

## Hot recombination of photogenerated ion pairs

Vladislav Gladkikh and Anatoly I. Burshtein<sup>a)</sup>  
Weizmann Institute of Science, Rehovot 76100, Israel

Serguei V. Feskov and Anatoly I. Ivanov<sup>b)</sup>  
Department of Physics, Volgograd State University, University Avenue 100, Volgograd 400062, Russia

Eric Vauthey<sup>c)</sup>  
Department of Physical Chemistry, University of Geneva, 1211 Geneva, Switzerland

(Received 7 July 2005; accepted 27 October 2005; published online 30 December 2005)

The recombination dynamics of ion pairs generated upon electron transfer quenching of perylene in the first singlet excited state by tetracyanoethylene in acetonitrile is quantitatively described by the extended unified theory of photoionization/recombination. The extension incorporates the hot recombination of the ion pair passing through the level-crossing point during its diffusive motion along the reaction coordinate down to the equilibrium state. The ultrafast hot recombination vastly reduces the yield of equilibrated ion pairs subjected to subsequent thermal charge recombination and separation into free ions. The relatively successful fit of the theory to the experimentally measured kinetics of ion accumulation/recombination and free ion yield represents a firm justification of hot recombination of about 90% of primary generated ion pairs. © 2005 American Institute of Physics. [DOI: 10.1063/1.2140279]

### I. INTRODUCTION

Most theories of electron transfer reactions in condensed media, reviewed in Refs. 1,2, incorporate as input data the thermal transfer rates between reactants separated by a distance  $r$ . These rates are controlled either by the tunneling near the intersection point of reactant and product levels or the system delivery to this point from the equilibrium position. It is usually assumed that the system motion along the reaction coordinate  $q$  proceeds faster than the modulation of the interparticle distance  $r$  by encounter diffusion and that the transfer always starts from the equilibrium position in the reactant well. If one of these conditions is violated, the encounter theory has to account for the occurrence of the process along  $\mathbf{r}$  and  $q$  simultaneously. This has been done once for a diffusion-controlled thermal ionization competing with the diffusion along the reaction coordinate.<sup>3</sup> In the present work, we consider the geminate recombination of ion pairs produced by bimolecular photoinduced electron transfer (ionization). The backward electron transfer proceeding before thermalization, known as “hot recombination,” does not need any thermal activation and is therefore more efficient and much faster than the subsequent thermal recombination that conventional theories are confined to.

The chemical system investigated here consists of perylene (Pe) in the first singlet excited state as electron donor in the presence of tetracyanoethylene (TCNE) in acetonitrile. The fluorescence quenching dynamics of Pe after excitation by an ultrashort optical pulse was recently studied both experimentally and theoretically.<sup>4</sup> It was concluded that

the electron transfer quenching results to both the ground and the excited state of the ion pair with the rates  $W$  and  $W^*$ , respectively,



Using the abbreviations,  $D$  for Pe and  $A$  for TCNE, we consider a four-level energy scheme (Fig. 1) including vibrational sublevels ( $n=0, 1, 2, \dots$ ) of the  $DA$  and  $D^+A^-$  states. According to this scheme, both the excited and the ground channels of ionization-recombination include hot transitions. These two ionization channels are depicted separately in Fig. 2. It is useful to introduce the probabilities  $\alpha$  and  $\alpha^*$  to produce equilibrated ion pairs through the ground and the excited channels, respectively. These pairs recombine thermally to the neutral ground state.

The overall reaction scheme includes the recombination of charged products assisted by vibrational and solvent relaxation. After the forward electron transfer generating the ion pair in the ground state, the population moves down diffusively and crosses a number of vibronic sublevels of neutral products before reaching the equilibrium. A fraction  $1-\alpha$  of the ion-pair population recombines during this stage, i.e., prior to thermalization, which is approximately equal to the time scale of the longitudinal solvent relaxation  $\tau_L$ . The remaining fraction of the ion-pair population ( $\alpha$ ) reaches equilibrium and recombines thermally with a rate  $W_R$  [see Figs. 1 and 2]. The fate of the excited ion-pair population is more complex [see Fig. 2]. These ion pairs are born near contact,<sup>4</sup> at a distance where electron transfer (either forward or backward) is essentially limited by the solvent relaxation ( $1/\tau_L$ ). These ion pairs undergo charge recombination to one of the vibrational states of the neutral products (dotted levels in Fig. 1) with approximately this rate. This is followed by the

<sup>a)</sup>Electronic mail: cfbursh@wisemail.weizmann.ac.il

<sup>b)</sup>Electronic mail: physic@vlink.ru

<sup>c)</sup>Electronic mail: eric.vauthey@chiph.unige.ch