₀ compared to excited states.

Adamantane 2,6-dithione (C=S groups on opposite sites)

- like mono thione: only one C=S group tilted, angles similar

Adamantane 2,4-dithione (C=S groups on adjacent sites)

- S₁, T₁: attraction between C=S groups
- slightly more attraction for S₁

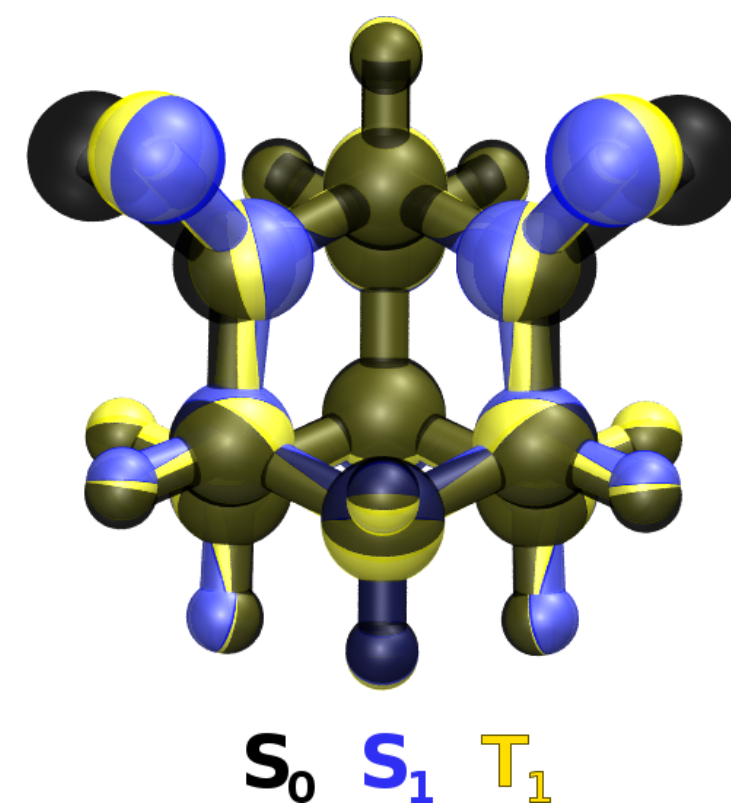


Fig. 6: 2,4-Dithione: Overlay of relevant states.

Adamantane trithiones

- both 2,4,6-trithione and 2,4,10-trithione directly comparable with 2,4-dithione
- excited states of 2,4,9-trithione: attraction between all three C=S groups

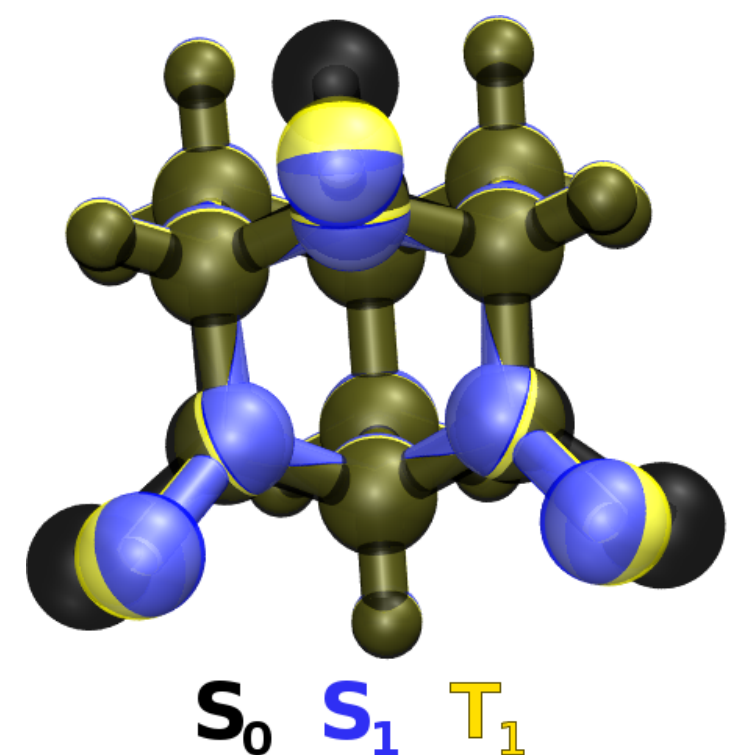


Fig. 7: 2,4,9-Trithione: Overlay of relevant states.

Intersystem Crossing

Adamantane thione

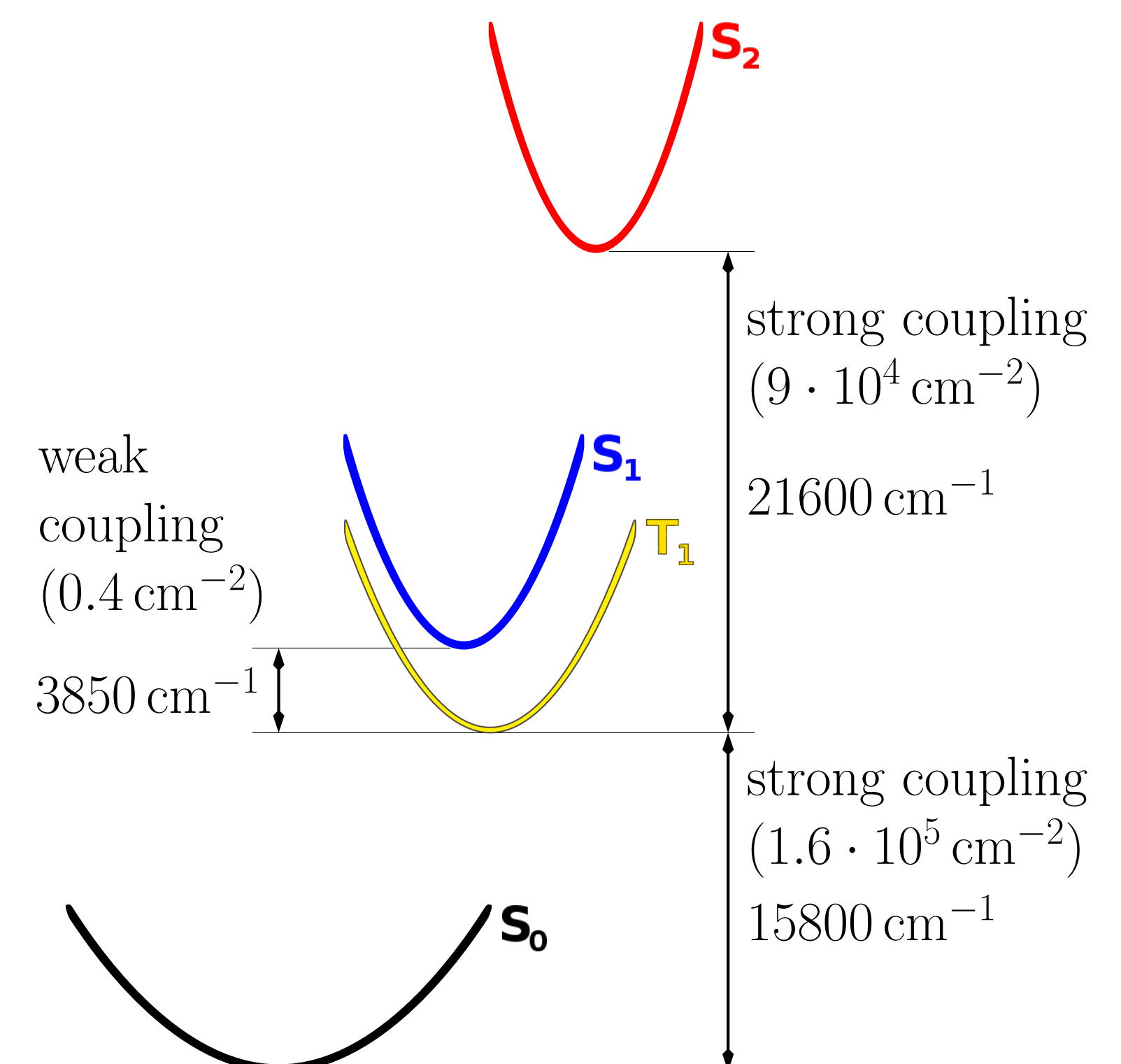


Fig. 8: Spin-orbit coupling matrix elements $|\langle S_a | \mathcal{H}_{\text{SO}} | T_1 \rangle|^2 / (hc)^2$ (CASSCF/6-311+G*) and adiabatic gaps $\Delta E_{IF}^0 / (hc)$ (B3LYP/TZVP).

- S₁ → T₁**
 - S₁ and T₁ have similar orbital character (n → π*) ⇒ weak spin-orbit coupling, predicted by El-Sayed's rule ⇒ $k_{S_1 \rightarrow T_1}^{\text{ISC}} \approx 10^5 \text{ s}^{-1}$
 - low compared to exp. findings: $\Phi_{\text{ISC}} \approx 1$, $k_f \approx 10^4$ [7] ⇒ maybe indirect population of T₁ via fast ISC to T₂?
- S₂ → T₁**
 - S₂: π → π* ⇒ strong coupling to T₁ ($k_{S_2 \rightarrow T_1}^{\text{ISC}} \approx 10^{10} \text{ s}^{-1}$)
 - moderately high rate compared to exp. data [8]: $\tau(S_2) = 0.3 \text{ ps}$, $k_f = 6 \cdot 10^8 \text{ s}^{-1}$, $k_{nr} = 3 \cdot 10^{12} \text{ s}^{-1}$
 - $\Phi_f = 1.7 \cdot 10^{-4}$, $\Phi_p^0 = 0.023$, $k_{S_2 \rightarrow S_1}^{\text{IC}} < 10^8 \text{ s}^{-1}$
 - according to Ref. [8] relaxation mainly via intermediate 'X' located on S₂-surface, with longer τ (200-250 ps)
- T₁ → S₀**
 - strong coupling, calculation of ISC-rate in progress
 - exp. data (combined for T₁ and T₂) [3]: $k_{T_1 \rightarrow S_0}^{\text{ISC}} = 2.3 \cdot 10^4 \text{ s}^{-1}$, $k_p = 4.7 \cdot 10^2 \text{ s}^{-1}$, $\Phi_p^0 = 0.020 \pm 0.004$, $\tau_p^0 = 43 \mu\text{s}$

Adamantane dithiones

- S₁ → T₁ and T₁ → S₀**
 - both dithiones similar (though spin-orbit coupling for 2,4-dithione preliminary, as CAS not yet converged):
 - $k_{S_1 \rightarrow T_1}^{\text{ISC}} \approx 10^5 \text{ s}^{-1}$ and $k_{T_1 \rightarrow S_0}^{\text{ISC}} \approx 10^6 \text{ s}^{-1}$

Adamantane trithiones

- S₁ → T₁**
 - 2,4,6- and 2,4,10-trithione – medium coupling (4 and 15 cm⁻²)
 - $k_{S_1 \rightarrow T_1}^{\text{ISC}} \approx 10^6 \text{ s}^{-1}$ for both
 - 2,4,9-trithione – very small energy gap (2570 cm⁻¹)
 - but weak coupling (0.2 cm⁻²)
 - $k_{S_1 \rightarrow T_1}^{\text{ISC}} \approx 10^3 \text{ s}^{-1}$
- T₁ → S₀**
 - 2,4,6-trithione – $k_{T_1 \rightarrow S_0}^{\text{ISC}} \approx 10^7 \text{ s}^{-1}$
 - 2,4,9- and 2,4,10-trithione – $k_{T_1 \rightarrow S_0}^{\text{ISC}} \approx 10^9 \text{ s}^{-1}$ for both

Conclusions

- employed cost efficient method for computing ISC-rates on thione derivatives of adamantane
- results in qualitative agreement with exp. data (available only for adamantane thione [8])
- first study of spin-orbit coupling effects of multiply thionated adamantanes

Outlook

- include more states (e. g. T₂, 'X')
- validate B3LYP geometries: CASSCF (or other multi-reference method)
- ISC-rates: use more general method [9] (beyond Condon approximation)
- investigate pentamantane derivatives

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- [9] M. Etinski, V. Rai-Constapel and C. M. Marian, *J. Chem. Phys.* **140**, 114104 (2014).