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Tuning the ion formation processes from triplet–triplet annihilation to triplet-mediated photoionization

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Abstract

Free ion formation in acetonitrile is examined through transient photoconductivity for a set of ketones excited at different wavelengths. According to the photophysical parameters of the ketones and the incident photon energy, two mechanisms can be operative: triplet–triplet annihilation (bimolecular process) and/or photoionization (monomolecular biphotonic process). By using a tunable laser, excited state mediated photoionization was studied. From the threshold energy (E_{thr}) required for this process to occur, ionization potentials in solution (I_{S}) were deduced and compared to the corresponding values in gas phase (I_{G}). A simple energetic model enables the determination of the oxidation potential (E_{ox}) of the ketones that are compared to the corresponding values obtained through electrochemical measurements.

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1. Introduction

Light absorption by a molecule in solution can lead to the formation of charged species. This photoionization process (PI) constitutes a primary step of importance in molecular photophysics and was extensively studied during the three past decades. PI corresponds to a relaxation pathway of the excited state of the solute molecule and therefore affects its fluorescence, intersystem crossing, and internal conversion characteristics. Moreover, PI is a multifacet phenomena, since its occurrence depends on numerous factors such as singlet and triplet state energies, excitation light energy and intensity, and the polarity of the medium [1–8]. In solution, photoionization occurs mainly because the photoionization energy (I_{S}) of a solute is substantially lower than in the gas phase (I_{G}) due to polarization stabilization of the cation and electron pair in the solvent, this stabilization depending dramatically on the overall polarity of the solvent. In acetonitrile (CH_3CN), formation of ions following excitation has been already reported for a variety of aromatic molecules [9–11].

In a recent paper, it was shown that nanosecond laser flash photolysis of benzophenone in CH_3CN

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results in the production of ions [12]. Free ions were evidenced by photoconductivity experiments. Interestingly, two different ionization mechanisms occur depending on the incident photon energy. Upon excitation at 355 nm (3.5 eV), the photocurrent rise times were observed on the microsecond time scale. The dependence of the photocurrent time profiles on the ground state concentration, laser pulse intensity, oxygen concentration, energetic considerations, indicated that the process of ion generation was a triplet–triplet annihilation (TTA) according to Scheme 1.

At higher photon energy (266 nm, 4.7 eV), an excited state mediated two-photon ionization occurred. This monomolecular biphotonic process results in photocurrent rise times within the laser pulsed (Scheme 2).

This change has been explained by the energy requirements of the two processes and the dipole-induced dipole solvation interaction has been shown to play the determinant role in the direct photoionization (Scheme 2) [12].

$$\mathrm{BP} \xrightarrow{h\nu,\ \mathrm{ISC}} {}^{3}\mathrm{BP}$$

$${}^{3}\mathrm{BP} + {}^{3}\mathrm{BP} \rightarrow \mathrm{BP}^{\bullet -} + \mathrm{BP}^{\bullet +}$$

Scheme 1.

$$\mathrm{BP} + 2h\nu \rightarrow \mathrm{BP}^{\bullet +} + e^{-}_{\mathrm{solv}}$$

Scheme 2.

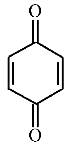
In this Letter, we first substantiate our proposed explanation by studying the time profiles of the photoconductivity signals for a series of aromatic ketones excited at two commonly used wavelengths: 355 and 266 nm. Second, the switching from a TTA to photoionization by using a tunable laser as an excitation source leads to the definition of a threshold excitation wavelength (λ_{thr}) corresponding to a threshold energy (E_{thr}) above which PI becomes operative. An experimental ionization potential in solution (I_{S}) can be then inferred from λ_{thr}.

2. Experimental

The nine aromatic ketones investigated are shown below.

All the experiments were performed in acetonitrile (Fluka, spectroscopic grade), with absorptivities adjusted to work at a constant absorbed energy.

Photocurrents were measured with a Q-switched Nd:YAG laser (JK Lasers 2000) producing 355 or 266 nm pulses of 19 ns duration. The photoconductivity cell was recently described in details [12,13]. For wavelength tuning experiments,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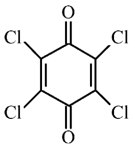
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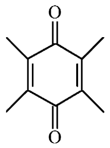
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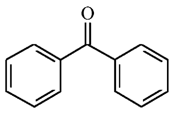
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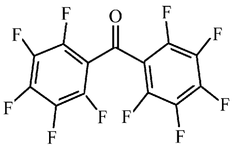
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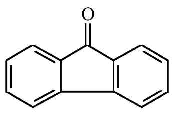
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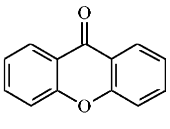
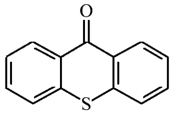
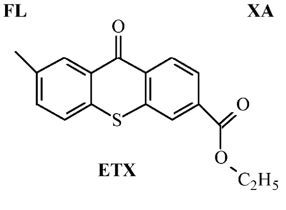

XA


TX


ETX

the excitation source was an optical parametric oscillator (OPO, Sunlite, Continuum) pumped with a Nd:YAG laser (Powerlite 9010, Continuum). The wavelength could be tuned from 450 to 1800 nm with an energy about 50 mJ/pulse at 550 nm. The frequency doubling system (FX1, Continuum) pumped by the OPO output is able to deliver 5 ns pulses from 225 to 450 nm with an average energy about 8 mJ. For the experiments, the energy was reduced down to 1 mJ/pulse.

Oxidation potentials of some ketones (BP, XA, TX, ETX, FL) were measured in acetonitrile by cyclic voltametry with 0.1 M of tetrabutylammonium hexafluorophosphate as supporting electrolyte and at scan rate 1 V/s (EG&G 173A potentiostat). The working electrode was a carbon disk with a diameter of 3 mm. The reference was a saturated calomel electrode in methanol. Ferrocene was added to all the solutions as an internal standard. Redox potentials were estimated from half peak potentials of the corresponding irreversible wave.

3. Results

3.1. 355 nm excitation

For each ketone, a photocurrent signal visible on the microsecond time scale was observed as reported for benzophenone in Fig. 1a. Comparison with the reference system BP/DABCO 20 mM (Fig. 1c) for which free ions are well known to be formed on the nanosecond time scale shows undoubtedly a much longer rise time. All the ketones studied exhibit the same behavior as reported for BP [12]: (i) at the same laser pulse intensity, the rise time of the photocurrent decreases with increasing the ground state concentration of the ketone ($^1K_0$), (ii) at the same ketone ground state concentration ($^1K_0$), the rise time of the photocurrent decreases with increasing laser intensity. In both cases, the net result is an increase in the triplet state concentration ($^3K^*$) that leads to faster ions formation kinetics according to Scheme 1. Therefore, the observation of a decreasing rise time for ion formation with increasing laser intensity or ketone ground state concentration demonstrates the occurrence of triplet–triplet annihilation.

3.2. 266 nm excitation

At higher excitation energy, the ketones can be sorted in two classes: (i) BQ, CA, DQ, and DF exhibit the same behavior as under 355 nm excitation, (ii) BP, XA, TX, ETX, and FL exhibit a photocurrent signal growing up faster than the time resolution of the experimental setup (Fig. 1c). Moreover, in the latter case the rise time does not depend on the laser intensity. This fact indicates

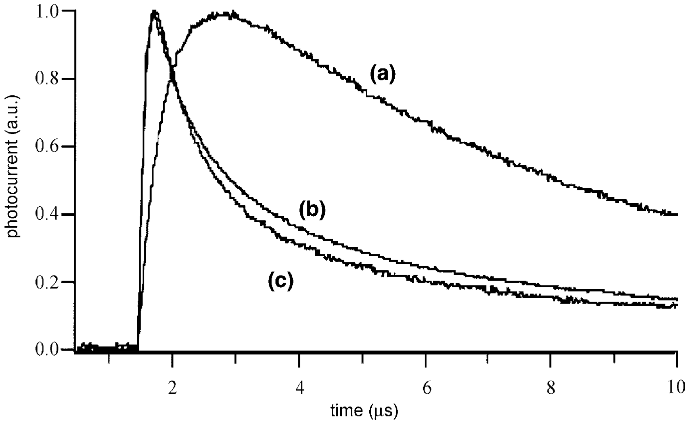


Fig. 1. Time profiles of the photoconductivity signal illustrating the two different ionization mechanisms of benzophenone in acetonitrile depending on the wavelength excitation. (a) Triplet–triplet annihilation at 355 nm, (b) photoionization at 266 nm. Curve (c) refers to the reference system benzophenone/DABCO 20 mM.

that the formation of ions is no longer due to T–T annihilation mechanism, but rather to a biphotonic photoionization as discussed in detail in [12] (Scheme 2). Although no attempt was made for determining the true quantum yield of both processes, it can be ascertained that for the TTA annihilation the quantum yield is only about 2%, whereas it is higher than 10% for direct photoionization under our experimental conditions. Table 1 summarizes the results obtained at both excitation wavelengths.

3.3. Threshold excitation wavelength λ_{thr}

Increasing the excitation energy favors excited state mediated photoionization. Indeed, a continuous shift from TTA to PI signals was observed as the excitation wavelength decreased, as exemplified in Fig. 2a in the case of XA. In order to characterize this switchover, it is convenient to define, according to the following procedure, a wavelength λ_{thr} below which the PI occurs. The contribution of the photoionization process was derived from the relative amplitude of the signal component with a rise time smaller than 50 ns. The onset of the sigmoïd curve obtained by plotting this relative amplitude as a function of the excitation wavelength leads to E_{thr} (Fig. 2b). Note that this procedure can be compared to the definition of the adiabatic ionization potential as the onset of the photoionization spectrum.

Since intersystem crossing in aromatic ketones is usually very fast, excited singlet states should not play a significant role in the ionization process (except for FL, vide infra). Therefore, starting from the lowest triplet state energy (E_{T}), the second photon must be sufficiently energetic (E_{thr}) to reach the energy level that corresponds to the ionization potential in solution (I_{S}), as illustrated in Fig. 3. Then I_{S} can be expressed as follows:

$$I_{\mathrm{S}} = E_{\mathrm{T}} + E_{\mathrm{thr}}. \qquad (1)$$

The pertaining data for the ketones investigated here are gathered in Table 2. As the molecules studied present nearly the same molecular volumes, no attempt was made for a precise correlation between $\Delta I = I_{\mathrm{G}} - I_{\mathrm{S}}$ and the molecular radius, as often done. However, it can be noted that on average ΔI amounts to 1.5 eV and that the lowest ΔI was obtained for the largest molecule (ETX). Recent values of ΔI obtained in acetonitrile for polycyclic aromatic hydrocarbons were reported in the range $\Delta I = 1.2$ eV for benzene to $\Delta I = 0.1$ eV for perylene [14]. Interestingly, extrapolation from these data to the ketones studied here would lead to $\Delta I \sim 0.8$ eV, i.e., twice lower as those obtained from our measurements. This significant difference may be attributable to the experimental detection used in [14]: photoelectron emission spectroscopy. As time-resolved photoconductivity measured the kinetics and quantum yields of ions formation directly, we will confidently use the I_{S} values determined in this work in the following.

Although, as stated in [5], the concept of ‘liquid phase photoionization potential is necessarily ambiguous’, inspection of the literature shows that from the experimental determination of I_{S} it is possible to evaluate the oxidation potential of the ketones according to [19]

$$I_{\mathrm{S}} = E_{\mathrm{ox}} + E_{\mathrm{RE}} + V_0, \qquad (2)$$

Table 1
Nature of the observed photocurrent rises as a function of the excitation wavelength

Molecule	355 nm excitation	Mechanism	266 nm excitation	Mechanism
BQ	Slow rise	TTA	Slow rise	TTA
CA	Slow rise	TTA	Slow rise	TTA
DQ	Slow rise	TTA	Slow rise	TTA
DF	Slow rise	TTA	Slow rise	TTA
BP	Slow rise	TTA	Fast rise	PI
FL	Slow rise	TTA	Fast rise	PI
XA	Slow rise	TTA	Fast rise	PI
TX	Slow rise	TTA	Fast rise	PI
ETX	Slow rise	TTA	Fast rise	PI

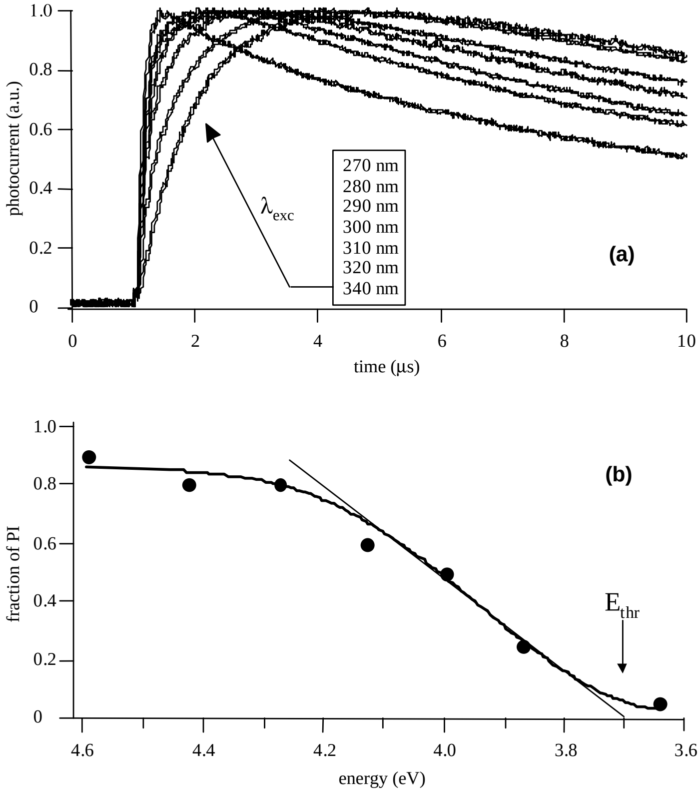


Fig. 2. (a) Switch (TTA → PI) of the ion generating mechanism for XA with the decrease of the excitation wavelength λ_{exc} and (b) definition of the threshold excitation energy (E_{thr}) for which PI appears.

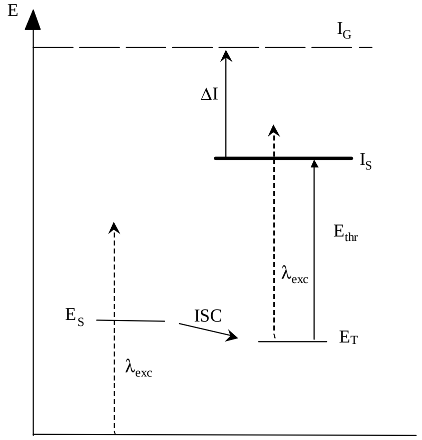


Fig. 3. Energy diagram for two-photon ionization.

where $E_{RE} = 4.71$ eV is the potential of the standard reference calomel electrode [19,20] and V_0 stands for the minimum energy of a 'quasi-free' electron in solvent relative to an electron in vacuum [19]. V_0 in acetonitrile was given as −0.14 eV [21].

Contrary to reduction potentials, data concerning oxidation potentials of ketones are rather scarce in the literature. To the best of our knowledge no reliable E_{ox} value for the five ketones investigated was available. This lack of data prompted us to perform electrochemical measurements, the results are reported in Table 2. A look at them reveals a quite satisfactory agreement between values deduced from Eq. (2) and direct electrochemical measurements, demonstrating that photoconductivity can be helpful when electrochemistry fails to work.

Fig. 4 shows that I_S and I_G are linearly correlated, a fact that gives confidence to the determination of I_S through Eq. (1). This helps to interpret the behavior of fluorenone. The value obtained

Table 2
Photophysical parameters, photoionization, and oxidation potentials derived from the experiments

	τ_s [a] (ns)	E_T (eV)	E_{thr} (eV)	I_G (eV)	I_S [b] (eV)	E_{ox}^{calc} [c] (V/SCE)	E_{ox}^{exp} [d] (V/SCE)
BP	0.016 [15]	3.00 [15]	4.3	9.05 [16]	7.30	2.73	2.65
XA	0.008 [15]	3.22 [15]	3.7	8.42 [16]	6.92	2.35	2.62
TX	0.07 [17]	2.76 [18]	3.65	7.85 [e]	6.41	1.84	1.75
ETX	1.25 [17]	2.55 [18]	3.8	7.70 [e]	6.35	1.78	1.76
FL [f]	21.5 [15]	2.20 [15]	3.8	8.36 [e]	6.56 [f]	1.99	2.11

[a] Singlet state lifetime in polar solvent or acetonitrile.
[b] According to Eq. (1).
[c] According to Eq. (2).
[d] This work.
[e] Measured in Fribourg.
[f] Photoionization occurs from S_1 ($E_S = 2.76$ eV).

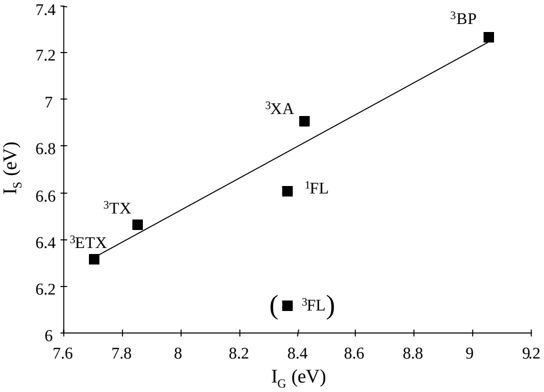


Fig. 4. Linear correlation between the gas phase ionization potentials I_G and the ionization potentials in acetonitrile I_S evaluated by Eq. (1).

from Eq. (1) would be $I_S = 6.0$ eV using the triplet state as starting excited state, and this value would be quite far away from the correlation. However, the fluorenone excited singlet state has a relatively long lifetime (21.5 ns) and since the laser pulse is significantly shorter (~5 ns), photoionization from the excited singlet state is favored. Correcting the I_S value by using $E_S = 2.76$ eV leads to $I_S = 6.56$ eV, a result that satisfies quite well the I_S vs. I_G correlation.

4. Conclusion

Light excitation of nine ketones in acetonitrile at 355 nm results in free ions formed by TTA as evidenced by transient photoconductivity. However, for some ketones, excitation at 266 nm can also lead to direct PI. The use of a tunable laser which facilitates the scanning of the excitation wavelength, allows (a) monitoring of the switch from TTA to PI and (b) direct evaluation of the ionization potentials I_S of the ketones in solution. Interestingly, the resulting E_{ox} values are in quite good agreement with those obtained through electrochemical measurement.

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