the $S_6^{\bullet-}$ ring eventually adopts in the crystal. Apparently, in Ph_4PS_6, this is the chair conformation **1a**.

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Conical Intersections in Charge-Transfer Induced Quenching**

Adalgisa Sinicropi, Uwe Pischel, Riccardo Basosi, Werner M. Nau,* and Massimo Olivucci*

A detailed knowledge of the molecular mechanisms that govern the chemically unproductive and thus undesirable quenching of excited states by external additives is essential for the rational development of efficient photochemical reactions, artificial photosynthetic systems, and functional photonic devices. We are currently employing high-level quantum chemical methods to provide a comprehensive quenching path mapping for n,π*-excited states of compounds such as ketones and azoalkanes. It was shown that quenching by hydrogen donors is induced by a conical intersection (CI) located halfway along the reaction coordinate for hydrogen abstraction (Figure 1a).[1, 2] Herein, we introduce a new quenching mechanism by electron donors that operates in a similar way through a CI, which is located halfway along a

[*] Prof. Dr. W. M. Nau, Dipl.-Chem. U. Pischel
Departement Chemie der Universität
Klingelbergstrasse 80, 4056 Basel (Switzerland)
Fax: (+41) 61-267-3855
E-mail: Werner.Nau@unibas.ch

Prof. Dr. M. Olivucci, A. Sinicropi, Prof. Dr. R. Basosi
Dipartimento di Chimica, Università degli Studi di Siena
via Aldo Moro, 53100 Siena (Italy)
Fax: (+39) 0577-234278
E-mail: olivucci@unisi.it

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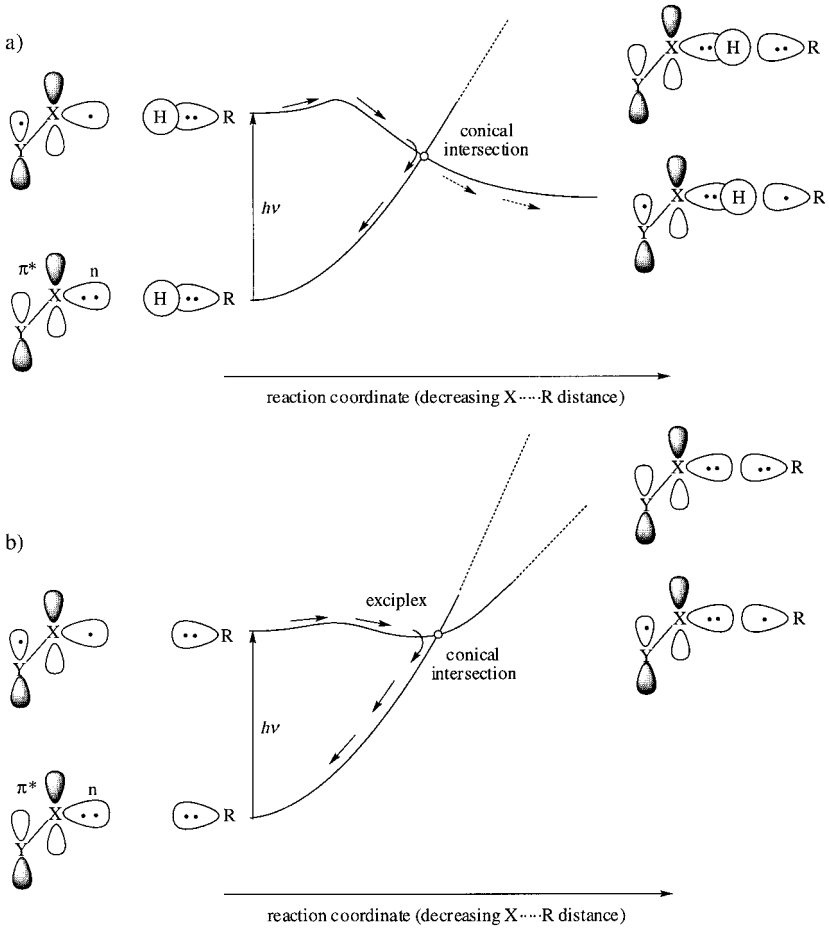

Figure 1. Modified correlation diagrams for the interaction of n,π*-excited states (X = O, N; Y = C, N) with hydrogen donors H–R (a) and electron donors R (b). The diagrams reflect the occurrence of transition states, exciplexes, and conical intersections along the reaction pathway. Dashed lines lead to strongly repulsive states.

charge transfer (CT) reaction coordinate (Figure 1b). While it is well known that quenchers can induce radiationless deactivation through reversible chemical reactions like hydrogen, proton, and electron transfer, the described quenching mechanisms are distinct since they require only a partial rather than a full hydrogen and electron transfer. This finding strongly supports the concept that common quenching mechanisms for excited states may be driven by photochemical reactions, including photoinduced electron transfer, which are interrupted ("aborted") at conical intersections located along the excited-state reaction path.

Akin to our previous study on direct hydrogen abstraction,[1] we have employed pyrazoline and 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) as computational and experimental models of the CT-induced quenching of n,π*-excited states. Most importantly, the azoalkanes allow a theoretical and experimental comparison of the singlet-state reaction, which is of primary interest in relation to the characterization of conical intersections. For the calculations, trimethylamine and dimethyl ether were chosen as prototypal quenchers with powerful and poor electron-donor abilities to rationalize the observed switch-over in quenching mechanism from CT (for amines and alkylbenzenes)[3–12] to hydrogen transfer (for ethers and alcohols).

pyrazoline DBO

We have employed ab initio CASSCF[13–16] and CASPT2[17, 18] calculations to map the minimum energy path for the approach of NMe_3 and OMe_2 to n,π* singlet-excited pyrazoline. The principal type of CT interaction (Figure 1b) involves electron donation from the quencher lone pair to the excited state nonbonding orbital of one azo nitrogen atom, which is half-vacant and thus electron deficient.[11, 12] Table 1 contains the calculated data for the two systems and Figure 2 shows the energy surfaces computed for the interaction of pyrazoline and NMe_3 or OMe_2.

The computed path starts at a long-distance point (LD) of negligible intermolecular interaction ($r \approx 3.7$ Å). Compression of the N···N bond length results in a slight (ca. 4 kJ mol^{-1}) increase in energy up to an energy maximum at $r \approx 3.3$ Å, which can be identified as a transition state (TS). Between $r \approx 3.3 - 2.1$ Å the excited state complex gains about 17 kJ mol^{-1} stabilization (ca. 8 kJ mol^{-1} including zero-point energy (ZPE) correction). This is accompanied by a significant CT (ca. 0.2 electrons, Table 1), which characterizes the resulting minimum structure at $r = 2.1$ Å as an exciplex (EX) with partial CT character. The resulting N···N bond can be regarded as a weak, polarized two-center–three-electron bond and described as a mixture of a covalent ($N{=}N^{\bullet}\cdots{:}NMe_3$) and an ionic configuration ($N{=}N^{\bullet -}\cdots{}^{+\bullet}NMe_3$).

Further progression along the reaction coordinate of Figure 2a leads to a conical intersection ($r = 2.0$ Å) and an additional increase of the CT character (Table 1). This S_1/S_0 potential energy surface crossing is located only about

Table 1. Calculated energies, dipole moments, and CT character of characteristic structures along the reaction coordinate for CT-induced quenching of n,π* singlet-excited pyrazoline.

Quencher	Structure[a]	E [Hartree][b]	ΔE	μ [kJ mol^{-1}][c]	Δq[e] [Debye][d]
NMe_3	LD (S_0)	−400.48778 (0.71)	−265.14	2.985	0.007
	LD (S_1)	−400.38670 (0.70)	≡0.00	2.684	0.006
	TS (S_1)	−400.38481 (0.70)	4.97 [5.10]	2.534	0.001
	EX (S_1)	−400.39113 (0.69)	−11.62 [−5.18]	1.840	0.226
	CI	−400.38997 (0.69)	−8.57	1.889	0.302
OMe_2	LD (S_0)	−381.16346 (0.74)	−268.11	2.573	0.001
	LD (S_1)	−381.06125 (0.73)	≡0.00	2.240	0.001
	CI	−381.00545 (0.72)	146.34[f]	2.216	0.192

[a] For the abbreviations LD, TS, EX, CI see Figure 2. [b] Calculated absolute energy at the CASPT2 level of theory. The weight of the CASSCF reference function in the first-order function is given in parentheses. [c] Calculated relative energies [LD(S_1) as reference]. ZPE-corrected values are given in square brackets. [d] Calculated (CASSCF level) dipole moments. [e] Amount of CT from the quencher to the azoalkane (CASSCF level). [f] The CASPT2 value of the lower root of the CASSCF optimized CI structure is given as an upper limit (circle at $r \approx 1.8$ Å in Figure 2b).

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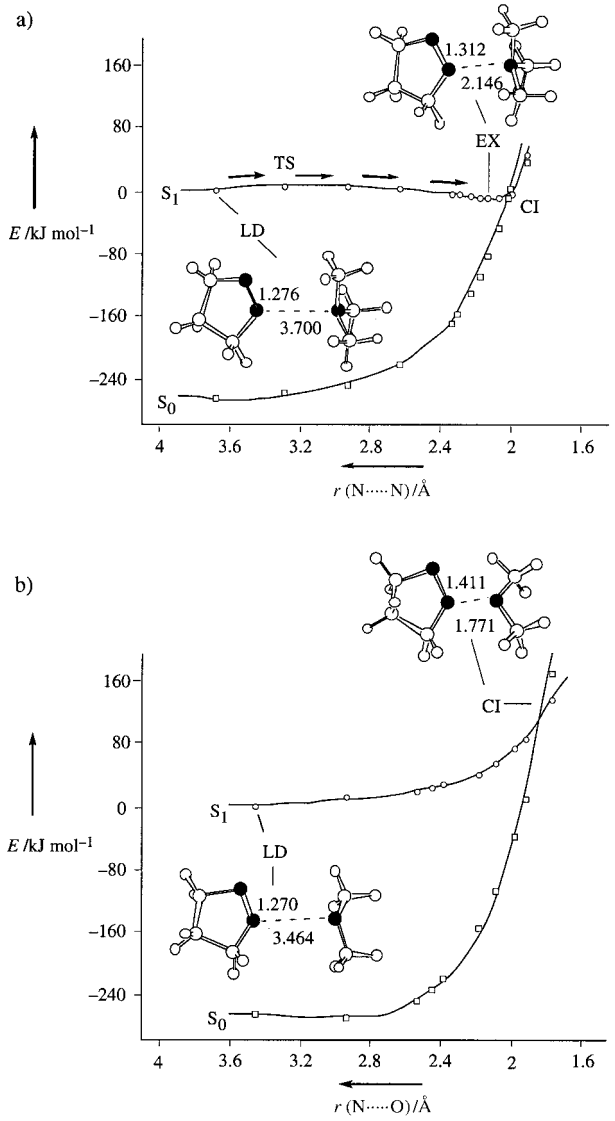

Figure 2. Energy profile (CASPT2 level) describing the quenching mechanism of pyrazoline by NMe_3 (a) and OMe_2 (b). The S_0 curve gives the ground state energy along the excited state reaction coordinate. The LD point represents a structure with a long bond length between the two involved nitrogen atoms. The reaction coordinate corresponds to a concurrent change of many geometrical parameters of the system (see ref.[13]). Only the values of the N···N bond lengths are reported for simplicity. LD = long-distance point; TS = transition state; EX = exciplex; CI = conical intersection.

3 kJ mol^{-1} above the exciplex and lies below the initial LD structure. The steep rise of the ground state energy surface towards the CI is due to a destabilizing four-electron two-orbital interaction (N=N:···:NMe_3). The strongly repulsive nature of both potential energy surfaces beyond the CI ($r <$ 1.9 Å) rapidly leads to mixing with upper excited states, thus preventing a further analysis within the framework of the correlation diagram (dashed lines in Figure 1b). While the CI exists already at the CASSCF level of theory, the LD → TS → EX → CI energy profile along the excited-state reaction coordinate in Figure 2a emerges only after inclusion of dynamic electron correlation (CASPT2 level). Expectedly, the inclusion of dynamic electron correlation is particularly important for structures with a mixed covalent CT character like exciplexes.[19]

The reaction mechanism in Figure 2a is transferable to triplet n,π*-excited states, where, however, the role of the CI is replaced by a singlet–triplet crossing.[20] A calculation of the triplet reaction for pyrazoline/NMe_3 confirms the existence of a singlet–triplet crossing with a molecular structure featuring a N···N bond with $r = 2.5$ Å, which is located about 52 kJ mol^{-1} above the corresponding triplet LD structure. Such a crossing provides a channel for intersystem crossing (ISC) to the S_0 surface and the rather pronounced radiationless deactivation in several triplet reactions of ketones and azoalkanes[3–9] may proceed through this type of quenching mechanism.

CASPT2 computations on DBO/NEt_3, an experimentally accessible system, proved unpractical, but a CI structure has been located at the CASSCF level with geometrical parameters similar to the pyrazoline/NMe_3 system. Nevertheless, a comparison of the computed quenching mechanism for pyrazoline (Figure 2a) with the information from fluorescence quenching experiments of DBO was of great interest since pyrazoline has previously proven to be an excellent theoretical model for DBO.[1] The experimental results for DBO are as follows: 1) Fluorescence quenching by amines leads to efficient radiationless deactivation (> 95%).[10, 11] 2) Steric effects suggest that exciplexes are involved.[12] 3) The activation energies (this work, measured from 283–323 K) for NEt_3 are 5.4 ± 0.8 kJ mol^{-1} in *n*-hexane and 7.1 ± 0.4 kJ mol^{-1} in acetonitrile. 4) The quenching rate constants ($k_q = 10^7$–10^8 M^{-1} s^{-1}) fall far below the diffusion-controlled limit[11] and the pre-exponential factors are consequently low: $\lg[A/(\text{M}^{-1}\text{s}^{-1})] = 8.9 \pm 0.2$ for NEt_3 in both *n*-hexane and acetonitrile (this work). 5) The fluorescence quenching by amines and other electron donors exhibits an inverted solvent effect, since it is slowed down in polar solvents (e.g., $k_q = 1.4$ versus 0.44×10^8 M^{-1} s^{-1} for NEt_3 in cyclohexane and acetonitrile).[11] 6) The quenching rate constants decrease for quenchers with weaker donor properties. For di-*n*-butyl ether, which has a much higher ionization potential than triethylamine (9.51 versus 7.50 eV)[11, 21] the value of k_q drops to 6.4×10^5 M^{-1} s^{-1} in acetonitrile (this work).

In agreement with the experimental findings 1) and 2), the computed reaction mechanism predicts that the interaction of singlet-excited azoalkanes with amines leads to fast and efficient radiationless deactivation with the involvement of an intermediary exciplex. This exciplex should be very short-lived since it resides in the vicinity of the CI. The fact that most of the previously postulated[3–12] exciplexes of n,π*-excited states have remained spectroscopically elusive with very few exceptions[4] may be due to their very short lifetime. Strikingly, with respect to the kinetic findings 3) and 4), the experimental activation energies and the computed TS for exciplex formation are in excellent agreement (ca. 4–8 kJ mol^{-1}). These values match those expected for solvent viscous flow,[22] that is, the involved exciplexes are real "encounter complexes".[4–7] Accordingly, the quenching by amines can be classified as an entropically controlled reaction, which is experimentally manifested in the low absolute quenching rate constants and the low Arrhenius *A* factors.

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Unfortunately, it cannot be decided whether this entropical control is related to stringent requirements to form the exciplex or undergo surface crossing at the CI.

With respect to the unusual observation of an inverted solvent effect (5), the dipole moments of the various structures have been suggested to play a key role.[11] Regardless of the significant amount of CT along the reaction coordinate, the computed data (Table 1) reveal a rapid *decrease* in dipole moment upon progression from the initial LD state (2.684 D) to EX (1.840 D) and CI (1.889 D). Our calculations indicate that the dipole moment induced by CT (pointing from the amine to the azoalkane) is counterbalanced by the inherent molecular dipole moment (pointing from the azoalkane to the amine, that is, in the opposite direction). This computational result confirms the peculiarity of the recently observed solvent effect.[11]

The viability of quenching by amines is made possible by a CT stabilization, which renders the CI and the exciplex energetically accessible. The degree of CT stabilization should decrease with decreasing donor ability of the quencher, which is reflected in the experimental finding 6) of a significantly slower quenching by ethers. Indeed, for OMe_2 as quencher of n,π* singlet-excited pyrazoline a CI along the reaction coordinate of decreasing N ··· O bond length is also computed (Figure 2b, Table 1). However, as expected from the poor donor properties of ethers, the amount of CT is lower than in the case of the amine (Table 1) and a reduced stabilization of the CI structure results upon inclusion of the dynamic electron correlation energy (CASPT2 level).[19] This has the consequences that an LD → TS → EX → CI energy profile does not apply for the ether (Figure 2b) and that the computed crossing lies too high in energy ($> 100\ kJ\,mol^{-1}$) to be accessible within the short lifetime of an excited state. Hence, CT-induced quenching by ethers appears unlikely to compete with the hydrogen abstraction mechanism,[1] which is expected to proceed with much lower activation energy. Indeed, our experiments (this work) yield an activation energy of $18.0 \pm 0.4\ kJ\,mol^{-1}$ (for di-*n*-butyl ether in acetonitrile) and a large deuterium isotope effect ($k_q(H)/k_q(D) = 4.2$ in neat diethyl ether). These results support a switch-over in quenching mechanism from a hydrogen abstraction for ethers (Figure 1a) to a CT process for amines (Figure 1b).

In summary, the CT-induced quenching of singlet-excited azoalkanes by amines occurs according to the LD → TS → EX → CI mechanism in Figure 1b. After partial CT from the quencher to the azoalkane (ca. 20–30%) the system enters an S_1/S_0 conical intersection which provides an efficient channel for radiationless deactivation to the ground state molecules. This CI occurs in the strict vicinity of the minimum energy point along the S_1 energy surface that corresponds to an exciplex with CT character. This novel quenching mechanism can be considered as an "aborted" charge transfer. Akin to the previously reported quenching through a partial hydrogen transfer[1] the present mechanism involves a partial electron transfer.

There are two underlying general conclusions which can be drawn from the computed reaction coordinates in Figure 2. First, the principal occurrence of a conical intersection (or a singlet–triplet crossing) appears to be insensitive to the donor and its electron-donating ability (cf. amine versus ether in Figure 2). This suggests that related quenching mechanisms of n,π*-excited states need also to be considered for other electron donors like alkylbenzenes[3–8] and olefins,[23–25] for which significant radiationless deactivation has also been observed. Second, one must consider the possibility of a full electron transfer as a follow-up reaction from the exciplex.[26] Such a mechanism of electron transfer, which requires an intermediary state with close proximity and orbital overlap between the reactants, can be referred to as an "inner-sphere" electron transfer.[5] This means that photoinduced electron transfer reactions, to the degree that they proceed by an inner-sphere mechanism, are likely to encounter competitive pathways of deactivation due to close-lying conical intersections and singlet–triplet crossings.

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[13] The geometry optimizations and reaction coordinate computations have been carried out at the CASSCF level of theory using a complete active space (CAS) including eight electrons in five orbitals [CAS(8,5)]. The orbitals comprise the π and π* N=N orbitals and the two N lone-pair orbitals of the pyrazoline fragment and the N lone-pair orbital of the amine NMe_3 or the p-type lone-pair orbital of the OMe_2 ether. The standard 6-31G* basis set (double-ζ + d-type polarization function on first- and seconds-row atoms) included in Gaussian 94[14] has been used. In order to test the reliability of this basis set we have also carried out computations with the augmented 6-31 + G* basis set which includes sp-type diffuse functions on all the first-row atoms. The results showed that the change in the CASSCF energy difference between the CI and LD points (the initial and final point of the path) is less than $8\ kJ\,mol^{-1}$. The reaction coordinates have been computed according to the following procedure: 1) The CI between the excited state (S_1) and ground state (S_0) was optimized by using the methodology available in Gaussian 94. 2) An S_1 relaxation path was computed starting from the optimized CI point and using the IRD method described in refs. [15, 16]. In both cases the resulting relaxation path is barrierless and leads to the LD structure. In order to compute a more accurate energetics we reevaluated it along a selected series of reaction co-ordinate points at the multireference Møller–Plesset perturbation theory (CASPT2) level[17] using MOLCAS-4.[18]

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[26] For the specific case of singlet-excited azoalkanes, electron transfer from the exciplex cannot compete with the radiationless deactivation due to the endergonic energetics ($\Delta G_{et} = 20 - 40\ kJ\,mol^{-1}$, refs. [11, 12]). Similarly, hydrogen transfer within the exciplex, which has been postulated for other systems,[3, 7, 10] is unlikely to compete for azoalkanes as revealed by the small amount of product formation (< 5%).

From a Racemate to a Pure Enantiomer by Laser Pulses: Quantum Model Simulations for H_2POSH**

Yuichi Fujimura, Leticia González, Kunihito Hoki, Dominik Kröner, Jörn Manz,* and Yukiyoshi Ohtsuki

Laser pulse control of chemical reactions is a hot topic in femtosecond chemistry.[1] After the theoretical design of various scenarios for laser pulse control,[2–7] experimental verifications have been demonstrated, initially for small molecules[8–10] but recently also for larger ones, for example selective laser pulse separation of different ligands from organometallic molecules.[11] A particular challenge in this field is the design of laser pulses for the selective preparation of enantiomers. The first suggestion was made by Shapiro and Brumer,[12] in which a laser pulse was used to convert a prochiral initial state of a symmetric precursor molecule ABA′ into a coherent superposition of two states with opposite symmetries, thus breaking the symmetry of the system. Subsequently, a second pulse should photodissociate the preexcited ABA′ system into selective enantiomers, either A + BA′ or AB + A′. A second scenario, presented for the model system H_2POSH assumed that the system is initially in its torsional ground state, which corresponds to a coherent 50%:50% superposition of left and right atropisomers.[13] An optimal laser pulse then drives the system to a coherent near 50%:50% superposition of the two lowest torsional states which have opposite symmetries, thus preparing a pure enantiomer. An alternative approach, introduced by Quack, suggests that it should be possible to selectively excite enantiomers, because they have slightly different energies due to interactions.[14, 15] Complementary to these proposals,[12–15] various methods have been developed for the subsequent laser pulse control of pure enantiomers, for example their stabilization[16] or the selective transformation of one enantiomer either into the opposite one[17] or into a superposition of chiral wavefunctions.[18]

Herein, we address the challenging problem of laser pulse preparation of a pure enantiomer from a racemate.[19] The corresponding initial state is an incoherent superposition of states representing enantiomers with opposite chiralities, in contrast to the previous papers[12, 13] which considered less demanding cases of pure initial states. Exemplarily, we shall simulate the laser pulse driven molecular dynamics from the racemate towards a pure enantiomer by using representative wavepackets for the torsional motion of the pre-oriented model system H_2POSH in the electronic ground state at low temperature.

H_2POSH forms a left and a right atropisomer depending on the negative or positive values of the P-O-S-H dihedral angle ϕ.[13] The corresponding double-well potential V along the torsional angle ϕ is shown in Figure 1 (adapted from reference [13]) together with the levels $E_{v\pm}$ of the torsional

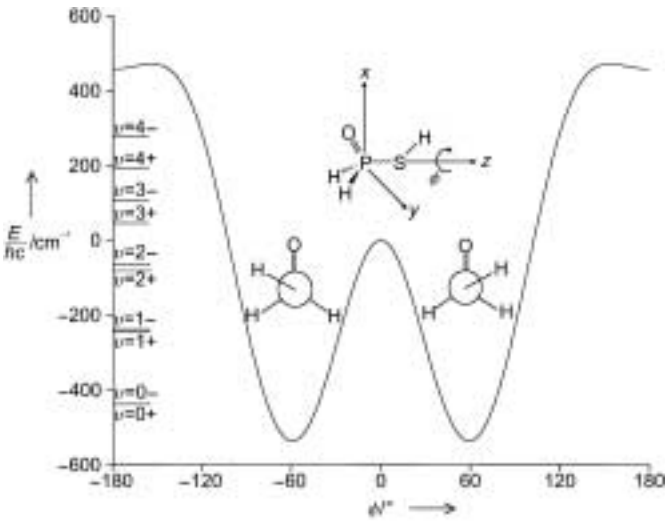

Figure 1. Double-well potential and torsional energy levels of the model H_2POSH (ab initio results adapted from ref. [13]).

[*] Prof. Dr. J. Manz, Dr. L. González, D. Kröner
Institut für Chemie, Physikalische und Theoretische Chemie
Freie Universität Berlin
Takustrasse 3, 14195 Berlin (Germany)
Fax: (+49) 30-838-54792
E-mail: manz@chemie.fu-berlin.de
Prof. Y. Fujimura, K. Hoki, Dr. Y. Ohtsuki
Department of Chemistry, Graduate School of Science
Tohoku University, Sendai 980-8578 (Japan)

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