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Theoretical investigation of charge transfer to solvent in photoexcited iodide–acetonitrile clusters

Qadir K. Timerghazin, Gilles H. Peslherbe [*]

Department of Chemistry and Biochemistry, Centre for Research in Molecular Modeling, 1455 de Maisonneuve Blvd. W., Concordia University, Montréal, Que., Canada H3G 1M8

Abstract

Photoexcitation of the iodide–acetonitrile complex leading to charge-transfer-to-solvent precursor states has been investigated with electronic structure theory calculations. The resulting vertical excitation energies are in good agreement with experimental results. The picture that emerges from the calculations is that, upon photoexcitation, an electron is transferred from one of the iodide valence p orbitals to the acetonitrile molecule, where it is stabilized by interactions with the acetonitrile dipole and the electrophilic hydrogen atoms of the methyl group. A similar picture applies to the photoexcitation of iodide–water clusters, but charge transfer to solvent appears much more obvious for iodide–acetonitrile clusters. © 2002 Published by Elsevier Science B.V.

1. Introduction

The role of solvation in the photochemical behavior of chemical species has been a long-standing issue, and charge transfer to solvent (CTTS) is undoubtedly one of the most pronounced cases of the solvent role in photochemistry [1]. Whereas many anions such as halides do not possess electronically bound excited states in the gas phase and undergo simple electron detachment when exposed to light of sufficient wavelength, they exhibit a strong and broad absorption band in a number of polar solvents. These absorption bands were assigned to transitions to bound excited states, hereafter called CTTS states, presumably supported by a concerted action of solvent molecules [1]. A number of theories, treating the solvent as a dielectric continuum which traps and stabilizes an excited electron, have been developed to model the CTTS phenomenon [2,3]. In the last few years, CTTS states were investigated by femtosecond spectroscopy [4,5] and modeled with quantum molecular dynamics [6,7].

Recent advances in experimental investigative techniques of chemical reactions in molecular clusters – an intermediate state between the gas and condensed phases [8], made it possible to investigate CTTS in clusters. Dipole-bound excited states resulting from photoexcitation of clusters containing an iodide ion and a few molecules of acetone [9], acetonitrile [10], water [11,12], nitromethane and methyl iodide [13] have been

[*] Corresponding author. Fax: +1-514-848-2868.

E-mail address: ghp@alcor.concordia.ca (G.H. Peslherbe).

recently observed experimentally and are thought to be precursors of the solution CTTS states. Bound excited states were also observed for iodide in clusters of highly polarizable xenon atoms $I^-(Xe)_n$ ($n \geqslant 4$) [14,15]. In the case of water clusters, two or more solvent molecules seem to be needed to stabilize the excited state, while acetone and acetonitrile complexes with iodide of 1:1 composition already demonstrate well-developed excited-state precursors of the bulk CTTS states. This suggests that the excited states of the anionic clusters are more stable with increasing solvent polarity. It was also shown that the larger the number of solvent molecules in the cluster, the larger the blue shift of the absorption maxima towards the bulk values [10,11,14]. Finally, it was observed that further evolution of photoexcited complexes of acetone, acetonitrile and water leads to dissociation into an iodine atom and a negatively charged solvent cluster $(S)_n^-$, where $S = CH_3CN$, $(CH_3)_2CO$ and H_2O [9,10,12]

$$I^-(S)_n \rightarrow \left[I^-(S)_n\right]^* \rightarrow I^\cdot + (S)_n^-$$
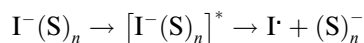
On the theoretical side, CTTS precursor states have only been investigated for iodide–water clusters [16–19]. It was shown that quantum-chemical calculations such as configuration interaction with single excitations (CIS) and time-dependent density-functional theory (TD-DFT) qualitatively reproduce experimentally observed trends for the dependence of the CTTS excitation energy on cluster size [16,18]. Chen and Sheu [17] studied the photoexcitation of $I^-(H_2O)_n$ and the resulting electron distribution in CTTS precursor states with the simple initial-guess method, and reported results in good agreement with experiment. Recently, the same approach was used for investigating the relaxation of iodide–water clusters following photoexcitation [19].

More detailed studies are needed to provide a thorough description of photoexcitation processes in ionic clusters. Of particular interest is the nature of the electronic transition to the CTTS state, i.e., the charge flow between ground and excited states. Furthermore, studies of photoexcitation processes in iodide clusters with molecules of varying polarity and polarizability should bring some more insight into CTTS phenomena. In this

Letter, we present a preliminary investigation of the excited states of the $I^-(CH_3CN)$ complex, and contrast our results to those for $I^-(H_2O)_3$ clusters, while we defer a more systematic and detailed investigation of $I^-(CH_3CN)_n$ clusters to a later publication. Vertical excitation energies are calculated with several quantum-chemical methods and successfully compared to experimental data. The charge flow between the ground and excited states is then analyzed in order to shed some light into the nature of the electronic transitions in these clusters.

2. Computational procedure

Cluster equilibrium geometries were optimized with second-order Møller–Plesset (MP2) theory [20] and vertical excitation energies were calculated by CIS [21], TD-DFT [22] with the B3LYP hybrid functional [23], and the coupled cluster (with single and double excitations) equation-of-motion approach (CCSD-EOM) [24]. For first row atoms, we used a standard 6-311++G(df, p) basis set [20]. For iodine, we employed an all-electron (AE) 6-311G basis [25] or a Stuttgart–Dresden–Bonn quasi-relativistic ECP46MWB effective core potential (ECP) [26], with valence basis sets augmented by diffuse s and p as well as polarization d and f functions [27]. Geometry optimizations were performed with the ECP basis set, while vertical excitation energies were calculated with both the AE and ECP basis sets. Atomic charges were calculated by Löwdin population analysis and the atoms-in-molecules (AIM) approach [28]. Calculations were performed with the GAUSSIAN 98 [29], GAMESS [30] and MOLPRO [31] quantum chemistry packages.

3. Results and discussion

The structure of iodide–acetonitrile complexes was previously investigated with the MP2/6-311+G* model chemistry [32]. These calculations predict the $I^-(CH_3CN)$ complex (shown in Fig. 1) to have C_{3v} cylindrical symmetry, with the ion residing on the methyl side along the acetonitrile
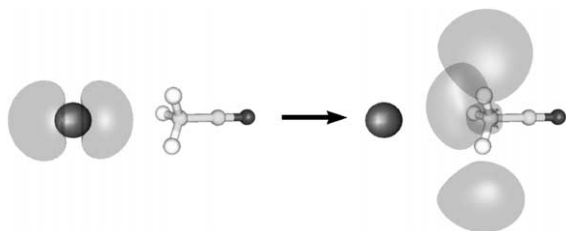
Fig. 1. Electronic density difference between the $I^-(CH_3CN)$ ground and excited states for the $\tilde{B}^1A_1 \leftarrow \tilde{X}^1A_1$ transition calculated with CIS/6-311++(df, p). The negative density difference isosurface is plotted on the left side, while the positive difference isosurface is plotted on the right side.

principal symmetry axis, at a distance of 3.70 Å from the methyl carbon. The binding energy of this complex was found to be 10.5 kcal/mol with CCSD(T)/6-311+G(2df, pd)//MP2/6-311+G* (including approximate zero-point energy and basis-set-superposition-error corrections), in good agreement with the experimental value of 11.10 ± 0.40 kcal/mol [33]. The complex was re-optimized with the larger basis set described in the previous section for consistency, but no change of consequence was observed in the geometry of the complex. The complex is stabilized mostly due to electrostatic interactions of the negatively charged iodide with the highly dipolar acetonitrile molecule, but some charge transfer is observed, as can be seen from the results of the ground-state population analyses in Table 1.

The results of excited-state calculations for the $I^-(CH_3CN)$ complex are collected in Table 1. All the methods employed (CIS, TD-DFT, CCSD-EOM) consistently suggest that the experimentally observed absorption of the $I^-(CH_3CN)$ complex corresponds to transitions to the first three singlet excited states, one doubly degenerate $\tilde{A}^1E$ state and one $\tilde{B}^1A_1$ state. Inspection of Table 1 shows that TD-DFT reproduces the experimental vertical excitation energies reported by Johnson and co-workers [10] within 0.2 eV, whereas CIS and CCSD-EOM overestimate the excitation energies by about 1.4 and 0.8 eV, respectively. Including higher-order excitations in the coupled cluster equation-of-motion approach may improve the calculated excitation energies, but one should note that a proper treatment of spin–orbit coupling

might be needed for truly quantitative results. [1] The energy difference between the ^1E and $^1A_1$ states is only 0.06 eV with TD-DFT, and other methods give even smaller differences. Calculations with AE basis sets tend to give higher excitation energies than with effective core potential bases. Finally, oscillator strengths calculated with a given method are very similar for both the $\tilde{A}^1E \leftarrow \tilde{X}^1A_1$ and $\tilde{B}^1A_1 \leftarrow \tilde{X}^1A_1$ transitions, but CIS predicts values about five times larger than TD-DFT.

To gain insight into the nature of the electronic transitions upon photoexcitation of the $I^-(CH_3CN)$ complex, we calculated the CIS electronic density difference between the ground and excited states. The density difference diagrams show areas of the molecule from where some negative charge is removed upon excitation (negative difference) and where it is promoted (positive difference). It is seen from Fig. 1 that the $\tilde{B}^1A_1 \leftarrow \tilde{X}^1A_1$ transition involves electron promotion from the iodide valence p_z orbital to diffuse orbitals mostly located on the methyl group of acetonitrile. The $\tilde{A}^1E \leftarrow \tilde{X}^1A_1$ transitions (not shown here) are similarly associated with electronic density moving out of the iodide valence p_x and p_y orbitals orthogonal to the complex symmetry axis. We note from Table 1 that the excitation energy for these transitions is lower than for the $\tilde{B}^1A_1 \leftarrow \tilde{X}^1A_1$ transition. This may be attributed to the fact that, in the ground-state cluster, electrons in the p_z orbital are stabilized by interactions with the solvent dipole – which is aligned with the p_z orbital – to a greater extent than those in the p_x and p_y orbitals. This picture of electrons being promoted from the iodide valence p orbitals to diffuse orbitals of the acetonitrile methyl group is representative of CTTS, and is further supported by the charge analysis of the excited complex. The Löwdin charge on iodine drops to zero in the excited complex, indicating full transfer of the iodide negative charge to the solvent. The AIM charge analysis also supports that picture of electron transfer to the solvent, but to a lesser extent, as the

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[1] Q.K. Timerghazin, G.H. Peslherbe, work in progress.

Table 1
Ground- and excited-state properties of the iodide–acetonitrile complex[a]

State		CIS		TD-DFT		CCSD-EOM		Experiment[b]
		AE[c]	ECP[d]	AE[c]	ECP[d]	AE[c]	ECP[d]	
$\tilde{X}^1A_1$	$q(I)_{Löwdin}$	−0.88	−0.89					
	$q(I)_{AIM}$	−0.97		−0.95				
$\tilde{A}^1E$	E	4.92	4.77	3.39	3.33	4.33	4.18	3.53
	f	0.091	0.100	0.021	0.023			
	$q(I)_{Löwdin}$	−0.04	−0.04					
	$q(I)_{AIM}$	−0.31						
$\tilde{B}^1A_1$	E	4.94	4.80	3.44	3.39	4.34	4.19	
	f	0.101	0.099	0.040	0.041			
	$q(I)_{Löwdin}$	−0.07	−0.08					
	$q(I)_{AIM}$	−0.33						

[a] $q(I)$ is the iodine atomic charge, E is the vertical excitation energy (in eV), and f is the oscillator strength.
[b] Taken from [10].
[c] All-electron 6-311++G(df, p) basis set for all atoms.
[d] Stuttgart–Dresden–Bonn ECP basis set for iodine, 6-311++G(df, p) basis set for all other atoms.

difference in the iodine charge between the ground and excited state is only about 0.7e.

For comparison with previous work on iodide–water clusters [16–19], we calculated the excited states of the C_3-symmetry $I^-(H_2O)_3$ cluster shown in Fig. 2. The total solvent dipole in this $I^-(H_2O)_3$ cluster is aligned along the complex symmetry axis and has a magnitude of 3.8 D very similar to that of acetonitrile (3.9 D). As for the $I^-(CH_3CN)$ complex, the results of our calculations, collected in Table 2, suggest that the first three lowest singlet
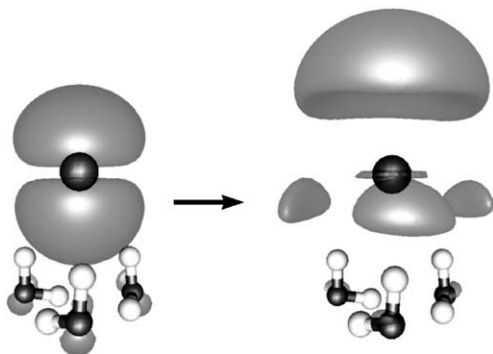

Fig. 2. Electronic density difference between the $I^-(H_2O)_3$ ground and excited states for the $\tilde{B}^1A_1 \leftarrow \tilde{X}^1A_1$ transition calculated with CIS/6-311++(df, p). The negative density difference isosurface is plotted on the left side, while the positive difference isosurface is plotted on the right side.

excited states of the cluster – $\tilde{A}^1E$ and $\tilde{B}^1A_1$ – are possible candidates for the experimentally observed CTTS precursor states. Our calculations of vertical excitation energies for $I^-(H_2O)_3$ are in good agreement with previous TD-DFT, CIS and initial-guess calculations [16,17]. Again, TD-DFT appears to perform well, reproducing the experimental excitation energy within 0.3 eV, while CIS and CCSD-EOM overestimate the excitation energy by 1.3 and 0.6 eV, respectively. All the methods employed consistently show a larger spacing between the $\tilde{A}^1E$ and $\tilde{B}^1A_1$ states for $I^-(H_2O)_3$ than for $I^-(CH_3CN)$. Both TD-DFT and CIS predict larger oscillator strengths for photoexcitation of the iodide–water cluster.

Analysis of the electronic density difference between the ground and excited states of the $I^-(H_2O)_3$ cluster, shown in Fig. 2, indicate that the transition to the $\tilde{A}^1E$ state involves electron excitation out of the degenerate iodide valence p_x and p_y orbitals, while the transition to the $\tilde{B}^1A_1$ state involves electron excitation out of the iodide valence p_z orbital (pointing towards the solvent cluster), very much like for the $I^-(CH_3CN)$ complex. However, the photoexcited electron seems to reside in the area above the iodine atom and not towards the solvent cluster, unlike for the $I^-(CH_3CN)$ complex. We note that initial-guess calculations by Chen and Sheu (cf. Fig. 1 in [17])

Table 2
Ground- and excited-state properties of the complex of iodide with three water molecules[a]

State		CIS		TD-DFT		CCSD-EOM	Initial guess[b]	TD-DFT[c]	CIS[c]	Experiment[d]
		AE[e]	ECP[f]	AE[e]	ECP[f]	ECP[f]				
$\tilde{X}^1A_1$	$q(I)_{Löwdin}$	−0.74	−0.73							
	$q(I)_{AIM}$	−0.90		−0.85						
$\tilde{A}^1E$	E	5.57	5.49	4.49	4.41	4.83	4.18	4.29	5.49	4.25
	f	0.125	0.160	0.072	0.078					
	$q(I)_{Löwdin}$	−0.25	−0.16							
	$q(I)_{AIM}$	−0.67								
$\tilde{B}^1A_1$	E	5.67	5.58	4.61	4.55	4.87				
	f	0.179	0.204	0.155	0.159					
	$q(I)_{Löwdin}$	−0.29	−0.21							

[a] $q(I)$ is the iodine atomic charge, E is the vertical excitation energy (in eV), and f is the oscillator strength.
[b] Taken from [17].
[c] CIS and TD-DFT results from [16].
[d] Taken from [11].
[e] All-electron 6-311++G(df, p) basis set for all atoms.
[f] Stuttgart–Dresden–Bonn ECP basis set for iodine, 6-311++G(df, p) basis set for all other atoms.

predict essentially the same distribution of the excited electron density for $I^-(H_2O)_3$. Population analyses in Tables 1 and 2 also indicate a higher negative charge on the iodine atom for the excited $I^-(H_2O)_3$ cluster than for the $I^-(CH_3CN)$ complex, and thus apparently much less electron transfer to solvent in the case of water. Thus, for iodide–water cluster, a picture emerges, which seems to contrast with that for acetonitrile, and in contradiction with CTTS upon photoexcitation.

This apparent contradiction can be elucidated if we compare the electronic structure of the corresponding solvent *anions* to that of the excited iodide clusters, taking into account the fact that the iodine core tends to repel the excited electron due to exchange repulsion, as recently discussed by Chen and Sheu [17]. In the dipole-bound acetonitrile anion, the excess electron is mostly located 'outside' the molecule, on the methyl group, as shown in Fig. 3. In many dipole-bound anions, the negative charge tends to settle on the electrophilic sites of the host molecule, which usually involve so-called 'dangling' hydrogen atoms [34,35]. A similar situation is observed for the $(H_2O)_3^-$ anion, where the excess electron is located above the plane of three hydrogen atoms, as shown in Fig. 3. We now consider the changes that would take place upon insertion of a neutral iodine atom into
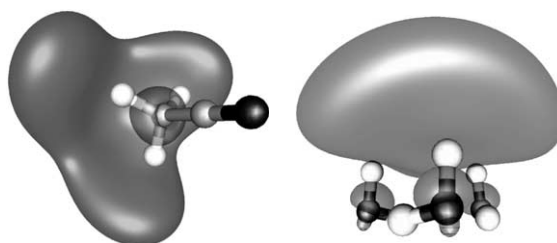

Fig. 3. Electronic density in the highest occupied molecular orbitals of the CH_3CN^- and $(H_2O)_3^-$ anions calculated with the MP2/6-311++G(df, p) model chemistry. The molecular geometries of acetonitrile and the water cluster are taken unrelaxed, from the iodide–solvent cluster structure.

these anions to form the excited iodide–solvent clusters. Repulsion with the iodine core shifts the excited electron into areas where it is still stabilized by the solvent dipole, but does not interact much with the occupied orbitals of the iodine atom. In the case of the acetonitrile complex, it is clear from Fig. 1 that the excited electron is located further towards the methyl group than it is in the bare acetonitrile anion because of repulsions from the iodine core. The stabilization of the excited electron by the acetonitrile dipole may be slightly less than that of the electron in the acetonitrile anion, but interactions with the electrophilic 'dangling' hydrogen atoms and the local C–H bond dipoles

may compensate for this loss of stabilization. As for the water cluster, the distance between the hydrogen atoms pointing at iodine and the iodine atom is smaller than that in the $I^-(CH_3CN)$ complex (2.82 vs. 3.54 Å), and the excited electron tends to shift to the area above the iodine atom, where it is stabilized by the solvent dipole, as seen from Fig. 2. Even if there is some electronic density located near the hydrogen atoms, the excited electron density is located above the iodine atom for the most part. However, even in this case where the excited electron does not seem to 'transfer' to the solvent, the excited state is essentially stabilized by the solvent. As was recently shown by Chen and Sheu [19], upon relaxation, the excited cluster ejects the neutral iodine atom, the excited electron passes around the iodine core and shifts to the water cluster, forming the $(H_2O)_n^-$ anion. Depending on cluster size, the nascent negatively charged solvent cluster may either vibrationally autodetach or rearrange in order to stabilize the excess electron [12]. In contrast, the relaxation of the excited $I^-(CH_3CN)$ complex is presumably a much simpler process, involving very little change in the excited electron density and simply ejection of the iodine atom from the cluster. This may explain the high yields of CH_3CN^- anions observed experimentally upon photoexcitation of the iodide–acetonitrile complex [10].

4. Concluding remarks

Charge-transfer-to-solvent (CTTS) precursor states of the iodide–acetonitrile complex have been investigated by means of quantum-chemical calculations and compared with those of iodide–water clusters. The calculated vertical excitation energies are found to be in good agreement with experimental results, and TD-DFT seems to perform particularly well for these systems. A detailed analysis of the electron density difference between the ground and excited states indicate that, upon photoexcitation, an electron is promoted from one of the iodide valence p orbitals to the acetonitrile molecule. In the case of iodide–water cluster photoexcitation, transfer of the electron to the solvent network is not as obvious and the excited

electron appears mostly located on top of the iodine atom, even though it is stabilized be a concerted action of the solvent. Analysis of the electronic density in the corresponding solvent anions shows that the apparent difference in the electronic structure of the excited $I^-(CH_3CN)$ and $I^-(H_2O)_3$ clusters can be rationalized in terms of the repulsion between the excited electron and the neutral iodine core, as well as the availability of solvent electrophilic sites which help stabilize the excess negative charge.

Acknowledgements

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