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# Electronic excited state of protonated aromatic molecules: protonated Fluorene

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## Abstract

The photo-fragmentation spectrum of protonated fluorene has been recorded in the visible spectral region, largely red shifted as compared to the first excited state absorption of neutral fluorene. The spectrum shows two different vibrational progressions, separated by 0.19 eV that are assigned to the absorption of two isomers. As in protonated linear PAHs, comparison with ab-initio calculations indicates that the red shift is due to the charge transfer character of the excited state.

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## Introduction

This paper belongs to a series of studies that are meant to characterise the optical properties of excited states of protonated aromatic molecules and particularly Polycyclic Aromatic Hydrocarbons (PAHs)<sup>1-8</sup>. We recently published the electronic spectra of linear protonated PAHs<sup>1</sup> for which the  $S_1$ - $S_0$  transitions are all in the visible region and do not show a monotonic red shift as a function of the molecular size, in contrast to their neutral analogues. Comparison with ab-initio calculations indicates that this behaviour is due to the charge transfer character of the excited states especially for PAH with even number of aromatic rings.

The protonation of fluorene is used to change the optical properties of conjugated polymers<sup>9</sup>. This allows the design and development of new organic emitter and sensor materials tailored toward particular needs. The effect of protonation on the monomer might be useful to understand the optical properties of larger systems. Besides, protonated polycyclic aromatic hydrocarbons have been suggested to be present in the interstellar medium, as potential carriers for the diffuse interstellar bands (DIBs) since attachment of highly abundant H atoms to ionized PAHs was measured to be fast<sup>10</sup>. Their spectroscopy is needed to allow comparison with astronomical observations.

Many efforts have been done recently to characterise the stability of the different conformers of protonated molecules through their infrared vibrational spectroscopy<sup>11-16</sup>. We will show in the present paper that the recent progress achieved by ab-initio methods is such that the electronic spectroscopy nowadays represents a quite accurate alternative to assign conformers through their electronic spectra.

## Methodology

The combination of experimental and theoretical methods used in this work has been described in details in a few papers recent papers<sup>1,6,8</sup>.

Briefly, the experiment combines a discharge at the exit of a supersonic expansion to produce cold protonated ions, a time of flight mass spectrometer to mass select these ions and a pulse tuneable laser to fragment them. The variation of the fragmentation efficiency versus the laser wavelength is very similar to the absorption spectrum. The multiphoton effects and the fragmentation threshold effect have already been discussed in details in previous papers.

The signal to noise in the experiment is not very good and the presented spectrum is the average of many scans. This is due to the presence of very hot molecules present at the same time than the cold ones responsible for the spectrum.

Concerning the ab-initio calculations, Turbomole suite was used<sup>17</sup>: the ground states properties (optimization and frequencies) are obtained with the RI-MP2 method and the excited states optimization and frequencies are obtained with the RI-CC2 method. The basis set used (SVP basis set (7s4p1d for carbon and 4s1p for hydrogen)) is quite small but it gives quite good results for these systems<sup>1</sup>. The isomers are noted  $H_n^+$  depending on which carbon atom the proton is attached, as shown in the insert of figure 1.

For the most stable isomer, a complete vibrational analysis has been performed after the excited-state optimization; the vibrational frequencies were calculated in both the ground and excited states, and then a Franck-Condon analysis was performed using the Pgopher software<sup>18</sup>.

## Results

### *Experimental*

The experimental spectrum is presented in figure 1: no signal has been recorded at wavelength higher than 550 nm.

As for linear protonated PAHs, the electronic absorption is strongly red shifted as compared to the absorption of neutral fluorene 296 nm (4.18 eV)<sup>19</sup>. The red shift is quite similar to the one observed in the case of Naphthalene<sup>1</sup>.

Clearly the spectrum shows two vibrational progressions, one starting at 479.8 nm (2.58 eV) and the other one at 447.6 nm (2.77 eV). The lowest energy one at 479.8 nm is less intense than the second one. The vibrational progression starting at 447.6 nm is well structured whereas the first progression hardly gets out of the experimental noise. These two progressions can correspond either to different electronic states or to different isomers. This is going to be clarified by the ab-initio calculations.

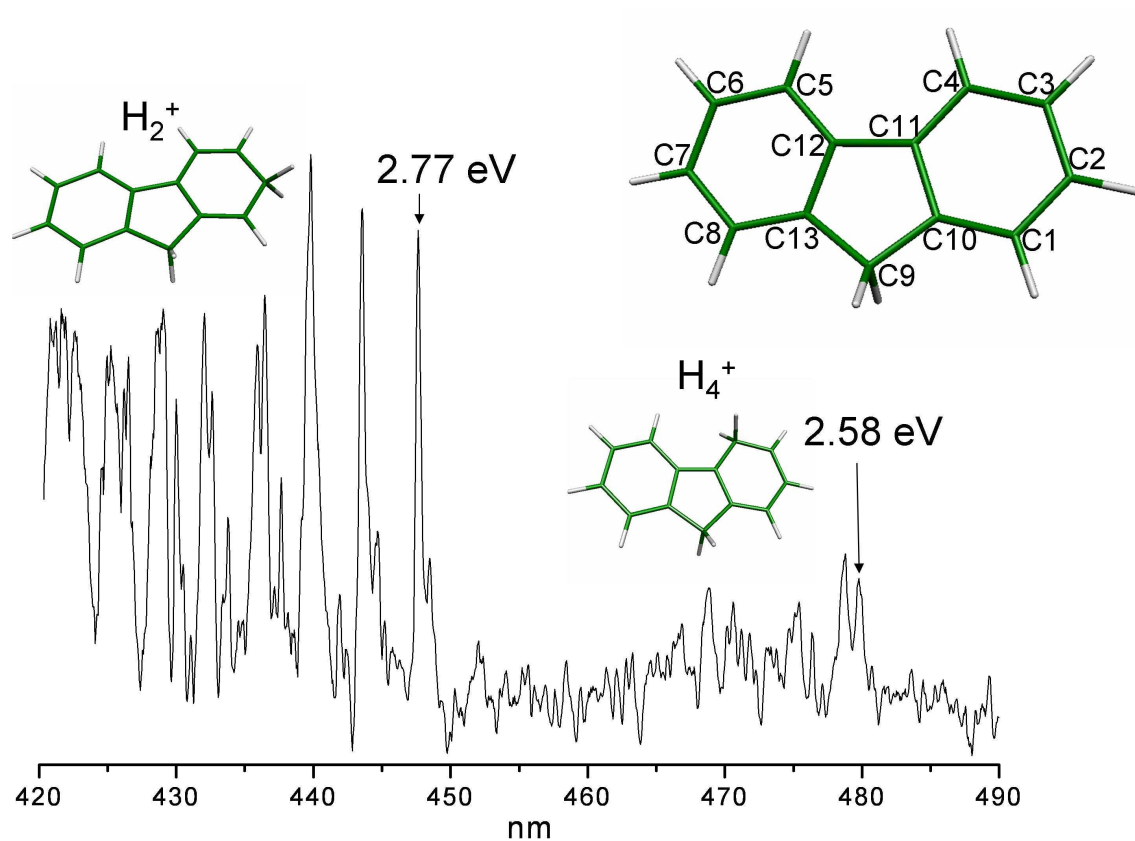


Figure 1

Figure 1: Photo-fragmentation spectrum of protonated fluorene. As in our previous experiments, a continuous background due to very hot molecules is present but has been subtracted in the figure. The molecules are drawn with the Molekel software.

### ***Ab initio calculations***

The results of the ab-initio calculations, ground state relative stabilities and transition energies are presented in table 1.

In the first column, the ground state energy of the different isomers is given relatively to the most stable  $H_2^+$  isomer. There are two isomers with similar energies,  $H_2^+$  and  $H_4^+$  : they have the highest  $S_0$ - $S_1$  calculated transitions energies, which are close to the observed band origins. Although not perfect there is a trend for the less stable isomers to have the lowest  $S_0$ - $S_1$  transitions. This has also been observed in the case of linear PAHs<sup>1</sup>. This might be quite general and will need to be investigated in more details.

*Table 1: Ab-initio calculations for the different isomers of protonated fluorene (see the insert figure 1 for the numbering of the carbon atoms). Column 2: ground state energies at the MP2 level, referred to the most stable isomer. Columns 3 and 4: the vertical transition energies of  $S_1 \leftarrow S_0$  and  $S_2 \leftarrow S_0$  and adiabatic transition  $S_1 \leftarrow S_0$  energies. The values in parenthesis are the oscillator strengths of the transitions. Column 5: difference in zero point energy between the ground and excited states. Columns 6 and 7: calculated transition energies in eV and in nm to be compared with experiment.*

	ground state	$S_1 \leftarrow S_0$ Vertical transition	$S_2 \leftarrow S_0$ Vertical transition	$S_1 \leftarrow S_0$ Adiabatic transition	zero point energy difference $\delta$ zpe	$S_1 \leftarrow S_0$ Adiabatic transition corrected for $\delta$ zpe	$S_1 \leftarrow S_0$ Adiabatic transition corrected for $\delta$ zpe
	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)	(nm)
$H_2^+$	0.00	3.20 (.038)	3.5 (.68)	2.91 (.029)	-0.156	2.76	449.2
$H_4^+$	0.09	2.91 (.53)	3.08 (.012)	2.74 (.046)	-0.155	2.59	478.7
$H_{10}^+$	0.31	2.91 (0.36)	3.20 (.075)	2.65 (.196)	-0.157	2.49	497.9
$H_3^+$	0.40	2.46 (.15)	2.76 (.005)	2.22 (.158)	-0.101	2.12	584.8
$H_1^+$	0.49	2.33 (.064)	2.59 (.006)	2.07 (.059)	-0.103	1.97	629.4
$H_{11}^+$	0.83	2.81(.058)	3.09 (.005)	2.1 (.001)	-0.093	2.01	616.8

The optimized geometry of the  $H_1^+$ ,  $H_2^+$ ,  $H_3^+$  and  $H_4^+$  stay planar in both the ground and the excited state. The  $H_{10}^+$  isomer is found quite low in energy but has lost the Cs symmetry. The ground and excited state geometries of the two most stable isomers,  $H_2^+$  and  $H_4^+$  are given in the supplementary information.

## Discussion

In previous experiments, we have seen that usually the lowest energy isomers are observed in the experiment, thus only the  $H_2^+$  and the  $H_4^+$  isomers that are the lowest in the ground state calculations are expected to be observed.

The spectrum can be assigned to these two lowest isomers since the calculated  $S_1 \leftarrow S_0$  transition energies are in very good agreement with the experimental band origins: the  $H_2^+$  is calculated at 2.76 eV and there is a band origin observed at 2.77 eV; the  $H_4^+$  is calculated at 2.59 eV and the first band origin is observed at 2.58 eV. Such a good agreement between the calculation (at this level of theory and basis set) and the experiment has already been observed for the linear protonated PAHs when the difference in the Zero Point Energy ( $\delta$  ZPE) between  $S_0$  and  $S_1$  is taken into account.

In order to test this assignment, the Franck Condon simulation can be compared with the experimental spectrum, at least for the most intense progression which is clearly evidenced. The result of the simulation is presented in figure 2.

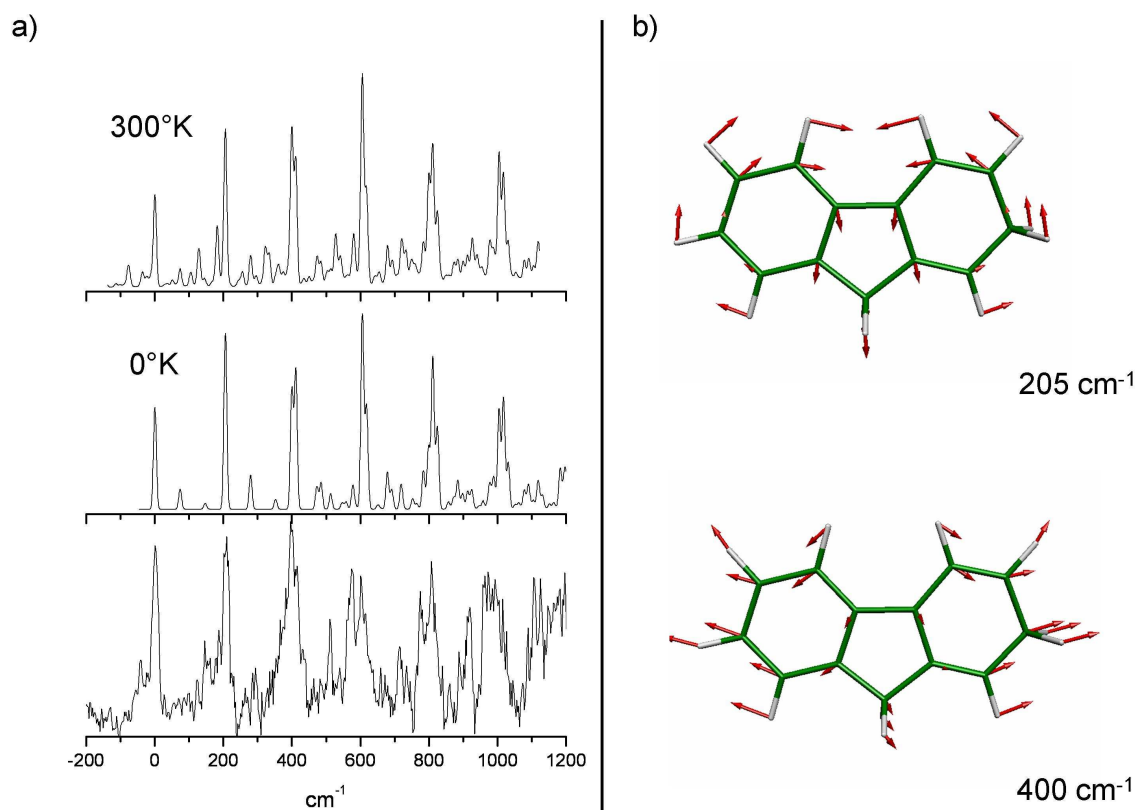


Figure 2

Figure 2 : Franck Condon simulation of the vibronic spectrum.

\*left part, lower trace: experimental spectrum of the band starting at 447.6nm, middle trace: Franck-Condon simulation at 0°K and upper trace: Franck-Condon simulation at 300°k

\*Right part, two most active vibrational modes in the spectrum.

The agreement between experimental data and theoretical calculation is quite good and is a strong support for the previous assignment. The 2 most actives modes are shown in figure 2b. They correspond to in plane deformations very similar to the modes that have been observed for protonated naphthalene and tetracene. The 205  $\text{cm}^{-1}$  mode is also quite similar to the mode observed in the neutral molecule<sup>19</sup> but is more active in the protonated species, which implies a stronger deformation upon excitation. In contrast to what was observed in anthracene, in the optimized geometries show no sign of out plane deformations neither in the ground nor in the excited state.

Another hypothesis could be that the two progressions are due to the 2 first excited states  $S_1$  and  $S_2$  of the most stable isomer. We think that we can rule this hypothesis because

the  $S_1$ - $S_2$  energy gap is 0.3 eV (for the vertical transition, see table 1), twice larger than the observed gap (0.19eV) and when the  $S_1$  and  $S_2$  states are optimized, the difference between the adiabatic transitions becomes even larger (0.46 eV).

The transition at 479.8 nm is assigned to the  $H_4^+$  isomer and its intensity is weaker than for the  $H_2^+$  since the ground state of this isomer is higher in energy by .09 eV.

The role of the charge transfer nature of the first excited state has been highlighted previously for protonated linear PAHs<sup>1</sup>. The same is true for protonated fluorene as shown in figure 3 where are depicted the HOMO and LUMO orbitals for the  $H_2^+$  isomer,

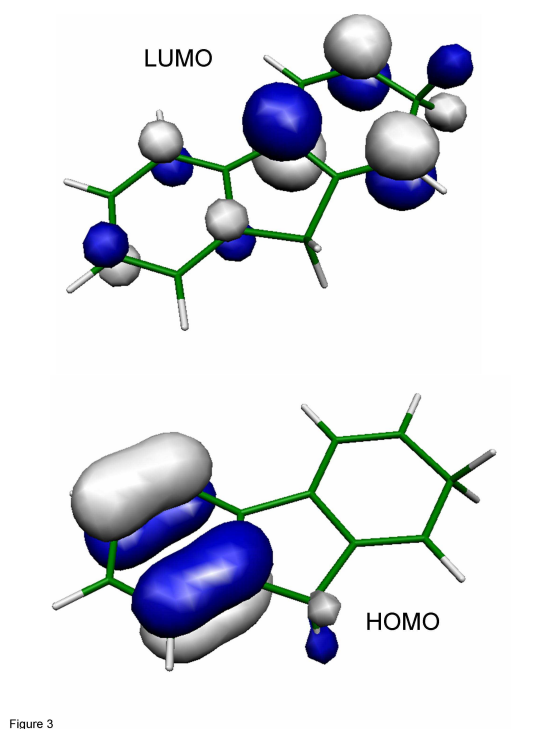


Figure 3 : Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital for the  $H_2^+$  isomer drawn using Molekel software. The cutting value is 0.05.

The  $S_1 \leftarrow S_0$  transition corresponds mainly to the HOMO-LUMO excitation and corresponds clearly to an electron transfer from the non protonated benzene ring to the protonated one. This charge transfer character is probably responsible for the larger deformation of the molecule upon excitation in the protonated species as compared to the neutral. The localisation of the electron on the non protonated part of the molecule has been explained in the case of the protonated benzene dimer: the ionisation potential of the protonated benzene is higher than the IP of the neutral homologue, because of the presence of a positive charge, thus the HOMO is more stabilised in the protonated moieties than on the neutral part. The first electronic transition basically corresponds to a transition from the



HOMO of the neutral part towards the LUMO of the protonated part. This is also an explanation why the electronic transitions are red shifted as compared to their neutral homologues.

The Diffuse Interstellar Bands (DIBs), observed in the visible to near infrared spectral range, provide a spectroscopic source of information about molecules present in the interstellar medium. However, none of them could be assigned to molecular carriers so far and it has been suggested that protonated PAHs could be possible carriers for the DIBs<sup>20</sup>. One of the consequences of the CT character of the first excited state is a relatively large change in geometry between the ground and the excited states, resulting in an important vibrational activity and a fairly low oscillator strength. The DIBs spectra do not show correlations between the bands observed, which means that they cannot belong to a molecular system with very active Franck Condon progressions. Thus the first excited state of protonated fluorene is probably not responsible for any DIB.

As for other PAHs, protonation leads to a strong red shift of the electronic absorption, which means that the proton affinity of the excited state is much larger than that of the ground state<sup>21</sup>. The proton affinity of fluorene in the ground state is 8.62 eV<sup>22</sup> and becomes 10.22 eV in the excited state. The effect of protonation on the optical properties of conjugated fluorene–pyridine copolymers<sup>9</sup> is to induce a large red shift of the fluorescence emission from 3.2 eV for non protonated polymers to 2.6 eV for protonated polymers. In the calculations<sup>9</sup> done to understand this effect, the proton is located on the pyridine moiety since the proton affinity of pyridine, 9.39 eV<sup>22</sup>, is higher than the proton affinity of fluorene in its ground state, but it is much lower than proton affinity of fluorene in its excited state. Besides, protonation of the pyridine molecule does not induce a shift of the electronic absorption, and the proton affinity of the excited state of pyridine should be similar to the ground state proton affinity. Thus, it is energetically very favorable to locate the proton on fluorene ring in the excited state, which implies that an excited state proton transfer is quite probable. This effect has not been considered previously<sup>9</sup> due the lack of knowledge on the optical properties of protonated molecules and it might be interesting to test this hypothesis by time resolved experiments.

## Conclusions

As for linear PAHs the protonation of fluorene leads to a strong red shift of the electronic transition as compared to the neutral molecule. This is due to the charge transfer

character of the excited state as in other PAHs. This strong shift of the electronic absorption implies a large increase of the excited state proton affinity, which can shade new perspectives on the excited state dynamics of protonated copolymers containing fluorene.

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