ultrafast spectroscopy on bimolecular photoinduced electron transfer reactions

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Introduction

Since the pioneering work of Weller and coworkers,[1,2] photoinduced bimolecular electron transfer (ET) reactions have been very intensively investigated. A typical scheme for photoinduced ET in polar solvents is shown in Figure 1. After excitation of one of the reactants, diffusion is required to bring the reaction partners at distances where charge separation (CS) can occur. The nature of the primary quenching product is still debated.[3] For weakly exergonic CS, $\Delta G_{CS} > \sim -0.4$ eV, it is generally accepted that the product is a contact ion pair (CIP), that is, two ions at a distance enabling a substantial overlap of their molecular orbitals. Therefore, CIPs often exhibit some charge transfer (CT) fluorescence. It should be noted, that CIPs could also be generated by direct excitation in the CT band of donor-acceptor complexes. As the product of more exergonic CS does in general not exhibit CT emission, it is often believed that it is not a CIP but rather a solvent-separated ion pair (SSIP). In polar solvents, all theses ion pairs can undergo charge recombination (CR) to the neutral ground state or dissociate into solvated free ions.

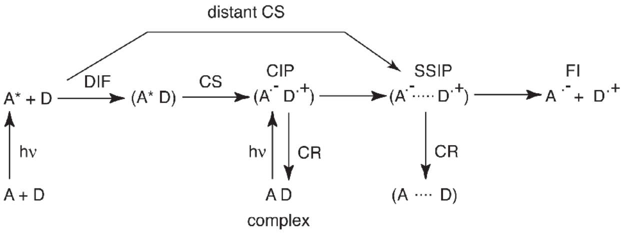


Figure 1. Reaction scheme of an intermolecular photoinduced electron transfer between an excited electron acceptor and a donor in polar solvents (the excited reactant could also be the electron donor).

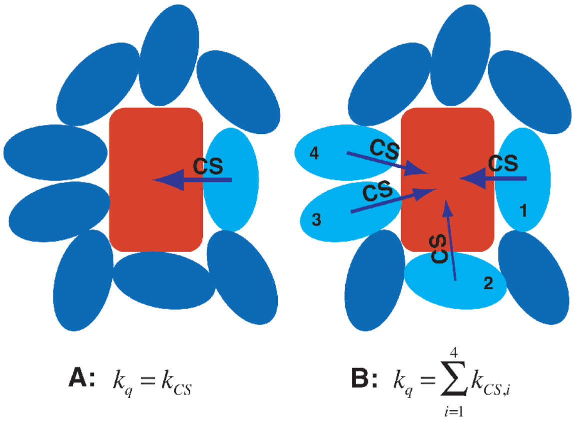
Despite an impressive number of studies, several questions still remain unanswered. Among them, one can mention:

- The inverted region predicted by ET theories,[4] that is, the decrease of the ET rate constant with increasing driving force in the high exergonicity regime, has been observed for intermolecular[5] and intramolecular CR[6], for charge shift[7] and for intramolecular CS[8] processes. There is however no convincing report of the inverted region for photoinduced intermolecular CS reactions. Why?
- As ET quenching involves both diffusion and CS, the intrinsic CS rate constant, k_{CS}, is not directly accessible when the process is diffusion controlled. This is the case as soon as $\Delta G_{CS} < -0.3$ eV even in a low viscosity solvent like acetonitrile.[1] Therefore, how large can be k_{CS} for an intermolecular process in liquids?
- What is the structure of the various intermediates involved in these ET quenching reactions?

These questions are almost as old as the field of photoinduced ET reactions. When they were first addressed, the experimental tools available to the photochemists were not as sophisticated as now. This was the beginning of laser flash photolysis, and processes occurring in time-scales shorter than several nanoseconds were not experimentally accessible.[9] Therefore, only hypotheses that could not really be verified at that time were proposed as answers to the above questions. Thanks to the impressive progress in the field of lasers and optoelectronics, we have now experimental tools that photochemists in the 1960s could not have even dreamed of. It is therefore worth to revisit this field and to see whether answers can now be proposed. In the following, we will describe some of the efforts of our group in this direction.

CS Dynamics Above the Diffusion Limit

The apparently most direct way to have access to CS dynamics above the diffusion limit is to use a quencher that also acts as the solvent. As the excited reactant is surrounded by a large number of solvent-quencher molecules, no translational diffusion is required prior to CS. This approach has been pioneered by Yoshihara and co-workers, who have reported quenching time constants of coumarins and ionic dyes in aniline derivatives as short as 60 fs.[10] As shown in Figure 2, the interpretation of the quenching rate



A: $k_q = k_{CS}$ **B:** $k_q = \sum_{i=1}^{4} k_{CS,i}$

Figure 2. Schematic representations of the possible interpretations of the excited state quenching in an electron donating solvent. The red rectangle represents the electron acceptor and the ellipses the solvent molecules.

constant, k_q, obtained in such experiments is ambiguous. If only one of the many electron donating-solvent molecules surrounding the excited reactant, typically of the order of 15-20, is able to act as a quencher, then $k_q = k_{CS}$. This has been assumed in most investigations in reacting solvents. However, if more than one solvent molecule is in a right configuration for quenching, then $k_q = \sum_i k_{CS,i}$. In this case, the intrinsic CS rate constant might be substantially smaller than the measured quenching rate constant.

In order to see whether it is possible to extract intrinsic CS rate constants with this approach, we have investigated the ET quenching of perylene (Pe) and substituted Pe, such as 3-cyanoperylene (PeCN), in several aniline derivatives.[11] The advantage of these acceptors compared to those used before, coumarins and ionic dyes, is the possibility to vary the nature of the solute-solvent interactions. Figure 3 shows time profiles of Pe and PeCN fluorescence intensity in N,N-dimethylaniline (DMA) measured by fluorescence up-conversion. The most striking feature is that the decay of PeCN S_1 population is about ten times faster than that of Pe, although the driving force for CS is about the same for both electron acceptors. These non-exponential decays, that can be reproduced with the sum of three exponential functions, have been analysed using a new simple orientational model (see Figure 4), where the donor-solvent molecules surrounding the excited acceptor are divided into three groups: donor molecules with an optimal orientation for CS, D_a, and donors for which quenching is only effective after some rotational or translational diffusion, D_b and D_c, respectively. For D_b and D_c molecules, CS is thus limited by rotational and translational diffusion, with rate constants that can be calculated or measured. As explained in more detail in reference 11, the rate constant of CS, k_{CS}, for D_a molecules and the average number of D_a, D_b and D_c molecules around an acceptor can be obtained with this orientational model. From this analysis, it appears that k_{CS} is of the order of 10^{12} s^{-1} for both Pe and PeCN in DMA, which is in agreement with the similar driving forces. However, the much faster decay time measured with PeCN is due to a larger average number of D_a molecules, 3-4 for PeCN compared to < 1 for Pe. This difference is ascribed to the occurrence of dipole-dipole interactions that are operative with the polar PeCN in anilines, but are absent with Pe. This number of D_a molecules was also found to depend on the driving force for ET quenching as well on steric interactions.

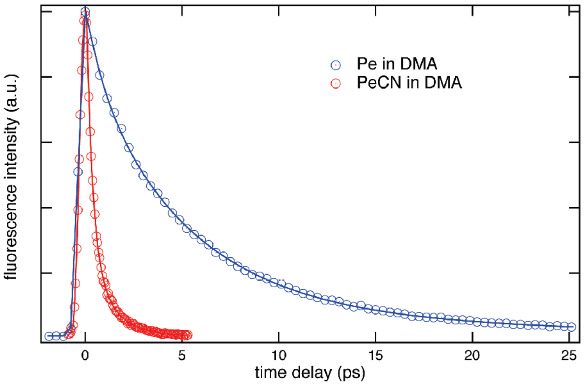


Figure 3. Time profiles of the fluorescence intensity of Pe and PeCN in DMA. The continuous line is the best fit of the orientational model.

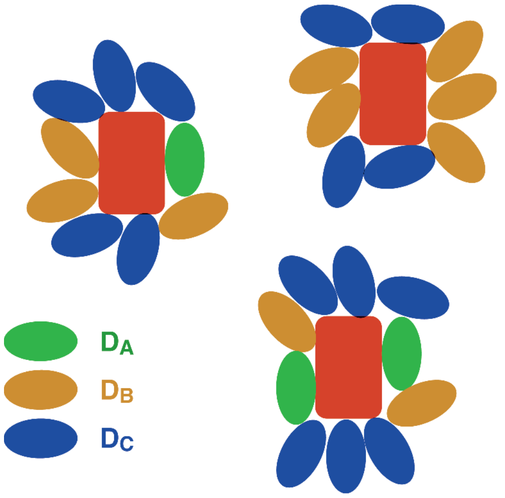


Figure 4. Schematic illustration of the orientational model with three possible solvent configurations around the excited acceptor. Each of these configurations is related to a distinct quenching rate constant. The probability of each configuration is computed and the fluorescence time profile is calculated.

From these studies, it appears that the determination of the intrinsic CS rate constant in reacting solvents is possible but more complex than previously assumed. Indeed, the identification $k_q = k_{CS}$ is only valid when the average number of D_a molecules is less than one, and, as shown in our investigations, this is obviously not always the case.

Formation of ET Product in an Electronic Excited State

As most radical ions have low lying electronic excited states (< 2 eV), excited ions can in principle be generated upon highly exergonic CS reactions as shown in Figure 5A. In this case, the quenching is no longer highly exergonic and can, according to Marcus theory, be ultrafast. This hypothesis, which was proposed many years ago to explain the absence of inverted region in intermolecular photoinduced CS processes,[1] has still been neither confirmed nor contradicted. This is due to the difficulty to spectroscopically detect excited radical ions in liquids.[12] Indeed, most radical ions do not fluoresce because of the very low radiative rate constant of the $D_1 \rightarrow D_0$ transition, and have a very short-lived (< 20-30 ps) excited state.[13] Because of these difficulties, we have considered a similar situation but for CR of ion pairs. In order to have an energy level scheme similar to that shown in Figure 5A for CR, we have investigated ion pairs formed upon CS of molecules in an S_2 state with weak quenchers.[14,15] As shown in Figure 5B, the resulting ion pairs have two CR pathways: a highly exergonic to the ground state and a weakly to moderately exergonic CR to the neutral product but with one of the partners in the S_1 state.

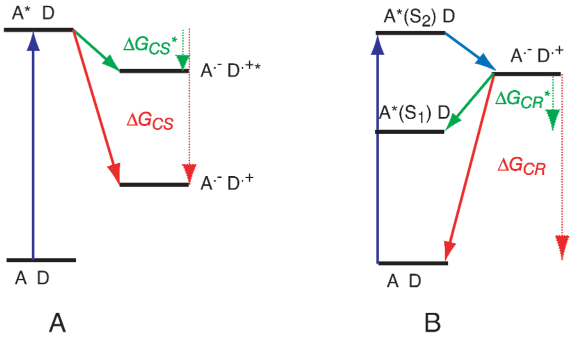


Figure 5. Energy level schemes with two competing CS (A) and CR (B) pathways.

We have first compared the systems Pe/DMA with azulene (AZ)/DMA.[14] These two systems have a very similar energy level scheme, the difference being the presence of an additional state for AZ/DMA. Although the energy gap for CR to the neutral ground state is the same for both A/D pairs, the free ion yield with Pe/DMA amounts to 67% while is it essentially zero for AZ/DMA. This difference is due to the rate constant of CR, which amounts to 2.5×10^8 s^{-1} for Pe/DMA and is larger than 2×10^{10} s^{-1} for AZ/DMA. In this case, a precise determination of k_{CR} cannot be obtained because CR is much faster than CS. The slow CR with Pe/DMA is due to the large driving force, CR occurring in the inverted regime. Similarly to AZ/DMA, a fast CR was measured with benzazulene (BA) and xanthione (XA), which have both a sufficiently long-lived S_2 state to undergo quenching.[14] Because of the very short S_1 lifetime of AZ, BA and XA, the population of the $A^*(S_1)$+D state upon CR could not be directly observed. Nevertheless, the much faster CR measured with these three systems clearly indicates that the presence of an additional state between the ion pair and the neutral ground state results in the suppression of the inverted region.

CR to the excited product could be clearly established with ion pairs formed upon CS between Zn-tetraphenylporphine (ZnTPP) in the S_2 state and weak quenchers such as acetophenone (ACP) and trimethoxybenzene (TMB).[15] Figure 6A shows the fluorescence spectrum of ZnTPP with various concentrations of TMB in acetonitrile. Addition of TMB results in a decrease of the S_2-S_0 fluorescence intensity but does not affect the yield of the S_1-S_0 emission. As indicated in Figure 6B, this is a simple and direct evidence of ion pair CR to the excited neutral product. Addition of TMB leads to a shortening of the S_2 lifetime as illustrated in Figure 7A, and ultrafast CR of the ion pair results in the population of the fluorescing S_1 state of ZnTPP (Figure 7B),

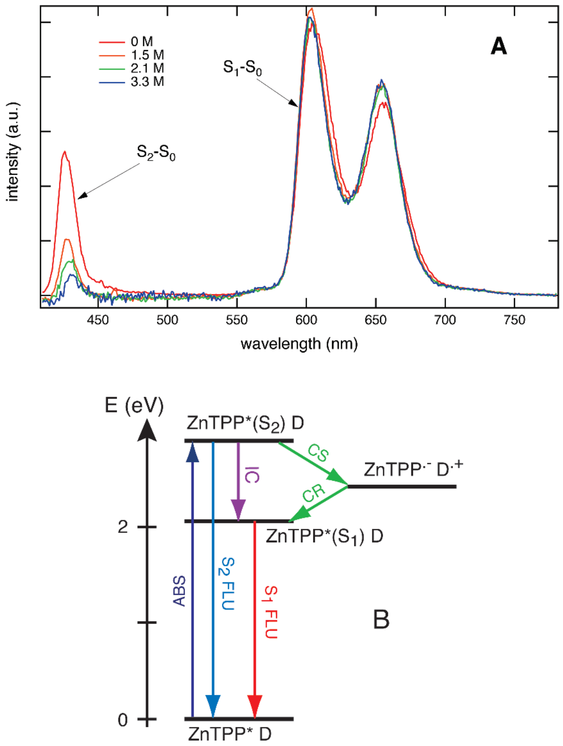


Figure 6. A) Fluorescence spectra of ZnTPP with various concentration of TMB in acetonitrile. **B)** Energy level scheme illustrating why S_2 fluorescence of ZnTPP is quenched, while the S_1 fluorescence is unaffected by the addition of D.

the CR to the neutral ground state being inoperative. The analysis of the fluorescence time profiles indicates that CR to the excited state occurs with a time scale of the order of 500 fs.

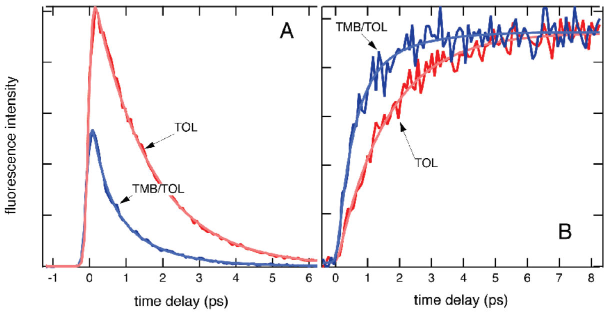


Figure 7. Time profiles of the S_2 (A) and S_1 (B) fluorescence intensity measured with ZnTPP in toluene and in a 1:1 TMB/toluene mixture. The smaller initial S_2 fluorescence intensity measured in TMB/toluene is due to quenching component that is too fast to be resolved.

These experiments show that, when energetically allowed, CR to an electronic excited product can be very efficient. There is no evident reason why this should not also be the case for CS. Although there is still no proof of the occurrence of this process, some recent investigations on the quenching of Pe by the strong acceptor tetracyanoethylene indicate that CS to the excited radical ion should be operative.[16]

Structure of the Intermediates in ET Quenching Reactions

As shown in Figure 1, many different intermediates are involved in intermolecular photoinduced ET reactions. However, their structure is not only still unknown but, with the exception of the few emitting CIPs, they cannot be easily differentiated, as their electronic absorption spectra are essentially the same. The most evident way to get structural information is time-resolved vibrational spectroscopy. Time-resolved resonance Raman experiments on the ET quenching of molecules in the triplet excited state have indeed shown that it is possible, in some cases, to observe the dissociation of an ion pair into free ions.[17] However, such experiments with singlet precursors are difficult because of the presence of fluorescence that may hide the Raman signal. Moreover, the high frequency vibrational modes of the ions are apparently only weakly affected upon pairing.

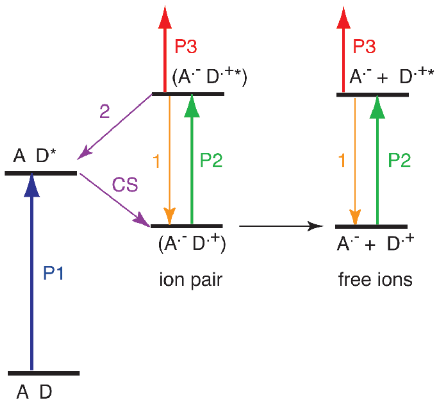


Figure 8. Energy level scheme for the pump-pump-probe experiments on photoinduced intermolecular ET processes.

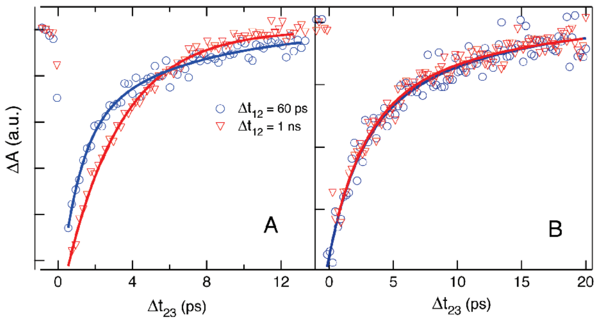


Figure 9. GSR dynamics of $Pe^{\cdot +}$ measured at different time delays after excitation of Pe in the presence of DCB (A) and FN (B) in acetonitrile.

Our recent experimental approach to this problem is pump-pump-probe spectroscopy. The principle is depicted in Figure 8. A first pump pulse, *P1*, triggers a photoinduced electron transfer reaction. After a variable time delay, Δt_{12}, a conventional pump-probe experiment is performed on the photoproduct with pulses *P2* and *P3*. For example, if *P2* and *P3* are at the same wavelength, the ground state recovery (GSR) dynamics of the photoproduct can be measured. Figure 9 shows the GSR dynamics of the perylene cation, $Pe^{\cdot +}$, at two different time delays, Δt_{12}, after the excitation of Pe in the presence of an electron acceptor, 1,4-dicyanobenzene (DCB) and fumaronitrile (FN).[18] In the case of DCB/Pe, the GSR dynamics is monoexponential at Δt_{12}= 1 ns, while it is biexponential at Δt_{12}=60 ps. On the other hand, the GSR dynamics with Pe quenched by FN is independent on Δt_{12}. The biexponential nature of the GSR dynamics implies the existence of two deactivation channels of the excited ion, $\mathrm{Pe}^{\cdot+*}$: the internal conversion from D_5 to D_0 (path 1) and a second one which might involve a CR to the $\mathrm{A}\cdot\mathrm{Pe}^{*}(S_1)$ state followed by CS to the $\mathrm{A}^{\cdot-}\cdot\mathrm{Pe}^{\cdot+}(D_0)$ state (path 2). As the free ion yield with the DCB/Pe pair is large (27%), we ascribe the Δt_{12} dependence of the GSR dynamics to a transition from $\mathrm{Pe}^{\cdot+}$ paired with $\mathrm{DCB}^{\cdot-}$ to free or "quasi-free" $\mathrm{Pe}^{\cdot+}$. In the latter case, the deactivation pathway 2 of $\mathrm{Pe}^{\cdot+*}$ is no longer operative because of the large inter-ionic distance and therefore the GSR dynamics of $\mathrm{Pe}^{\cdot+}$ is monoexponential.

With FN/Pe, the second deactivation channel is still open at Δt_{12}= 1 ns. With this system, the free ion yield is very small (~ 2%). Moreover, time-resolved fluorescence measurements indicate that, with the acceptor concentration used, the quenching of $\mathrm{Pe}^{*}(S_1)$ by FN is still not finished at Δt_{12}= 1 ns. Consequently, the $\mathrm{Pe}^{\cdot+}$ population probed at Δt_{12}= 1 ns should mostly consist in "fresh" ion pairs.

The occurrence of pathway 2 is presently being studied by performing three-color pump-pump-probe measurements. If this deactivation channel is indeed efficient, we will have a powerful tool to investigate the interconversion of ion pairs and maybe even to estimate the interionic distance.

Such pump-pump-probe experiments are not limited to the measurements of population dynamics. We plan to perform impulsive stimulated Raman and photon-echo measurements on the ET quenching products in the near future.

Conclusion

We hope to have convinced the reader that there is still a lot of interesting work to be done before a deep understanding of intermolecular photoinduced electron transfer reaction in solution is reached. Understanding these "simple" prototypic processes is important for chemistry, where most reactions are bimolecular and take place in liquids.

Acknowledgment

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References

1. Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, 8, 259.
2. Leonhart, H.; Weller, A. *Z. Phys. Chem. N. F.* **1961**, 277; Weller, A. *Pure & Appl. Chem.* **1982**, *54*, 1885.
3. Muller, P.-A.; Högemann, C.; Allonas, X.; Jacques, P.; Vauthey, E. *Chem. Phys. Lett.* **2000**, *326*, 321; Vauthey, E. *J. Phys. Chem. A* **2001**, *105*, 340; Gould, I. R.; Farid, S. *Acc. Chem. Res.* **1996**, *29*, 522; Mataga, N.; Miyasaka, H. *Adv. Chem. Phys.* **1999**, *107*, 431; Zhong, C.; Zhou, J.; Braun, C. L. *J. Phys. Chem. A* **2004**, *108*, 6842.
4. Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.
5. Vauthey, E.; Suppan, P.; Haselbach, E. *Helv. Chim. Acta* **1988**, *71*, 93; Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794.
6. Wasielewski, M. R.; Niemczyk, N. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080; Beddard, G. S.; Irvine, M. P.; Harrison, R. J.; Sanders, J. K. M. *Chem. Phys.* **1986**, *104*, 315.
7. Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440; Guldi, D. M.; Asmus, K. D. *J. Am. Chem. Soc.* **1997**, *119*, 5744.
8. Mataga, N.; Chosrowjan, H.; Shibata, Y.; Yoshida, N.; Osuka, A.; Kikuzawa, T.; Okada, T. *J. Am. Chem. Soc.* **2001**, *123*, 12422.
9. Porter, G. *Chemistry in Microtime*; Imperial College Press: London, 1997.
10. Rubstov, I. V.; Shirota, H.; Yoshihara, K. *J. Phys. Chem. A* **1999**, *103*, 1801; Yoshihara, K. In *Electron Transfer: From Isolated Molecules to Biomolecules*; Jortner, J., Bixon, M., Eds.; John Wiley: New York, 1999; Vol. 107, pp 371.
11. Morandeira, A.; Fürstenberg, A.; Gumy, J.-C.; Vauthey, E. *J. Phys. Chem. A* **2003**, *107*, 5375; Morandeira, A.; Fürstenberg, A.; Vauthey, E. *J. Phys. Chem. A* **2004**, *108*, 8190.
12. Breslin, D. T.; Fox, M. A. *J. Phys. Chem.* **1994**, 98, 408.
13. Gumy, J.-C.; Vauthey, E. *J. Phys. Chem. A* **1997**, *101*, 8575; Brodard, P.; Sarbach, A.; Gumy, J.-C.; Bally, T.; Vauthey, E. *J. Phys. Chem. A* **2001,** *105*, 6594.
14. Muller, P.-A.; Vauthey, E. *J. Phys. Chem. A* **2001**, *105*, 5994.
15. Morandeira, A.; Engeli, L.; Vauthey, E. *J. Phys. Chem. A* **2002**, *106*, 4833.
16. Pagès, S.; Lang, B.; Vauthey, E. *J. Phys. Chem. A* **2004**, *108*, 549; Gladkikh, V.; Burshtein, A. I.; Angulo, G.; Pagès, S.; Lang, B.; Vauthey, E. *J. Phys. Chem. A* **2004**, *108*, 6667.
17. Vauthey, E.; Phillips, D.; Parker, A. W. *J. Phys. Chem.* **1992**, 96, 7356; Vauthey, E.; Parker, A. W.; Phillips, D.; Nohova, B. *J. Am. Chem. Soc.* **1994**, *116*, 9182.
18. Pagès, S.; Lang, B.; Vauthey, E. In *Femtochemistry and Femtobiology: Ultrafast Events in Molecular Science*; Hynes, J. T., Martin, M., Eds.; Elsevier Science Publishers: Amsterdam, 2004; pp 319.

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Lily of the Valley
by Roald Hoffmann

Seek shelter, said the man.
But where will I find her?
You jump to conclusions, kid—

that she's a woman, for one.
It might just be the way a leaf
curls, plumb weighed down

by porcelaneous bells,
odoriferous bells, the ... Yes,
I butted in ... Convallaria majalis.

But you see, I went on—
it was dark in that house
and I was whirling with a wraith,

helter-skelter, beds, toys
and lamps to bump in—then
she threw me off spinning,

and stood there, arms akimbo—
Have you danced with her?
He said—don't ask; I told you

seek shelter. Bizarre, I said,
so I should build a hut, when
I can't drive a nail straight,

crosscut? I'll help you, he said.
So we walked into the valley
found a porch of an abandoned house

and sat there a spell. I saw a wasp
dragging a larva bigger than itself.
In the yellowing light of afternoon

we raised up walls, even tacked up
a dusty photograph of a couple
holding hands. Before I knew it

the sun had set, I was alone, and
through the loosely thatched roof
I could see the Pleiades.