Chemical Physics Letters 661 (2016) 206–209

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

On the ultrashort lifetime of electronically excited thiophenol

Virginia Ovejas [a], Marta Fernández-Fernández [a], Raúl Montero [b,*], Asier Longarte [a]

[a] Departamento de Química Física, Universidad del País Vasco (UPV/EHU), Apart. 644, 48080 Bilbao, Spain
[b] SGIker Laser Facility, Universidad del País Vasco (UPV/EHU), Leioa, Spain

ARTICLE INFO

Article history:
Received 11 July 2016
In final form 31 August 2016
Available online 1 September 2016

ABSTRACT

The relaxation dynamics of thiophenol, excited from the onset of the S_1 ($1^1\pi\pi^*$) state absorption, to the more intense S_3 ($2^1\pi\pi^*$) state band (290–244 nm), has been studied by time resolved ion yield spectroscopy. Along the studied energy range, the reached excited states relax in less 100 fs. These results evidence that the photophysics is dominated by the non-adiabatic coupling between the initially excited S_1 and $S_3\,{}^1\pi\pi^*$ states, and the dissociative character ${}^1\pi\sigma^*$ state. Contrarily to phenol, the $1^1\pi\pi^*/{}^1\pi\sigma^*$ crossing is reached from the origin of the $1^1\pi\pi^*$ state absorption, through a nearly barrierless pathway.

1. Introduction

Due to their role as chromophore in many natural compounds, the photophysics and photochemistry of aromatic phenols and thiols have intrigued physical chemists since long ago. As a consequence, the extensive knowledge gained during this time on the relaxation of these molecules after photoexcitation, has directly contributed to understand fundamental phenomena related to non-adiabatic couplings as internal conversion (IC), tunneling or hydrogen transfer, among others [1–23], while at the same time, has opened the door to the study of more complex systems as aminoacids, peptides, DNA bases, etc. [24–29]. A decisive piece to build the actual picture of the photochemistry of phenols in particular, and aromatic molecules in general, has come from the theoretical and experimental characterization of dark ${}^1\pi\sigma^*$ type excitations (see Refs. [7,8] for recent reviews). In the case of phenol, the relevant ${}^1\pi\sigma^*$ state (we use the terms $1^1\pi\pi$, ${}^1\pi\sigma^*$, $2^1\pi\pi^*$, to label the diabatic states and potential energy surfaces (PES), and S_0, S_1, etc. for the corresponding adiabatic states and PES) results from the mixing of the O(3 s) $\leftarrow \pi$ and O—H(σ^*) $\leftarrow \pi$ transitions. The latter provides strong dissociative character as the O—H bond stretches, while at the same time, intersects the ground state forming a conical intersection (CI). Since the ${}^1\pi\sigma^*$ state of phenols exhibits a strong impact on the photophysics and photochemistry of these molecules, mediating the H atom detachment and the ground state ultrafast IC channels, the access to this state highly determines their excited states dynamics [9–23]. In general, the ${}^1\pi\sigma^*$ surfaces appears at energies higher than $1^1\pi\pi^*$ state, and exhibit a very weak oscillator strength. However, they can be accessed by non-adiabatic coupling to the bright ${}^1\pi\pi^*$ states [9,16]. In the case of phenol and substituted phenols, the lifetime of the S_1 state, and consequently, of the subsequent relaxation events, is determined by the location of the $1^1\pi\pi^*/{}^1\pi\sigma^*$ CI. At excitation energies below the crossing point the ${}^1\pi\sigma^*$ surface is reached slowly (~1 ns) by tunneling [12,15,20,23], while at wavelengths shorter than 248 nm some population can be directly promoted to the ${}^1\pi\sigma^*$ [17].

The substitution of O by S permits, while still retaining the same basic electronic structure, to modify three fundamental aspects of the problem: the $1^1\pi\pi^*(S_1)/{}^1\pi\sigma^*(S_2)$ energy gap, the topology of the ${}^1\pi\sigma^*$ state surface and the oscillator strength of the latter, which now can also be populated by direct photoexcitation. Several studies have explored the photoinduced processes that the thiophenol molecule undergoes, by detecting the kinetic energy resolved H atoms produced after excitation in the near part of its UV spectrum (290–225 nm) [30–37]. The obtained data exhibit fundamental differences with the observations made for phenol which have been convincingly explained by the modified topology of the $1^1\pi\pi^*/{}^1\pi\sigma^*$ CI predicted by theoretical calculations [38]. These experimental and computational studies have provided a detailed picture of the relaxation routes of thiophenol, however, to the best of our knowledge, no time-resolved studied of the thiophenol excited states dynamics is available up to date, being this the main motivation for the present work. We have tracked the temporal evolution of the molecule after excitation in the 290–240 nm wavelength interval, which covers the absorption of the $1^1\pi\pi^*$, the ${}^1\pi\sigma^*$ and the $2^1\pi\pi^*$ states. The collected data nicely complement the information extracted from previous works, while offers new insight on the relaxation mechanisms that thiophenol undergoes.

---

* Corresponding author at: SGIker Laser Facility, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU), Apart. 644, 48080 Bilbao, Spain.

E-mail address: raul.montero@ehu.eus (R. Montero).

http://dx.doi.org/10.1016/j.cplett.2016.08.082
0009-2614/

2. Experimental methods

Thiophenol dynamics has been tracked by time resolved multiphoton ionization using different probe wavelengths. The experimental setup is described in detail elsewhere [39]. The measurements were carried out in a time-of-flight mass spectrometer equipped with a pulsed valve (Parker Series 9) that fires at 100 Hz, an 80 cm flight tube and a dual plate MCP detector. The sample was seeded in an Ar supersonic expansion at room temperature. The laser pulses were generated in a Ti:Sapp oscillator-regenerative amplifier system (Coherent Mantis-Legend) that provides a 1 kHz train of 35 fs pulses. Two optical parametric amplifiers were used to obtain the pump pulse in the range 290–240 nm and the probe at 1360 nm. Additional experiments were carried out at the fundamental 800 nm and the second harmonic 400 nm probe wavelengths. A fused silica pulse compressor was used only for the pump pulses. The temporal overlap of the pump and probe pulses was controlled by optical delay line (APE Scandelay 150) with a resolution of 5 fs. Typically, two seconds are required to complete a single full delay scan, while samples are averaged for 45 min to obtain a transient.

The pump intensities were reduced to avoid saturation effects and contributions from higher excited states. In all the experiments the one color (pump and probe only) signal was negligible respect to the two color ionization. The probe beams intensities were estimated to be, $\sim 10^{10}$ W/cm^2 for the 400 nm and 10^{11} W/cm^2 for the 800, and 1305 nm probe wavelengths. The relative polarization was set at 54.7° to avoid rotational contributions. The instrumental response function, 50–100 fs, and the $\Delta t = 0$ reference position were determined by the simultaneous measurement of the non-resonant ionization of ethylene.

3. Results and discussion

The temporal evolution of the thiphenol$^+$ mass channel has been recorded after exciting in the 290–244 nm UV range, which in principle covers the absorption of the $1^1\pi\pi^*$, $^1\pi\sigma^*$ and $2^1\pi\pi^*$ states while probing with different ionizing probes.

Fig. 1 shows the thiophenol$^+$ 1 + 3′ decay (IP = 8.30 eV) recorded with the 290 and 800 nm pump and probe wavelengths, respectively, together with the ethilene$^+$ 1 + 5′ non-resonant ionization (IP = 10.51 eV), used for the determination of the instrumental response function. Both signals are modeled by Gaussians centered at $\Delta t = 0$, being that of the ethilene$^+$ slightly narrower due to the higher order of the ionization process. From this measurement we can conclude that at 290 nm the thiophenol S_1 state is not promoted by the pump photon, although some pump + probe resonances could be met in the ionization process [41]. The observation agrees with the action spectra for forming H^+ fragments registered by Devine et al. [33] whose onset is located at 286 nm. On the other hand, in the UV spectra in n-hexane the $1^1\pi\pi^*$ absorption seems to extend to slightly longer wavelengths, up to 295 nm, due to thermal and solvent effects [40].

Fig. 2 exhibits the thiophenol$^+$ decays registered at 281 nm with three different probe wavelengths, 1365 (1 + 5′), 800 (1 + 3′) and 400 (1 + 2′) nm. The differences in the measured lifetimes lie into the error bars, ruling out any influence of the probe wavelength in the observed dynamics. Two temporal components are required to fit the decays: a Gaussian resembling the instrumental response function (in the following τ_0 component) and a τ_1 exponential lifetime whose value varies between 50 and 59 fs depending on the probe wavelength. While τ_0 is assigned to the thiophenol$^+$ molecules that are non-resonantly ionized analogously to the 290 nm experiment, τ_1 is the lifetime of the S_1 excited state prepared by the pump pulse (see below).

Fig. 3 summarizes the thiophenol$^+$ transients recorded across the 285–244 nm excitation range. The τ_1 lifetime is noticeable from the onset of the S_1 state absorption to the shortest excitation wavelength tried at 244 nm, experiencing a modest shortening as the excitation energy increases. For the 244 nm excitation, which overlaps with the more intense band of the UV spectrum attributed to the $S_0 \rightarrow S_3$ $(2^1\pi\pi^*)$ transition, the τ_0 component is not required to obtain a good fit of the transient due to the much higher oscillator strength of this excitation (see below).

The τ_1 lifetime, which reflects the excited state dynamics, can be correlated with previous experimental and theoretical findings. It is remarkable that the prepared excited state decays with the ultrafast τ_1 lifetime even when excited at the onset of the $1^1\pi\pi^*$ state absorption. It is also well established that the $1^1\pi\pi^*$ state is reached at lower excitation energies than the dissociative character $^1\pi\sigma^*$ state [33,36,38]. Consequently, the τ_1 lifetime measured for the $1^1\pi\pi^*$, together with the formation of fast H^+ fragments

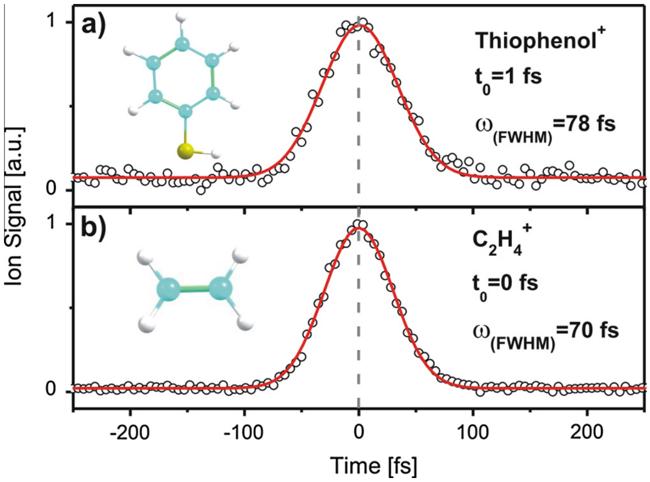

Fig. 1. Transient ionization signals recorded simultaneously at thiophenol$^+$ (a) and ethylene$^+$ (b) mass channels using 290 nm and 800 nm as pump and probe wavelengths respectively. The red line is the result of the fit with a Gaussian function centered at t_0 that reproduces the instrumental response function. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

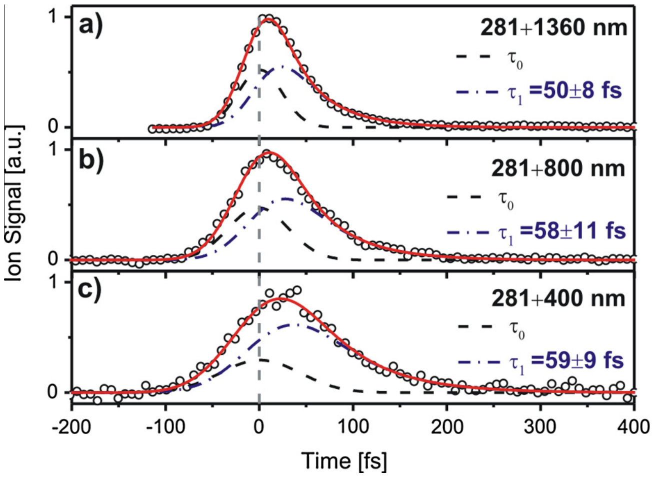

Fig. 2. Thiophenol$^+$ signals recorded at 281 nm excitation using 1360 nm (a), 800 nm (b) and 400 nm (c) as probe wavelengths. Red lines represent the result of an exponential fit with two components: a Gaussian function (τ_0 component) with t_0 and width given by the reference signal (black line) and an exponential decay τ_1 (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)