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# Solvation of charge in aromatic/noble gas Van der Waals clusters

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## Abstract

The results of an experimental study of the ionisation threshold in the various structural isomers of the Van der Waals clusters aniline-(argon)<sub>n</sub> ( $n = 1-5$ ) and 4-fluorostyrene-(argon)<sub>n</sub> ( $n = 1-2$ ) using resonant two-photon ionisation are reported. The data validate and generalise the site-specific modified shift additivity rule. They show an interesting influence of the localisation of argon atoms at the surface of the chromophore on the value of the net shift of the ionisation potential. Interpretation of the results involves evaluation and balancing between the charge-induced-dipole interaction and dispersion interaction. © 1997 Elsevier Science B.V.

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## 1. Introduction

The problem of the solvation of charge is one of the fundamental questions for understanding many chemical reactions in solution. In recent years the use of microclusters to study the progressive construction of solvent shells around a chromophore has allowed going into the details of solvation processes on a nanometer scale. Among many cluster systems the anionic clusters made of water or ammonia molecules present pure examples for the solvation of the negative charge [1], in which the degree of delocalisation of the charge among the cluster has been investigated. Alternatively, the solvation of the positive charge can be studied using cationic clusters, through the degree of solvent-charge interaction

as measured by the shift in the ionisation potential (IP). However, such studies are difficult in neat clusters, since the usual ionisation techniques like photoionisation or electron impact are unable to locate the adiabatic threshold. They are sensitive to vertical thresholds, and important rearrangements occur in the cluster immediately after ejection of the negative charge. Then the use of microclusters becomes a route for this prospect. Then the use of microclusters, in which a chromophore molecule is embedded into the solvent molecules, becomes a route for this prospect. Indeed in that case the charge is removed from orbitals of the chromophore, and the degree of rearrangement is much smaller. Therefore adiabatic IPs can be measured.

We report in this Letter new experimental results for the shift in the IP induced by the adduction of 1 to 5 argon atoms to aromatic chromophores. Specifically, IP shifts have been measured for 6 different

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structural isomers of aniline-(argon)<sub>n</sub> Van der Waals (VdW) clusters and for 2 isomers of 4-fluorostyrene-(argon)<sub>n</sub> VdW clusters. These new data complete our previous measurements [2,3] on aniline-(argon)<sub>n</sub> by 3 new isomers, and are original for 4-fluorostyrene-(argon)<sub>n</sub> monomer and clusters.

Concerning aniline-(argon)<sub>n</sub> Van der Waals clusters, our group has demonstrated, in a previous work [4], the existence of a site specificity relative to the shift of the  $S_1 \rightarrow S_0$  transition. Indeed, there are two main binding sites on the aniline microsurface; the “ring” site and the “NH<sub>2</sub>” one. When an argon atom occupies one or the other site, the origin of the  $S_1 \leftarrow S_0$  transition is shifted in a specific way: the shift is 53 cm<sup>-1</sup> to the red when an argon atom occupies the “ring” site and about 35 cm<sup>-1</sup> to the blue when an argon atom occupies the “NH<sub>2</sub>” one. More recently [5], we have experimentally recorded the  $S_1 \leftarrow S_0$  absorption spectrum of the previously theoretically predicted [4] (4/1) aniline-(argon)<sub>5</sub> isomer. We have also demonstrated the existence of a new kind of site: the “hydrogen” one and measured the shift of the origin of the  $S_1 \leftarrow S_0$  transition induced by an argon atom adsorbed in this “hydrogen” site: this shift is about 25 cm<sup>-1</sup> to the red.

On the other hand, we have observed in aniline-(argon)<sub>n</sub> clusters, from the measurements of IP shifts in 4 different structural isomers [3], that this site specificity was also characteristic of a shift in the ionisation potential. Depending on the occupied site, it was found that the ionisation potential is specifically shifted by 114 cm<sup>-1</sup> to the red when an argon atom occupies the “ring” site, and by 200 cm<sup>-1</sup>, also to the red, when an argon atom occupies the “NH<sub>2</sub>” one.

We are now able to confirm these results with the recording of a new series of ionisation efficiency spectra of the aniline-(argon)<sub>n</sub> clusters with much better signal-to-noise ratio than previously [3], which includes 3 new isomers, i.e. (2/0), (3/1) and (4/1)<sup>1</sup>.

Such results appeal for the investigation of the same processes in a similar system but involving a

different aromatic solute molecule. In the 4-fluorostyrene molecule, the structure is such that the substituent -CH=CH<sub>2</sub> vinyl group breaks the symmetry of the aromatic ring. Then two inequivalent binding sites appear next to this substituent, as was shown in our previous work [6] on the spectroscopy of the  $S_1 \leftarrow S_0$  transition in 4-fluorostyrene-(argon)<sub>n</sub> ( $n = 1-4$ ) VdW clusters. In this case the spectroscopy is richer because of the existence of three different kinds of sites: one “ring” site and two different “substituent” sites. The modified shift additivity rule [4] was tested by assigning a specific shift to each site: 40 cm<sup>-1</sup> to the red for the “ring” site, 39 cm<sup>-1</sup> to the blue for the first substituent site and 20 cm<sup>-1</sup> to the red for the second substituent site. However, it was shown that the formation of a trimer of argon atoms in the case of the (3/*n*) isomer family subsequently modifies the position of the argon atoms relative to the aromatic molecule and thus the shift additivity rule fails to provide accurate predictions of the global shift for any such isomer.

In the present work we have investigated the validity of the shift additivity rule for the IP shift in this 4-fluorostyrene-(argon)<sub>n</sub> system. It turned out that accurate determination of the IP of the 4-fluorostyrene free molecule was also necessary.

## 2. Experimental

Most of the experimental apparatus used in this study has already been described in a previous publication [7]. The “ICARE” apparatus has been modified by the insertion of a new time-of-flight mass spectrometer between the skimmer and the magnetic bottle. The mass resolution of this new spectrometer is about 200 for an average mass of 300 amu.

The resonant 2-photon 2-color ionisation (R2P2CI) technique has been used to obtain the photoionisation efficiency spectra of the clusters of interest. The tuning of one laser frequency to a resonance in the  $S_1 \leftarrow S_0$  transition of one selected isomer enables the optically selection of a single isomer of a given size. Then the scanning of the second laser frequency through the threshold region allows the recording of the PI profile. The first excitation step needing photons of about 295 nm in all cases, we used the frequency-doubled output of a

<sup>1</sup> A ( $p/q$ ) isomer of an aromatic-(M)<sub>n</sub> VdW cluster ( $n = p + q$ ) is built with  $p$  atoms or molecules on one side of the aromatic plane and with  $q$  atoms or molecules on the other side.

YAG-pumped 590 nm dye laser beam. The ionisation step (second colour) was realised by two different lasers, depending on the nature of the aromatic chromophore:

- for the aniline-(argon)<sub>n</sub> clusters, we used a 354 nm laser beam from a FL2002 Lambda Physics dye (DMQ) laser pumped with a 308 nm (XeCl) excimer laser beam;

- for the 4-fluorostyrene-(argon)<sub>n</sub> clusters, we used a KDP-crystal frequency-doubled 590 nm laser beam delivered by a Quantel TDL III dye laser (containing Rh6G) pumped with a 532 nm frequency-doubled Nd:YAG laser beam.

The ions were extracted with a static electric field of 500 V/cm for the aniline-(argon)<sub>n</sub> clusters, and with a delayed pulsed field for the 4-fluorostyrene-(argon)<sub>n</sub> clusters so that these clusters were ionised in zero-field.

### 3. Results and discussion

#### 3.1. Aniline-(argon)<sub>n</sub> clusters ( $n = 1-5$ )

Fig. 1 shows a set of photoionisation efficiency spectra for different ( $p/q$ ) structural isomers of aniline-(argon)<sub>n</sub> clusters ( $n = p + q = 2$  to 5) as a function of the energy of the ionising photon. The photoionisation efficiency spectra of the monomer and of the first two (1/0) and (1/1) clusters have also been measured under the same conditions, but are not displayed in Fig. 1 for reasons of clarity. They had already been measured in our previous

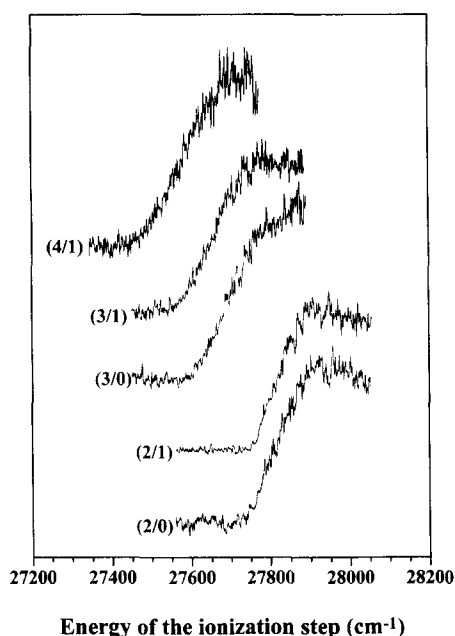


Fig. 1. Photoionisation efficiency spectra for different structural ( $p/q$ ) isomers of aniline-(argon)<sub>n</sub> ( $n = p + q = 0$  to 4) VdW clusters.

work [1,2], and the values of the IPs which had been derived were found to be in good agreement with independent determinations by different groups [8,9]. We recall that the value of the threshold energy in the ionisation step has been taken at the beginning of the signal onset. From a comparison with our previous work, a large improvement in the signal-to-noise ratio is clearly visible. The width of the step function ranges from about 100 cm<sup>-1</sup> for the (2/0) and

Table 1

Values of the measured threshold energy of the ionisation step at  $E = 500$  and 0 V/cm for different structural isomers of aniline-(argon)<sub>n</sub> clusters. From the values of the shift of the origin of the  $S_1 \leftarrow S_0$  transition relative to the monomer taken from previous work [10] the IPs at  $E = 0$  V/cm are deduced (right column). The new values concerning the (2/0), (3/1) and (4/1) isomers are in bold

Species (cm <sup>-1</sup> )	Threshold energy of the ionisation step at $E = 500$ V/cm (cm <sup>-1</sup> )	Energy of the ionisation step at $E = 0$ V/cm (cm <sup>-1</sup> )	$S_1 \leftarrow S_0$ transition shift relative to the monomer (cm <sup>-1</sup> ) [10]	Ionisation potential
an	28112 ± 2	28239 ± 2	–	62268 ± 2
an-Ar: (1/0)	28055 ± 5	28182 ± 5	– 53.2	62158 ± 5
an-Ar <sub>2</sub> : (1/1)	28000 ± 5	28127 ± 5	– 107.4	62049 ± 5
	(2/0) <b>27781 ± 8</b>	<b>27908 ± 8</b>	– 20.8	<b>61916 ± 8</b>
an-Ar <sub>3</sub> : (2/1)	27740 ± 8	27867 ± 8	– 74.4	61822 ± 8
	(3/0) 27588 ± 8	27715 ± 8	+ 21.9	61766 ± 8
an-Ar <sub>4</sub> : (3/1)	<b>27542 ± 10</b>	<b>27669 ± 10</b>	– 31.0	<b>61667 ± 10</b>
an-Ar <sub>5</sub> : (4/1)	<b>27460 ± 10</b>	<b>27587 ± 10</b>	– 56.0	<b>61560 ± 10</b>

Table 2

Values of the IP shifts (in  $\text{cm}^{-1}$ ) at  $E = 0$  V/cm for different structural isomers of aniline-(argon) $_n$  clusters deduced from previous work (see text) and from this work. The new values concerning the (2/0), (3/1) and (4/1) isomers are in bold

Species		This work	Ref. [2]	Ref. [3]	(ZEKE) [8]	(ZEKE) [9]
an-Ar:	(1/0)	$-110 \pm 7$	$-96 \pm 5$	$-116 \pm 10$	$-111$	$-113$
an-Ar <sub>2</sub> :	(1/1)	$-219 \pm 7$	$-194 \pm 6$	$-226 \pm 10$	$-219$	$-220$
	<b>(2/0)</b>	<b><math>-352 \pm 10</math></b>				
an-Ar <sub>3</sub> :	(2/1)	$-446 \pm 10$		$-412 \pm 15$		
	(3/0)	$-502 \pm 10$		$-533 \pm 15$		
an-Ar <sub>4</sub> :	<b>(3/1)</b>	<b><math>-601 \pm 12</math></b>				
an-Ar <sub>5</sub> :	<b>(4/1)</b>	<b><math>-708 \pm 12</math></b>				

(2/1) isomers to about  $200 \text{ cm}^{-1}$  for the (3/1) and (4/1) isomers.

The values of the threshold energies of the ionisation step in the electric field  $E = 500$  V/cm are given, in wavenumbers, in the first column of Table 1 for all the measured species. Their correspondence in zero-field, i.e. values up-shifted<sup>2</sup> by  $127 \text{ cm}^{-1}$ , are given in the second column. The values of the shift of the  $S_1 \leftarrow S_0$  transition, which has been used to optically select every cluster isomer by the first photon excitation, are recalled from our previous work in the third column. Finally the IPs are listed in the last column of Table 1 as the sums of the energies of the two steps.

Table 2 contains the same data expressed in terms in the shifts of the IPs with respect to the monomer IP for different isomeric clusters of aniline-(argon) $_n$ , together with the results previously obtained with the same method in our group [2,3] and by Takahashi et al. [8] and Zhang et al. [9] with a ZEKE technique. Two remarks can be made: (i) Due to the better signal-to-noise ratio the present results are more accurate than our previous measurements; (ii) the values obtained by the R2P2CI threshold technique are in good agreement with those obtained by the ZEKE technique, which confirms that the R2P2CI is a simple and reliable method for studying the IP shift of this kind of species. As a matter of fact the absolute values of the IPs measured in the present

work are also found to be in agreement with the ZEKE measurements within a few  $\text{cm}^{-1}$ .

To strengthen the previously [3] discussed specificity of the site relative to the shift of the IP, we can extract from these new IP shifts the site's contribution. Thus, it is possible to examine, as introduced in the lines above, the validity of the modified, site specific, shift additivity rule. Table 3 gives the contributions of the different sites to the IP shift, and recalls their contributions to the shift of the  $S_1 \leftarrow S_0$  transition. From the first two lines of Table 2 [(1/0) and (1/1) isomers], it is easy to extract the contribution of the main "ring" site:  $-110 \text{ cm}^{-1}$ . From it and lines 3 to 6 of Table 2, we find that the contribution of the "NH<sub>2</sub>" site is about  $-235 \text{ cm}^{-1}$  for the (2/ $n$ ) family of isomers [ $-242 \text{ cm}^{-1}$  for the (2/0) isomer and  $-227 \text{ cm}^{-1}$  for the (2/1) one] and about  $-194 \text{ cm}^{-1}$  for the (3/ $n$ ) family ( $-196 \text{ cm}^{-1}$  for the (3/0) isomer and  $-191 \text{ cm}^{-1}$  for the (3/1) one). Finally, the contribution of the "hydrogen" site is  $-107 \text{ cm}^{-1}$ , which is close to that of the "ring" site.

It is remarkable that, contrary to what occurs for the shift in the  $S_1 \leftarrow S_0$  transition, all sites produce a red shift. Also striking is the sensitivity of this shift to the kind of site, the "NH<sub>2</sub>" site's shift being about twice as large as the "ring" or the "hydrogen" sites. However, finer behaviour can be observed. The IP shift contribution of an "NH<sub>2</sub>" site differs in the (2/ $n$ ) and (3/ $n$ ) families, i.e. when only one, or two, of this kind of site is occupied by argon atoms placed on the same side of the aromatic plane. The difference, of the order of  $40 \text{ cm}^{-1}$ , is significant. A similar, but much smaller (about  $4 \text{ cm}^{-1}$ ), difference is also present in the shifts produced by the occupation of these sites in the  $S_1 \leftarrow S_0$

<sup>2</sup> This correction represents the dependence (red-shift) of the IP of a species with an extraction electric field value of  $500 \text{ V/cm}$ . We have previously [2] found that this dependence with the electric field  $E$  is equal to  $5.7 \sqrt{E}$ .

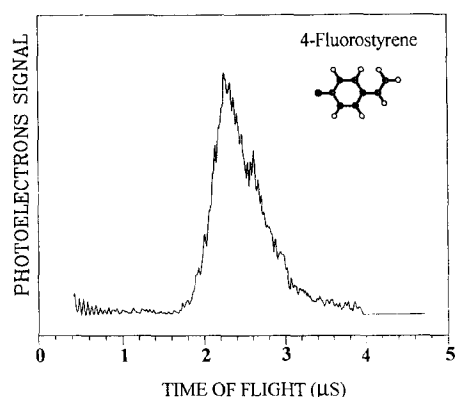


Fig. 2. Photoelectron spectrum of 4-fluorostyrene monomer obtained by ionisation with 2 photons of the same colour through the first electronically excited state  $S_1$  located at  $34314\text{ cm}^{-1}$ .

transition (see Table 3). This can be explained by a difference in the equilibrium positions of the argon atoms relative to the surface of the aniline substrate. Indeed, when argon atoms occupy two adjacent “ $\text{NH}_2$ ” sites in the same half solvation layer (case of  $(3/n)$  isomers,  $n = 0$  or  $1$ ), the system is more symmetric than when only one “ $\text{NH}_2$ ” site is occupied (case of  $(2/n)$  isomers,  $n = 0$  or  $1$ ). In previous investigations of the most stable structures by molecular dynamics simulation [4], a difference in equilibrium positions of the argon atom relative to the substrate for symmetric and non-symmetric structures was observed as a feature of the potential energy surface used for the aniline–(argon) $_n$  system. Such a detailed knowledge of the spectroscopic shifts induced by the various adsorption sites should be helpful for making predictions for aniline–(argon) $_n$

clusters of larger size, and then allow further assignments.

A final remark can be done about the width of the step functions in the recordings. By nature this width should reflect the extension of the Franck–Condon distribution upon VdW modes in the  $S_1 \leftarrow D_0^+$  transition ( $D_0^+$  being the ground electronic state of the ion). The stabilisation energy involved in this transition can be evaluated from Table 3 for each type of site:  $\approx 56\text{ cm}^{-1}$  for the ring site,  $\approx 250\text{ cm}^{-1}$  for the “ $\text{NH}_2$ ” site,  $\approx 80\text{ cm}^{-1}$  for the hydrogen site. It is expected that the larger this stabilisation energy, the larger the change in the equilibrium configuration. Thus the clearly larger value of this width observed when two “ $\text{NH}_2$ ” sites are occupied (isomers  $(3/0)$ ,  $(3/1)$ ,  $(4/1)$ ) must be due to such a large difference in equilibrium configurations between the  $S_1$  and  $D_0^+$  states.

### 3.2. 4-fluorostyrene–(argon) $_n$ clusters ( $n = 1$ and $2$ )

The study of VdW induced IP shifts in 4-fluorostyrene–(argon) $_n$  ( $n = 1$  and  $2$ ) clusters requires a preliminary measurement of the IP of the 4-fluorostyrene free molecule. Indeed, the IP of this species has only been measured with low accuracy in the gas phase by photoelectron spectroscopy [11], so that first searches to localise the ionisation threshold by R2PI were unsuccessful. Then our first goal has been to obtain a reasonably accurate value for the IP of 4-fluorostyrene. We knew that this IP was not higher than  $68628\text{ cm}^{-1}$  since two photons from the same laser tuned to the resonance of the  $S_1 \leftarrow S_0$  transition at  $34314\text{ cm}^{-1}$  [12] were able to ionise the molecule.

Table 3

Contributions to the IP shift and to the  $S_1 \leftarrow S_0$  transition shift due to each type of site derived from the results for different structural isomers of aniline–(argon) $_n$ . The new values concerning the  $(2/0)$ ,  $(3/1)$  and  $(4/1)$  isomers are in bold

Site	Species	Site's contribution to the IP shift ( $\text{cm}^{-1}$ )	Site's contribution to the shift of the $S_1 \leftarrow S_0$ transition ( $\text{cm}^{-1}$ ) [10]
ring site	an–Ar: (1/0)	$-110 \pm 7$	$-53.2$
	an–Ar $_2$ : (1/1)	$-109 \pm 14$	$-53.7$
	<b>an–Ar<math>_2</math>: (2/0)</b>	<b><math>-242 \pm 17</math></b>	<b><math>+34.2</math></b>
$\text{NH}_2$ site	an–Ar $_3$ : (2/1)	$-227 \pm 17$	$+33.0$
	an–Ar $_3$ : (3/0)	$-196 \pm 9$	$+37.6$
	<b>an–Ar<math>_4</math>: (3/1)</b>	<b><math>-191 \pm 10</math></b>	<b><math>+38.2</math></b>
hydrogen site	<b>an–Ar<math>_5</math>: (4/1)</b>	<b><math>-107 \pm 24</math></b>	<b><math>-25.0</math></b>

Our molecular beam apparatus [7] was equipped with a magnetic bottle photoelectron spectrometer, we took advantage of this capability by looking at the kinetic energy of the R2PI ejected electrons.

Fig. 2 shows the photoelectron spectrum of the 4-fluorostyrene molecule which has been obtained when photoionising with 2 photons of  $34314\text{ cm}^{-1}$ , which has been recorded with an extraction field of  $2.5\text{ V/cm}$ . The time-of-flight (TOF) distribution is characterised by a single delayed unresolved peak: its maximum is located at  $t = 2.30 \pm 0.04\text{ }\mu\text{s}$ . In this electron spectrometer, the TOF of the electrons can be related to the kinetic energy  $E$  of the electrons by [13]:

$$t = t_0 + \frac{843.0}{\sqrt{E + V_0 + V_{\text{EXT}}}},$$

843.0 is a characteristic parameter of the spectrometer depending on the length of the flight-tube;  $t_0$  (ns) represents a synchronisation temporal shift;  $V_0$  (eV) represents the residual contact potential due to the fact that the extraction electrodes can accommodate some electric charge;  $V_{\text{EXT}}$  (eV) represents the extraction voltage (potential difference).

The use of this time–energy relation requires some information about the residual contact potential. This one was estimated on the basis of similar measurements done with aniline whose IP is accurately known. We can confidently consider that:  $-250\text{ meV} < V_0 < -150\text{ meV}$ . On the other hand the electrons travel a 1 mm path in the extraction field before entering the E-field free region. Thus  $V_{\text{EXT}} = 250\text{ meV}$ . And finally we find for the electrons at the peak of the TOF distribution:  $34\text{ meV} < E < 134\text{ meV}$ .

Thus the IP seems to be nearly twice the energy of the  $S_1 \leftarrow S_0$  transition. This idea is confirmed by

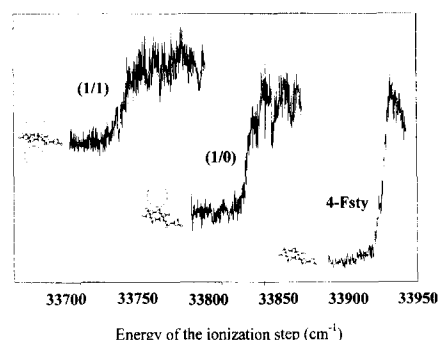


Fig. 3. Photoionisation efficiency spectra of 4-fluorostyrene monomer, and of the two (1/0) and (1/1) isomers of the 4-fluorostyrene–(argon) $_n$  VdW clusters.

the fact that the fragmentation signal in previously recorded R1C2P spectra of 4-fluorostyrene–(argon) $_n$  VdW clusters was small [6]. The width of the TOF distribution is about  $0.6\text{ }\mu\text{s}$ , which converts into about  $60\text{ meV}$ . This spreading is rather smaller than the above energy range resulting from poor knowledge of the contact potential. Indeed the electrons arriving at later times should have been created with basically zero kinetic energy, while those arriving at earlier times should have been formed with all the kinetic energy available. This implies that only low-frequency states (torsional modes) have been populated in the ion. This argument tends to set the IP of 4-fluorostyrene at about  $60\text{ meV}$  below the energy input by the two photons, i.e.  $68628\text{ cm}^{-1}$ .

This measurement represented a useful first step allowing restriction of the energy range to scan with the laser photons in order to obtain a value for the IP with an accuracy of about  $10\text{ cm}^{-1}$ . Indeed we quickly localised the threshold energy for the ionising photon, originating from the second colour laser. Fig. 3 shows the ionisation efficiency spectra of the

Table 4

Values of the shifts for the 2 structural isomers (1/0) and (1/1) of 4-fluorostyrene–(argon) $_n$  clusters. The shift of the origin of the  $S_1 \leftarrow S_0$  transition is taken from previous work, the energy of the ionisation step, the IP's and IP shifts are obtained from this work

Species	$S_1 \leftarrow S_0$ transition shift relative to the monomer [12] ( $\text{cm}^{-1}$ )	Energy of the ionisation step ( $\text{cm}^{-1}$ )	Ionisation potential ( $\text{cm}^{-1}$ )	IP shift ( $\text{cm}^{-1}$ )
4-fsty	–	$33918 \pm 5$	$68232 \pm 5$	–
4-fsty–Ar (1/0)	–39.6	$33825 \pm 10$	$68099 \pm 10$	$-133 \pm 15$
4-fsty–Ar <sub>2</sub> (1/1)	–82.0	$33730 \pm 10$	$67962 \pm 10$	$-270 \pm 15$

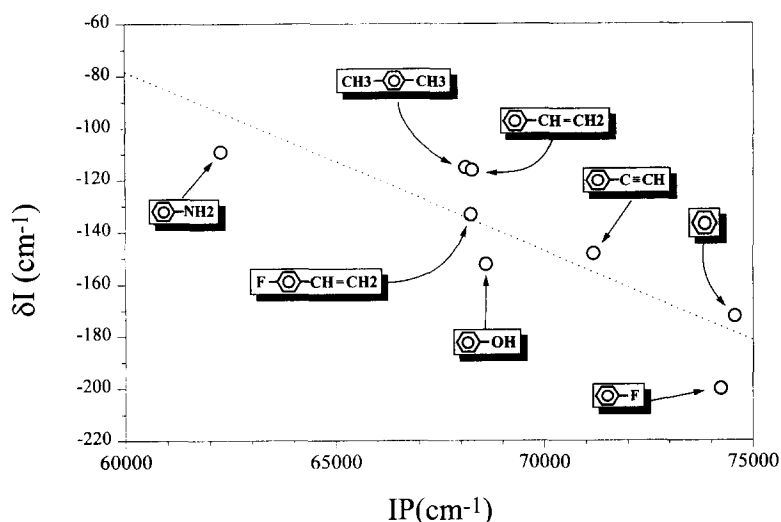


Fig. 4. The IP solvent shift of a series of substituted benzene VdW clusters with argon as a function of the IP of the free aromatic molecule.

4-fluorostyrene monomer and the first two 4-fluorostyrene-(argon)<sub>n</sub> (*n* = 1, 2) VdW clusters as a function of the ionisation step energy. These spectra have been obtained in zero-field.

Table 4 summarises the results obtained for these species. The first column recalls the previously [14] obtained values of the shifts of the *S*<sub>1</sub> ← *S*<sub>0</sub> transition, the second one the threshold energy of the ionising step, and the third one the absolute values of

the IPs. The last column indicates the resultant VdW shifts of the clusters. These results call for some comments.

– First, we can check that the value obtained for the IP of the 4-fluorostyrene molecule, i.e.  $68232 \pm 5 \text{ cm}^{-1}$  lies inside the proper range, within about  $100 \text{ cm}^{-1}$  from the value predicted from the photoelectron spectrum. This result illustrates how it can be useful to associate photoelectron spectroscopy and laser spectroscopy.

– Second, the VdW shift for the IP of the *n* = 2 cluster,  $-270 \pm 10 \text{ cm}^{-1}$ , is, within experimental accuracy, equal to twice that of the *n* = 1 cluster,  $-133 \pm 10 \text{ cm}^{-1}$ . This result is not unexpected, since it has already been observed in most aromatic molecule/rare gases atom VdW clusters. Following the site specific shift additivity rule [4], it confirms that the two argon atoms in the 4-fluorostyrene-(argon)<sub>2</sub> cluster occupy equivalent sites, and that these sites are of the same type as the only occupied in the 4-fluorostyrene-argon complex. Consequently the two probed isomers respectively have (1/0) and (1/1) structures. This was already derived from a previous study of the shift of the *S*<sub>1</sub> ← *S*<sub>0</sub> transition [6].

The values of the IP shifts of the 4-fluorostyrene-argon and aniline-argon (1/0) VdW clusters have the same order of magnitude as those observed for similar VdW species built with a substituted benzene molecule and one argon atom. To

Table 5

Values (in  $\text{cm}^{-1}$ ) of the IPs for a series of substituted benzene molecules and of the IP shifts of the VdW clusters of the same molecules with one argon atom

Species	Ionisation potential of the monomer ( $\text{cm}^{-1}$ )	IP shift of the aromatic-argon VdW clusters ( $\text{cm}^{-1}$ )	References
Aniline	62268	-110	This work
Paraxylene	68110	-115	17
4-fluorostyrene	68232	-133	This work
Styrene	68267	-116	18
Phenol	68600	-152	19
Phenylacetylene	71175	-148	18
Fluorobenzene	74230	-200	20
Benzene	74555	-172	21



illustrate this affirmation, it can be interesting to plot the values of these IP solvent shifts in a series of clusters of mono and di-substituted benzene as a function of the absolute values of the IPs of the aromatic free molecules. This is shown in Fig. 4, on the basis of the values gathered in Table 5 (data from Refs. [17–21] and this work). A correlation clearly appears between the two quantities: IP of the monomer and IP shift of the VdW cluster. Aniline, which is the molecule with the smallest IP, also has the smallest IP shift. Such a good correlation has already been observed and discussed by our group [2], and by Mons et al. [15] in the case of the shift of the  $S_1 \leftarrow S_0$  transition. We consider this as a fairly strong indication that the reduction of the dispersion interaction energy upon ionisation plays an important role in reducing the binding energy of the argon atom to the aromatic cation, in spite of the presence of the induction interaction, which is expected to be much larger than the observed solvent shifts, even when taking into account the delocalisation of the charge into the ring orbitals [16].

#### 4. Conclusions

Improved data and new results have been presented about the shift in energy of the IP induced by the binding of argon atoms in well-defined solvation sites onto two single-ring aromatic molecules. It has been found that this shift is extremely sensitive to the precise localisation of the rare gas atom relative to the various chemical bonds of the chromophore molecule. In particular in the case of aniline the value of this shift is increased by about a factor of two when one argon atom is displaced from the region above the  $\pi$ -electron cloud in the ring to the region next to the amino group. Such changes must be the consequences of local variations of inductive and dispersive interactions, and, as shown here, particularly the latter. A more quantitative evaluation of these various terms would require a careful study combining approximate quantum chemistry methods and semi-empirical approaches. While waiting for the results of such studies one can nonetheless con-

clude that, rather unexpectedly, the binding of a rare gas atom by VdW interaction appears to be a sensitive probe of the local charge density on an atomic scale.

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