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G. Sciaini, R. Fernández-Prini, D. A. Estrin, and E. Marceca

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Short-range and long-range solvent effects on charge-transfer-to-solvent transitions of I^- and K^+I^- contact ion pair dissolved in supercritical ammonia

G. Sciaini

INQUIMAE-DQIAQF, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, C1428EHA Buenos Aires, Argentina

R. Fernández-Prini

INQUIMAE-DQIAQF, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, C1428EHA Buenos Aires, Argentina and Unidad de Actividad Química, Comisión Nacional de Energía Atómica, Avenida del Libertador 8250, 1429 Buenos Aires, Argentina

D. A. Estrin and E. Marceca^{a)}

INQUIMAE-DQIAQF, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, C1428EHA Buenos Aires, Argentina

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Vertical excitation and electron detachment energies associated with the optical absorption of iodide ions dissolved in supercritical ammonia at 420 K have been calculated in two limiting scenarios: as a solvated free I^- ion and forming a K^+I^- contact ion pair (CIP). The evolution of the transition energies as a result of the gradual building up of the solvation structure was studied for each absorbing species as the solvent's density increased, i.e., changing the NH_3 supercritical thermodynamic state. In both cases, if the solvent density is sufficiently high, photon absorption produces a spatially extended electron charge beyond the volume occupied by the solvated solute core; this excited state resembles a typical charge-transfer-to-solvent (CTTS) state. A combination of classical molecular dynamics simulations followed by quantum mechanical calculations for the ground, first-excited, and electron-detached electronic states have been carried out for the system consisting of one donor species (free I^- ion or K^+I^- CIP) surrounded by ammonia molecules. Vertical excitation and electron detachment energies were obtained by averaging 100 randomly chosen microconfigurations along the molecular dynamics trajectory computed for each thermodynamic condition (fluid density). Short- and long-range contributions of the solvent–donor interaction upon the CTTS states of I^- and K^+I^- were identified by performing additional electronic structure calculations where only the solvent interaction due to the first neighbor molecules was taken into account. These computations, together with previous experimental evidence that we collected for the system, have been used to analyze the solvent effects on the CTTS transition. In this paper we have established the following: (i) the CTTS electron of free I^- ion or K^+I^- CIP presents similar features, and it gradually localizes in close proximity of the iodine parent atom when the ammonia density is increased; (ii) for the free I^- ion, the short-range solvent interaction contributes to the stabilization of the ground state more than it does for the CTTS excited state, which is evidenced experimentally as a blueshift in the maximum absorption of the CTTS transition when the density is increased; (iii) this effect is less noticeable for the K^+I^- ion pair, because in this case a tight solvation structure, formed by four NH_3 molecules wedged between the ions, appears at very low density and is very little affected by changes in the density; (iv) the long-range contribution to the solvent stabilization can be neglected for the K^+I^- CIP, since the main features of its electronic transition can be explained on the basis of the vicinity of the cation; (v) however, the long-range solvent field contribution is essential for the free I^- ion to become an efficient CTTS donor upon photoexcitation, and this establishes a difference in the CTTS behavior of I^- in bulk and in clusters. © 2007 American Institute of Physics. [DOI: 10.1063/1.2723723]

INTRODUCTION

Electron photodetachment from isolated atomic, molecular, and ionic species to the continuum is nowadays a well-understood process, which has been extensively used to in-

vestigate the system's reactive channels in the excited state.^{1–3} In the presence of solvent molecules, the situation changes radically due to the strong coupling of the system ground and excited states with the interacting solvent field.⁴ Visible or UV photoexcitation of many anionic solutes in solution and in clusters frequently leads to the appearance of optical charge-transfer absorption bands, located at lower en-

^{a)}Author to whom correspondence should be addressed. Electronic mail: marceca@qi.fcen.uba.ar

ergies than the vacuum detachment threshold; they are normally referred to as charge-transfer-to-solvent (CTTS) transitions.⁵ The excitation responsible for such bands can be described as a promotion of an electron from the solute donor to a somewhat diffuse state which is bound by the interacting field of the surrounding solvent molecules. The absorption energy of CTTS bands has been used to give an insight into the structure of the solvent surrounding a photoexcitable solute; these studies have contributed to the understanding of many features of the solvation phenomenon in recent years.⁶ However, most of the results are limited to describing the spatial delocalization of the excited electron within the first solvation shell of the donor, apparently neglecting the effect that distant solvent molecules could have on the stabilization of the system or the presence of a counterion close to the donor, as is the case of ion pairs.

The CTTS excitation has been studied in many systems starting with polar liquids in the 1960s; the studies of this process were reviewed by Blandamer and Fox⁵ who gave abundant references. In a more recent review,⁷ the importance of electron transfer as a “critical link” was highlighted for the understanding of many electron photoexcitation processes. More recently, dynamic aspects of the CTTS excitation and electron photodetachment from halide ions, mostly iodide, in water clusters^{4,8–10} and in aqueous solution^{11–14} have been extensively investigated with the object of characterizing the solvent restructuring associated with the phenomenon. Although the electronic structure of iodide CTTS excited states and their evolution along the solvent coordinate are well known at present, less information exists about other types of CTTS donors. In particular, photoabsorption by ion pairs was rarely taken into account since most of these experiments were performed in solutions of polar liquid solvents at temperatures close to their triple point. Under these conditions alkali metal halide solutions that have been routinely used to generate CTTS states will have the solvated free halide ion as the only optically absorbing species; hence, the influence of the counterion to the CTTS excitation can be neglected. Only for very high ionic strengths it has been suggested¹⁵ that ion pairing could affect the overall dynamics of the process. It is reasonable to expect that halide ions which form an ion pair can still act as an efficient CTTS donor when photoexcited in solution.^{16,17} Recent experiments of photodissociation of NaI pairs^{18,19} in water and ammonia clusters, as well as the results derived from the electronic structure calculation of the excited state of different ion pairs in small aqueous clusters,^{20,21} motivated us to study the UV absorption of K^+I^- pairs dissolved in a bulk solvent environment. Our experimental results¹⁶ and model calculations¹⁷ showed that the photoexcitation of the K^+I^- contact ion pair (CIP) dissolved in ammonia also occurs by a CTTS mechanism. We observed that for a reduced density $\rho_1^* > 0.07$ ($\rho_1^* = \rho_1/\rho_{1t}$, where ρ_1 is the molar density of ammonia and ρ_{1t} corresponds to the triple point) photon absorption produces a spatially extended electronic charge beyond the volume occupied by the CIP solvated solute core. This excited state resembles that of a typical CTTS state produced by an excited anion in solution of polar liquid solvents. Figure 1 depicts the spatial distribution of the CTTS electron

FIG. 1. Illustrative picture of the CTTS state for an I^- ion (a) and a K^+I^- contact pair (b) dissolved in ammonia, from a typical snapshot of a simulation run at a fluid density $\rho_1^* = 0.827$ and $T = 420$ K. The solvent molecules are not shown in the figure for the sake of clearness. Isovalue contours were obtained as shown in Fig. 3(b), see text for further details.

excited from an I^- ion and from a K^+I^- contact ion pair dissolved in ammonia, for a typical snapshot of a simulation run at a fluid density $\rho_1^* = 0.827$ and $T = 420$ K.²²

Supercritical ammonia in the reduced density range $\rho_1^* = 0.07$ – 0.83 was chosen as the solvent medium because by varying its density it was possible to have either free iodide ions or K^+I^- CIPs with sufficiently high concentrations to observe their optical absorption.¹⁶

The optical excitation of iodide anions in supercritical NH_3 revealed that not only the free solvated anion but also the CIP species act as efficient CTTS donors.¹⁶ However, the two CTTS states will exhibit marked differences between them due to the proximity of the potassium counterion to the donor in the CIP; K^+ ions dominate the solvent structure around the photoexcitable species producing substantial alterations with respect to the solvation structure in free iodide ion.

In this work, using electronic structure calculations, we describe the vertical excitation and electron detachment energies of CTTS states associated with the optical absorption of iodide ions in two limiting scenarios: as a solvated free I^- ion and forming a K^+I^- CIP. We compare the results obtained for the two donor species and also analyze the evolution of the two CTTS states as a result of the gradual building up of the solvation structure surrounding the donor species as the solvent's density is increased, i.e., changing the NH_3 supercritical thermodynamic state. The results of our calculations will show that the long-range solvent effect strongly contributes to the stabilization of the CTTS states generated by photoexcitation of I^- , while this interaction is almost absent when the donor species is the CIP. Hence, we confirm in agreement with Bradforth and Jungwirth²³ that the information provided by the study of molecular clusters that contain the I^- ion cannot be directly related to the behavior observed in the bulk because the role of distant solvent molecules is absent in the confined systems. On the other hand, a different behavior was found for the CTTS electronic transition of the K^+I^- CIP in bulk solvent, which we conclude can be easily related to that in clusters.

Classical molecular dynamics simulations with periodic boundary conditions followed by quantum mechanical calculations have been carried out for the system consisting of one I^- ion surrounded by ammonia molecules for the ground, first-excited, and electron-detached electronic states; the main set of the results was obtained for a system having the ion solvated in a box containing 215 NH_3 molecules. Aver-

ages were obtained from 100 randomly chosen microconfigurations along the molecular dynamics trajectory computed for each thermodynamic condition (fluid density). The results were compared with previous and new calculations made on the system formed by K^+I^- CIPs dissolved in ammonia.⁶

COMPUTATIONAL METHOD

The calculations were performed following the computational procedure proposed by Bradforth and Jungwirth²³ for the excited state of iodide anions dissolved in water, which combines a molecular dynamics trajectory-sampling technique with an efficient quantum electronic structure calculation method. Recently, we have successfully applied this method to ammonia solutions of K^+I^- CIPs in supercritical conditions.^{6,17} In the present work, we use the same procedure to describe the CTTS states for I^- in NH_3 and give a description of the computational method validation.

Molecular dynamics *NVT* runs with classical model intermolecular potentials and periodic boundary conditions were carried out to sample the configurational space of I^- dissolved in supercritical ammonia, using the AMBER8 package.²⁴ The runs were made for one I^- ion dissolved in a box containing 215 ammonia molecules at a temperature of 420 K, and the evolution of the system was monitored over 200 ps, after 50 ps of equilibration, using a time step of 0.4 fs. Different values of ρ_1 for the simulation runs were obtained by adjusting adequately the volume of the simulation box. The *ab initio* electronic structure calculations were done for randomly chosen snapshots along the molecular dynamics trajectories, according to the method described below.

The solvent's intermolecular interaction was represented by the rigid ammonia model proposed by Impey and Klein.²⁵ These model NH_3 molecules have partial charges located on four sites and a Lennard-Jones core. Although the model underestimates the dielectric constant of the fluid²⁶ ($\epsilon_D=9.8$ versus the experimental value $\epsilon_D^{\text{expt}}=18.2$ at 298 K) it provides a good representation of the structure of liquid ammonia^{25,26} and it was also used to describe adequately the behavior of solvated electrons in supercritical ammonia.²⁷ As a consequence of the lower ϵ_D values obtained with the model, it might be expected that the experimental long-range solvent effects on the photoexcitation of I^- would be somewhat larger than those calculated using this model. Iodide ions interact with ammonia particles through their charges and Lennard-Jones cores. The Lennard-Jones coefficients for the $\text{I}^- \cdots \text{NH}_3$ interaction was chosen such that the minimum energy of the pair gave results close to the experimental or the *ab initio* calculated values, as reported elsewhere.^{28–30} Further details about the simulation runs and the interaction parameters used were given in Ref. 16.

Although highly demanding quantum multiconfigurational procedures would be generally required for studying low-lying excited states in detail, *ab initio* single-reference quantum methods can still provide important semiquantitative information about the excited state of systems such as iodide ions in solution. This approach has been successfully

employed for I^- dissolved in water²³ and for K^+I^- ion pairs dissolved in ammonia.^{16,17} In the following paragraphs we shall show that the lowest electronic state having a triplet spin multiplicity for I^- (and for K^+I^- ion pairs) dissolved in ammonia provides a very good description of the excited CTTS state of the system, which agrees with the observations of Bradforth and Jungwirth²³ for aqueous solutions of iodide ions. We used the GAUSSIAN98 package³¹ to calculate the energy and charge distribution of the lowest electronic state for the singlet and triplet spin multiplicities, employing the Hartree-Fock (HF) method and the Møller-Plesset second order perturbation theory (MP2). The correctness of this approximation which ignores the effect that the spin multiplicity causes on the excited CTTS state is based on the fact that upon excitation the $5p$ electron remains very loosely bound to the iodine core and consequently its space-charge distribution and energy will be almost unaltered by a change on the wave function spin. On the following paragraphs, we will refer to CTTS excited states calculated using the previous approximation as HF-CTTS states. Single-excitation configuration interaction (CIS) method was used to establish the validity of this approximation for the donor species dissolved in ammonia. The CIS calculation showed a small singlet-triplet energy splitting for the excited state of about 0.3 eV for $\rho_1^*=0.827$ and the difference was even smaller at lower densities, reaching the value of 0.0 eV for $\rho_1^*=0$ when the photoexcited electron detaches from the iodine core.

The electronic structure of iodide ions was computed using a basis set augmented by diffuse basis functions. The effect of the solvent was incorporated in the Hamiltonian by adding an external potential given by the same point-charge model employed in the molecular dynamics simulations. The inclusion of diffuse basis for the solute became crucial because of the high spatial extension of the electron density in the excited state. For the iodine atom, we have employed LANL2DZ basis functions with a pseudopotential core. This basis set was augmented by inclusion of a very diffuse *s* set with eight exponents forming a geometric series with a factor of 2 with the lowest exponent of 1.406×10^{-3} , plus a *p* set with an exponent of 0.500 and six exponents forming a geometric series with a factor of 2 and a lowest exponent of 4.688×10^{-4} and, finally, a *d* basis with an exponent of 0.100 was added. We found that these basis functions were suitable for describing this type of system since the MP2 calculation yielded an ionization potential for the bare iodide ion which showed excellent agreement with the experimental result,³² and reproduced adequately the values of the vertical excitation energy (E_{max}) and vertical ionization potential [also referred to as vertical detachment energy (VDE)], corresponding to the aqueous iodide clusters $\text{I}^-(\text{H}_2\text{O})_N$, $N=2-6$, reported in the literature.⁸

The contours shown in Fig. 2 are two qualitative representations of how the electron spatial distribution changes when the ground state is photoexcited to the first singlet [panel (a)] or triplet [panel (b)] states for a K^+I^- CIP dissolved in supercritical ammonia at $\rho_1^*=0.591$ and $T=420$ K. The calculations were done using CIS and the contours result from subtracting the electron density function corresponding to the ground electronic state from that of each excited state,

FIG. 2. Illustration of the spatial distribution of the excited electron (light gray: negative-sign contour) and location of the electron density before the transition (dark gray: positive-sign contour) for a K^+I^- pair dissolved in ammonia at a fluid density $\rho_1^*=0.591$ and $T=420$ K, calculated using CIS. The contours result from subtracting the electron density function of the ground state from those of the first excited singlet (a) and for the first excited triplet (b). For both panels, the cutoff isodensity value is $0.0004 \text{ \AA}^{-3}$.

using the same snapshot of a simulation run. The spatial distribution of the excited electron for the K^+I^- pair after the transition is represented by negative-sign isodensity contours, shown in light gray in Fig. 2. The similarity exhibited by both contours supports the assumption that for our system the spin multiplicity has very little influence on the characteristics of the excited state.

The positive-sign isodensity contours, shown in dark gray in Fig. 2, represent the location of the electron density before the transition (ground state). The shape of the contours resembles a p atomic orbital, which under these conditions is orthogonal to the CIP axis and centered on the iodine atom. The visual comparison done in Fig. 2 for the CIP was repeated for the donor I^- dissolved in ammonia and an even smaller difference due to the higher symmetry was found for this system.

Further evidence supporting the correctness of using HF-CTTS wave functions may be found in Fig. 3, where the highest occupied orbital of the HF-CTTS state for K^+I^- CIP dissolved in supercritical ammonia at $\rho_1^*=0.591$ and $T=420$ K is depicted together with the negative-sign isodensity contour resulting from the difference of the CIS electron density functions (shown previously in Fig. 2). It can be verified that both computation methods yield very similar representations of the spatial distribution of the excited electron.

When using single-reference methods such as HF or MP2, E_{max} was calculated by averaging over about 100 ran-

FIG. 3. Illustration of the spatial distribution of the excited electron for a K^+I^- pair dissolved in ammonia at a reduced fluid density $\rho_1^*=0.591$ and $T=420$ K: (a) negative-sign contour resulting from subtracting the electron density function of the ground state from that of the first excited singlet (calculated using CIS); (b) contour of the highest occupied orbital of the HF-CTTS excited state. For panel (a), the cutoff isodensity value is $0.0004 \text{ \AA}^{-3}$; for panel (b), the cutoff value on the wave function amplitude is $0.023 \text{ \AA}^{-3/2}$.

FIG. 4. Illustration of the spatial distribution of a CTTS excited electron for I^- dissolved in ammonia at a fluid density $\rho_1^*=0.236$ and $T=420$ K. Contour of the highest occupied orbital of the HF-CTTS state for (a) first neighbor quantum $6-31++G^*$ ammonia molecules (the remaining NH_3 molecules were taken as point charges), and (b) all the solvent structure is modeled by a collection of point charges. For both panels, the cutoff value on the wave function amplitude is $0.011 \text{ \AA}^{-3/2}$.

domly selected molecular dynamics microconfigurations the energy difference between the lowest electronic states having triplet and singlet spin multiplicities. Additionally, HF and MP2 values for VDE were computed as the energy difference between the state generated by removing one electron from the system and the ground state, averaged over about 100 snapshots during the simulation. When the CIS method was employed, E_{max} was taken as the energy difference of the first excited singlet and the ground states. As we are interested to study how the solvent structure gradually perturbs the energetics associated with the charge transfer process, all the calculations were repeated for different ρ_1^* at $T=420$ K.

We have already shown^{6,17} that due to the characteristics of the CTTS states, the effect of the solvent field on the excitation of K^+I^- pairs can be adequately represented by a simple distribution of point charges around the quantum donor species. In Fig. 4 we show that the same assumption applies to the free I^- dissolved in ammonia, since a similar spatial distribution is obtained for the CTTS excited electron in both situations: (i) the first neighbors are treated quantum mechanically [panel (a)], or (ii) all the solvent interacting field is modeled by a distribution of molecules represented by point charges [panel (b)]. In the figure, the gray surfaces represent the HF contours of the highest occupied molecular orbitals (HOMOs) of the excited state, calculated using a typical snapshot taken from the simulation run at a reduced density $\rho_1^*=0.236$ and a temperature $T=420$ K.

Figure 4 shows that although the Pauli exclusion of the CTTS excited electron for the ammonia electrons is absent in the HOMO contour calculated using the point-charge solvent field [smooth electron distribution on panel (b)], the symmetry and spatial extent of the excited electron are very similar for both representations.

Quantum I^- ions and K^+I^- ion pairs dissolved in the point-charge model ammonia proved to be an adequate description of the system since, for several snapshots, this approach yielded values of E_{max} and VDE which reproduced within less than 0.2 eV the values obtained if the first solvation shell was also included in the quantum calculation. The fact that the CTTS transition energy and the vertical detachment energy resulted almost unaffected when the solvent

TABLE I. Vertical excitation energy ($E_{\max}$) and vertical detachment energy (VDE) of I^- and K^+I^- dissolved in ammonia at $T=420$ K and different fluid densities obtained using the HF, MP2, and CIS computation schemes.

ρ_1^*	$\text{I}^- (sv)$					$\text{K}^+\text{I}^- (sv)$				
	$E_{\max} \text{ (eV)}$			VDE (eV)		$E_{\max} \text{ (eV)}$			VDE (eV)	
	HF	MP2	CIS	HF	MP2	HF	MP2	CIS	HF	MP2
0.071	3.56	4.07	4.45	3.66	4.22	4.43	4.81	5.32	6.73	7.28
0.236	3.79	4.26	4.68	4.01	4.57	4.52	4.89	5.41	6.76	7.32
0.426	4.06	4.48	4.94	4.32	4.88	4.68	5.02	5.57	6.86	7.41
0.591	4.27	4.66	5.15	4.56	5.11	4.84	5.16	5.72	7.02	7.57
0.827	4.53	4.88	5.39	4.86	5.41	4.99	5.28	5.87	7.08	7.63

model was substituted by quantum mechanically treated molecules was already observed by Bradforth and Jungwirth²³ for the iodide-water system. This indicates that the excited electron is distributed over the empty space that exists within the solvent structure, and consequently a complete description of the electronic structure of the solvent molecules becomes unnecessary.

RESULTS

Table I summarizes the values obtained for $E_{\max}$ and VDE of I^- dissolved in ammonia at 420 K and at different fluid densities obtained using the HF, MP2, and CIS calculation schemes. In the same table, we have included new and already published^{6,17} results which were obtained for K^+I^- CIP dissolved in ammonia, under the same conditions; in this way it will be easier to underline the differences between both photoexcitable species.

All the methods show the same dependence of $E_{\max}$ and VDE against ρ_1^* , although for a given donor species we obtained higher absolute values for $E_{\max}$ when going from HF to MP2 (about 0.3–0.5 eV) and from MP2 to CIS (also 0.4–0.6 eV). Concerning the VDE values, we observed an increase of about 0.4–0.5 eV when going from HF to MP2. These differences are typical of the use of different calculation procedures; nevertheless an important characteristic can be drawn from the data reported in Table I. Along the explored ρ_1^* range, the values corresponding to the difference $\Delta E_{\max}$ (and ΔVDE) between the excitation (and electron detachment) energies of the donors I^- and K^+I^- are very similar for all the calculation procedures considered in this work, exhibiting a difference of only 0.1 eV. This indicates that the effect on the excited electron produced by incorporating a K^+ cation in the close vicinity of the iodide ion is correctly

described by the HF, MP2, and CIS calculations. For simplicity, throughout the paper we shall focus on the results obtained using the MP2 approach because it yields better values for $E_{\max}$ in comparison to the experimental measurements.¹⁶

With the purpose of analyzing the short- and long-range contributions of the solvent-donor interaction upon the CTTS states of I^- and K^+I^- , we have repeated the calculation of the electronic structure over all the snapshots used in Table I, but this time taking into account only the solvent interaction due to the first neighbor molecules, modeled as a distribution of point charges. First neighbor NH_3 molecules were those closer than the first minimum of the radial distribution function¹⁶ $g_{\text{ion-N}}$ (0.55 nm for I^- and 0.40 nm for K^+); for the free iodide, they were those at $r \leq 0.55$ nm from I^- , and for the CIP they were those at $r \leq 0.40$ nm from K^+ or $r \leq 0.55$ nm from I^- . Excitation and detachment energies obtained using MP2 when only the contribution to the solvent interaction of the first solvation shell was taken into account are shown in Table II, denoted by $E'_{\max}$ and VDE' , respectively. The table also gives the values of $E_{\max}$ and VDE reported in Table I for the MP2 calculation.

First, we shall concentrate on the behavior of the donor $\text{I}^-(sv)$. According to our previous experimental work,¹⁶ these and the calculated values of $E_{\max}$ (and $E'_{\max}$) for this species in Table II exhibit marked shifts to the blue when ρ_1^* increases. This effect was observed over the whole range of fluid densities and is considered a direct consequence of the ionic character of the ground electronic state of I^- for which a progressive stabilization due to the denser solvent structure is expected to occur. At the same time, it must be considered that the solvent interaction on the excited CTTS state is much weaker than that on the ground state, because of the

TABLE II. MP2 vertical excitation ($E_{\max}$) and detachment energies (VDEs) of I^- and K^+I^- dissolved in ammonia at $T=420$ K and different fluid densities. (') indicates that the solvent interaction was restricted to the first neighbor molecules in the calculations. All values are tabulated in eV.

ρ_1^*	$\text{I}^- (sv)$				$\text{K}^+\text{I}^- (sv)$			
	$E_{\max}$	$E'_{\max}$	VDE	VDE'	$E_{\max}$	$E'_{\max}$	VDE	VDE'
0.071	4.07	3.89	4.22	3.89	4.81	4.76	7.28	7.26
0.236	4.26	3.93	4.57	3.93	4.89	4.79	7.32	7.30
0.426	4.48	4.11	4.88	4.11	5.02	4.91	7.41	7.42
0.591	4.66	4.30	5.11	4.30	5.16	5.02	7.57	7.49
0.827	4.88	4.48	5.41	4.49	5.28	5.13	7.63	7.59

FIG. 5. Vertical detachment energy of the CTTS state for the species I^- as a function of ρ_1^* . The values were calculated using MP2 and a point-charge distribution for the solvent structure. ■: VDE^* , all solvent molecules; ○: VDE'^* , only the first neighbor solvent molecules.

larger degree of delocalization of the electronic charge. Concerning the values of E_{max} and E'_{max} in Table II, they differ by about 0.35 eV from each other and present the same trend when plotted against ρ_1^* , indicating that the first solvation shell is responsible for most the stabilization effect described above.

The values of VDE shown in Table II for I^- also experience a blueshift when plotted against ρ_1^* due to the increasing stabilization of the ionic ground state with respect to the electron detachment level. On the other hand, the stabilization energy of the CTTS state with respect to the level of detachment (vertical detachment energy of the excited state), which is denoted by $\text{VDE}^* = \text{VDE} - E_{\text{max}}$, is very small for I^- indicating that, within the studied density range, the CTTS electron remains very loosely bound after the excitation. However, at higher densities the stabilization energy of the CTTS state due to the interaction with ammonia molecules increases weakly and reaches the value $\text{VDE}^* \approx 0.5$ eV at $\rho_1^* = 0.827$.

An interesting feature emerges when we notice that the values of E'_{max} and VDE' given in Table II for the species I^- are almost identical, indicating that no further significant stabilization energy occurs for the CTTS state ($\text{VDE}'^* \approx 0$) when the calculations take into account NH_3 molecules beyond the first solvation shell. The distinct behavior of VDE^* and VDE'^* as a function of the fluid density for this donor reveals that the long-range contribution to the solvent stabilization is significant for the existence of CTTS bound states in the solutions of I^- dissolved in ammonia. In Fig. 5 the quantities VDE^* and VDE'^* are plotted against the density for this system.

If the difference ($\text{VDE}^* - \text{VDE}'^*$) is due to the long-range contribution to the solvent field stabilization, we can conclude that the CTTS state of I^- dissolved in ammonia will be favored by an increase in the fluid density. This result has been already observed by Bradforth and Jungwirth²³ in aqueous solutions of I^- .

The behavior of the donor $\text{K}^+\text{I}^-(\text{sv})$ is very different. In this case, the blueshifts of E_{max} (and E'_{max}) caused by an increasing ρ_1^* are smaller than for I^- since the solvent struc-

FIG. 6. Ground (and CTTS excited) state energy of the species $\text{K}^+\text{I}^-(\text{sv})$ and $\text{I}^-(\text{sv})$ as a function of ρ_1^* . The energy of the state attained after vertical electron detachment is taken as equal to zero. Solid lines: all solvent molecules; dotted lines: only the first neighbor solvent molecules. Representative transitions (vertical excitation and detachment from the excited state) are indicated by arrows, for each donor.

ture is mainly determined by the ammonia- K^+ interaction and the solvent effect is similar for the ground and CTTS states (see Table II). Moreover, the blueshift is nearly absent according to the experimental measurements¹⁶ of E_{max} performed for this system.

As a consequence we found that the long-range contribution to the solvent field stabilization is much weaker for the donor $\text{K}^+\text{I}^-(\text{sv})$, since the calculated values for the vertical excitation and detachment energies show very small variations when the solvent interaction is restricted to the first neighbor NH_3 molecules. The values obtained for E_{max} (and VDE) differ from those corresponding to E'_{max} (and VDE') less than 0.15 eV (cf. Table II). A plausible explanation for this observation is that the presence of the K^+ ion mostly determines the optical properties exhibited by the donor $\text{K}^+\text{I}^-(\text{sv})$. This is due to two reasons: (i) the K^+ ion creates a more rigid first solvation shell around the ion pair¹⁷ and (ii) its positive charge was found essential in order to attain a bound CTTS state for the system. Electronic structure calculations of snapshots along the molecular dynamics trajectories in which the charge of the cation was removed did not result in a bound electronic excited state, in spite of the fact that the solvent field was the same as that for the CIP with a charged potassium ion.

DISCUSSION

Assuming that the energy of the electronic state generated after vertical electron detachment is equal to zero, the data shown in Table II can be used to represent how the energy of the ground (and the excited CTTS) state of $\text{K}^+\text{I}^-(\text{sv})$ and $\text{I}^-(\text{sv})$ varies as a function of the ammonia density. This is illustrated in Fig. 6 which shows more clearly the different behavior found for the donors $\text{I}^-(\text{sv})$ and $\text{K}^+\text{I}^-(\text{sv})$ upon the photoexcitation and electron detachment processes, and how these phenomena are coupled to the solvent structure. The energy curves plotted as solid lines correspond to the calculations performed for the entire system and the dotted lines indicate that only the interaction of the donors with the solvent molecules in the first solvation shell

is considered. The most remarkable feature is the fact that for $I^-(sv)$ the energy of the ground (and the excited CTTS) state is substantially reduced by extending the solvation structure from the first neighbor to more distant NH_3 molecules. The stronger long-ranged ion-solvent effect exhibited by the ground (and the excited CTTS) state of $I^-(sv)$, represented schematically in Fig. 6 by a hatched region between the solid and the dotted lines, increases with ρ_1^* . This agrees with the change of the dielectric constant of the medium. In particular, the long-range effect of the solvent interaction stabilizes the CTTS state of $I^-(sv)$ and prevents the excited electron to reach the detachment threshold. Being a long-range effect, we observed that its value increases somewhat for a larger simulation box, remaining the qualitative behavior of the system unchanged. From calculations done on a few boxes of different sizes, we estimate that at the thermodynamic limit the difference will not exceed 0.5 eV. Consequently, the long-range effect for I^- in bulk ammonia is expected to be more pronounced than that shown in Fig. 6. On the other hand, for K^+I^- CIPs dissolved in ammonia the long-range solvent interaction is almost absent; this is represented in the left panel of Fig. 6 by the close proximity of the solid and dotted lines. For this species, the size of the simulation box did not alter the calculated values.

The fact that the energy of the ground (and the excited CTTS) state of the ion pair $K^+I^-(sv)$ only exhibits a hardly noticeable change when the long-range CIP-solvent interaction is taken into account, even at the highest fluid densities, reveals that the electric field of the CIP fades away very rapidly with the distance from the ion pair as a consequence of the efficient dielectric screening caused by the nearest solvent molecules; this is due to the fact that the contact pair essentially acts as a dipole, hence having a shorter-range electrostatic interaction.³³ We have already observed for this system¹⁷ that a tight solvation structure, formed by four NH_3 molecules located in the interionic region of the K^+I^- CIP, appears at very low density and is very little affected by changes in ρ_1^* . The CIP and the four interionic NH_3 neighbors, oriented so that they bridge both ions, can be considered as a moiety which preserves essentially the same structure along the molecular dynamics trajectory.

The interaction between the free iodide ion and NH_3 molecules decreases less rapidly as a function of the distance and consequently the long-range solvation effect is clearly observed for this system. The relative importance of long-range versus short-range solvent interaction increases at higher fluid density, because of the larger number of solvent molecules present around the donor. For this reason, it must be borne in mind that the use of I^- dissolved in confined systems in order to understand solvation phenomena in the bulk solvent has to be done with caution, since in the confined systems the interaction with solvent molecules is mainly restricted to those molecules that surround closely the donor species.

Finally, we will analyze the effect of the short-range solvent interaction on the CTTS transition of $K^+I^-(sv)$ and $I^-(sv)$ dissolved in ammonia. First, we will focus on the excited CTTS state. For both donor species, we have calculated the solvent-averaged mean distance between the ex-

FIG. 7. Solvent-averaged electron-iodine mean distance $\langle r_{I-e^-} \rangle$ and electron dispersion σ_{e^-} of the HF-CTTS excited state for the species $K^+I^-(sv)$ (squares) and $I^-(sv)$ (circles), as a function of the reduced medium density ρ_1^* , at $T=420$ K. The averaged values were obtained from about 100 randomly selected molecular dynamics microconfigurations.

cited electron and the iodide core $\langle r_{I-e^-} \rangle$, as well as the dispersion of the excited electron σ_{e^-} . These two quantities were defined according to the following expressions:

$$\langle r_{I-e^-} \rangle = \langle \langle \psi_{CTTS} | \mathbf{r} | \psi_{CTTS} \rangle - \langle \psi_n | \mathbf{r} | \psi_n \rangle \rangle, \quad (1)$$

$$\sigma_{e^-} = \langle (\langle r_{I-e^-}^2 \rangle - \langle r_{I-e^-} \rangle^2)^{1/2} \rangle, \quad (2)$$

where $\langle r_{I-e^-}^2 \rangle$ was evaluated as

$$\langle r_{I-e^-}^2 \rangle = \langle \langle \psi_{CTTS} | \mathbf{r}^2 | \psi_{CTTS} \rangle - \langle \psi_n | \mathbf{r}^2 | \psi_n \rangle \rangle. \quad (3)$$

The wave functions in Eqs. (1)–(3) have been calculated taking the position of the iodine atom as the center of coordinates and using the HF approach. The HF-CTTS excited state was represented by the ψ_{CTTS} wave function and the system remaining after the electron detachment by ψ_n . The values $\langle r_{I-e^-} \rangle$ and σ_{e^-} were calculated using the same averaging procedure employed before for $E_{\max}$ and VDE, i.e., about 100 randomly selected microconfigurations were taken from the molecular dynamics runs, for each density condition, at $T=420$ K. In Fig. 7 the values obtained for $\langle r_{I-e^-} \rangle$ and σ_{e^-} are plotted as a function of ρ_1^* .

We have found that the CTTS electron of $K^+I^-(sv)$ or $I^-(sv)$ presents similar features when the density is increased. For both donor species, the mean position of the excited electron gradually localizes closer to the parent iodine atom and, at the same time, the electron dispersion decreases as a function of ρ_1^* and converges towards a common value. These observations agree with the fact that, when the fluid density is sufficiently high, the CTTS electron wave function is squeezed into the small voids existing among the solvent molecules located in close proximity of the iodine parent atom. Under these conditions, the short-range solvent interaction on the CTTS state will experience only minor variations with the density of the fluid. This is shown in Fig. 6,

where the energy curves corresponding to the CTTS states of $K^+I^-(sv)$ and $I^-(sv)$ have small slopes for $\rho_1^* > 0.7$.

As expected when ρ_1^* increases the short-range solvent interaction lowers the energy of the ground state corresponding to the species $K^+I^-(sv)$ and $I^-(sv)$, the effect being more noticeable for the free ion than for the ion pair (cf. Fig. 6). The presence of a K^+ counterion in the CIP is responsible for increasing to about 2 eV the stability of the $K^+I^-(sv)$ ground and CTTS states with respect to those of $I^-(sv)$, over the whole density range. The stabilization due to the presence of the K^+ in the CIP is responsible for having a bound CTTS state for the system.

CONCLUSION

In this paper we have established the following: (i) the CTTS electron of free I^- ion or K^+I^- CIP presents similar features, and it gradually localizes in close proximity of the iodine parent atom when the ammonia density is increased; (ii) for the free I^- ion, the short-range solvent interaction contributes to the stabilization of the ground state more than it does for the CTTS excited state, which is evidenced experimentally as a blueshift in the maximum absorption of the CTTS transition when the density is increased; (iii) this effect is less noticeable for the K^+I^- ion pair, because in this case a tight solvation structure, formed by four NH_3 molecules wedged between the ions, appears at very low density and is very little affected by changes in the density; (iv) the long-range contribution to the solvent stabilization can be neglected for the K^+I^- CIP, since the main features of its electronic transition can be explained on the basis of the vicinity of the cation; (v) however, the long-range solvent field contribution is essential for the free I^- ion to become an efficient CTTS donor upon photoexcitation, and this establishes a difference in the CTTS behavior of I^- in bulk and in clusters. Therefore, the different range of the solvent interaction depending on the type of donor species must be taken into account; this will also affect the comparison between the photoexcitation behavior of donors containing iodide in bulk solvents and in clusters.

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