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Electronic properties of liquid ammonia: A sequential molecular dynamics/quantum mechanics approach

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The electronic properties of liquid ammonia are investigated by a sequential molecular dynamics/quantum mechanics approach. Quantum mechanics calculations for the liquid phase are based on a reparametrized hybrid exchange-correlation functional that reproduces the electronic properties of ammonia clusters [$(NH_3)_n$; $n=1-5$]. For these small clusters, electron binding energies based on Green's function or electron propagator theory, coupled cluster with single, double, and perturbative triple excitations, and density functional theory (DFT) are compared. Reparametrized DFT results for the dipole moment, electron binding energies, and electronic density of states of liquid ammonia are reported. The calculated average dipole moment of liquid ammonia (2.05 ± 0.09 D) corresponds to an increase of 27% compared to the gas phase value and it is 0.23 D above a prediction based on a polarizable model of liquid ammonia [Deng *et al.*, J. Chem. Phys. **100**, 7590 (1994)]. Our estimate for the ionization potential of liquid ammonia is 9.74 ± 0.73 eV, which is approximately 1.0 eV below the gas phase value for the isolated molecule. The theoretical vertical electron affinity of liquid ammonia is predicted as 0.16 ± 0.22 eV, in good agreement with the experimental result for the location of the bottom of the conduction band ($-V_0=0.2$ eV). Vertical ionization potentials and electron affinities correlate with the total dipole moment of ammonia aggregates. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2804420]

I. INTRODUCTION

Liquid systems are important in several different areas of natural sciences. They are essential in many chemical reactions affecting molecular properties compared to the isolated *in-vacuum* situation. Among these systems, polar liquids have a special place. In addition, protic liquid systems are very important in physical, chemical, and biological processes. Hydrogen bond (HB) networks[1] characterize the structure of these liquids leading to solvent properties of fundamental interest. This is the case of water that has been of extraordinary interest as well as of ammonia, where much less studies have been devoted. The structural and electronic properties of these molecular liquids are relevant in understanding chemical reactivity in solution since energy transfer can be related to thermal (and charge) induced fluctuations of the network. Although the structure, energetics, and dynamics of HB networks have been the subject of several investigations, their electronic properties are not very well understood and deserve further analysis.[2] One relevant aspect concerns the relationship between the local structure of the HB network and electronic properties such as the dipole moment, ionization energy, and electron affinity. Experimental information on the density of states (DOS) and electronic properties of water were recently reviewed.[2] However, in comparison with water, experimental or theoretical information on the electronic properties of liquid ammonia is scarce, although experimental studies on the ammoniated electron[3–5] and metal atom-ammonia solutions[6] have been reported. Experimental data on the ammoniated electron were also important for comparison with the hydrated electron, which has been the subject of several investigations.[7–10] Theoretical studies on the solvated electron in liquid ammonia,[11] electronic states of small metal-ammonia clusters,[12] and adiabatic dynamics of the ammoniated electron[13] have been reported by Klein and co-workers. These works on excess electrons in ammonia and water reflect the importance of understanding the binding of electrons to polar molecular species.[14]

In this work, we study the electronic structure of liquid ammonia. Initially, we investigate the electronic properties of

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small gas-phase free ammonia clusters that are obtained from geometry-optimized, minimum-energy configurations. This would correspond to the situation found in cluster chemical-physics such as jet cooling. Then, by adopting a sequential molecular dynamics/quantum approach, statistically uncorrelated configurations composed of different numbers of ammonia molecules are sampled from the simulation of liquid ammonia for subsequent quantum mechanics (QM) calculations. In this situation, the structures of the selected aggregates are supermolecular configurations generated by molecular dynamics (MD). By using different numbers of molecular units we investigate how the electronic properties depend on the size of the quantum system and we also consider the effects of the boundaries, where the outer surface of the ammonia aggregate interfaces with the *vacuum* (nonembedded clusters) or with the electrostatic embedding provided by the atomic charges of the remaining ammonia molecules (embedded clusters). As we will see this is an important issue for small clusters and allows us to establish a distinction between the nonembedded cluster and the liquid situation, where surface effects are minimized by the presence of embedding charges.

Sequential computer simulation/quantum mechanics studies[15,16] of the electronic properties of liquids[17–19] were recently reported. The present approach to study electronic properties of liquid ammonia is thus based on the use of computer simulation to generate the structure of the liquid and afterwards density functional theory (DFT) calculations on these structures. For the DFT calculations, a reparametrized hybrid exchange-correlation functional that reproduces *ab initio* electron binding energies of small ammonia clusters is proposed. As discussed below, it is of interest to make a reappraisal of the usual exchange-correlation parametrization to obtain orbital energies that represent a good approximation to electron binding energies. Therefore, we initially report *ab initio* and DFT predictions for the electron binding energies of small ammonia clusters in the geometry-optimized gas phase. Next, we present DFT results for the dipole moment, electronic density of states, and ionization energies of liquid ammonia, using the supermolecular structures selected from the MD simulation. The polarization due to the electronic environment is studied by obtaining the in-solution dipole moment and comparing with the in-vacuum situation. In addition, the present estimate for the average dipole moment in liquid ammonia is compared with a result reported by Deng *et al.*[13] based on a model for liquid ammonia that includes the dipole polarizability of the nitrogen atom. We also discuss the energetics of vertical electron attachment (VEA) to neutral ammonia clusters and its relationship with the total dipole moment of the aggregates. Electron attachment to neutral water clusters has been recently investigated by Turi *et al.*[20] who pointed out the similarity of this process with experiments on electron attachment to cold water clusters under collision-free conditions.[21]

II. COMPUTATIONAL DETAILS

A. Quantum mechanics calculations

Full geometry optimizations (with a very tight convergence criterion) of small ammonia clusters $[(NH_3)_n;\ n=1-5]$ were carried out with frozen-core Møller-Plesset second-order perturbation theory (MP2). The optimized structures are shown in Fig. 1. We are not aware of experimental or theoretical electron binding energies of ammonia clusters and two theoretical approaches were adopted for estimating these energies. The first was Green's function (GF) or electron propagator theory as implemented in the GAUSSIAN-03 suite of programs.[22] In this case, outer valence orbital binding energies were calculated with the partial third-order quasiparticle theory of the electron propagator (P3).[23] In Green's function schemes,[24,25] orbital energies and spectral intensities are available as pole position and pole strengths, respectively, of the spectral representation of the Green's function.[23–26] The second approach was coupled cluster with single and double excitations, and perturbative treatment of triples[27–30] [CCSD(T)], and it was restricted to total energy difference calculations of the neutral and ionic systems to predict the first vertical ionization potentials (IPs) and electron affinities (EAs).

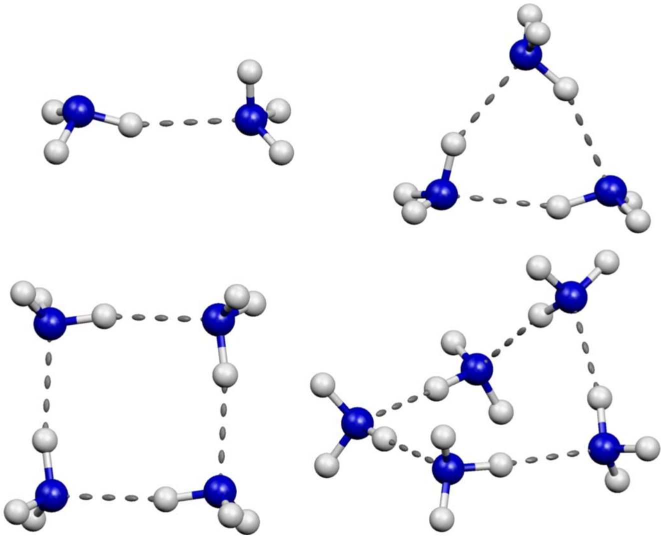

FIG. 1. (Color online) MP2/aug-cc-pVDZ optimized structures of ammonia clusters $(NH_3)_n$, $n=2-5$. Symmetry species and total dipole moments (*D*) are $n=2(C_s)$, $\mu_T=2.32$; $n=3(C_{3h})$, $\mu_T=0$; $n=4(C_{4h})$, $\mu_T=0$; $n=5(C_1)$, $\mu_T=0.13$.

The applications of GF and CCSD(T) are naturally limited to small clusters. To overcome this limitation we are exploring the possibility to predict electron binding energies and electron affinities of ammonia aggregates using DFT calculations. The physical meaning of DFT orbital energies has been recently discussed.[31–33] In an exact DFT theory the energy (with opposite sign) of the highest occupied molecular orbital (HOMO) corresponds to the ionization energy and can be calculated as the difference between the neutral and corresponding ionized systems. However, in approximate DFT theories the two procedures generally give different results (see Ref. 31). Moreover, recent investigations indicate that for occupied orbitals, Kohn-Sham energies are a good approximation to electron binding energies.[19,31–33] We have adopted the following procedure for predicting Kohn-Sham orbital energies. The modified Perdew-Wang functional (MPW1PW91) proposed by Adamo and Barone[34,35] has been reparametrized to reproduce the electron binding energies of small ammonia clusters. The parametrization was based on the representation of the exchange-correlation functional[34,35]

$$E_{xc} = (1 - \alpha)E_x^{\mathrm{HF}} + \alpha(E_x^{\mathrm{Slater}} + \Delta E_x^{\mathrm{mPW}}) + E_c^{\mathrm{local}} + \Delta E_c^{PW91}, \tag{1}$$

where $\Delta E_x^{\mathrm{mPW}}$ is the modified Perdew-Wang exchange-correlation functional and E_c^{local} is the local correlation functional contribution. In the absence of experimental results we will take CCSD(T) calculations as reference. By varying α in expression (1) we have found that when $\alpha=0.30$, the HOMO energy is identical to the first ionization potential of the ammonia dimer calculated from the total energy difference at the CCSD(T)/aug-cc-pVDZ level (10.01 eV). The calculations performed with the standard MPW1PW91 functional ($\alpha=0.75$) will be called standard DFT and the MPW1PW91 functional with $\alpha=0.30$ will be called reparametrized DFT. All quantum mechanical calculations made here use the correlation-consistent aug-cc-pVDZ basis set.[36,37]

B. Molecular dynamics simulation

To simulate liquid ammonia the interaction potential developed by Impey and Klein[38] was used. This model was adopted since it provides a good description of the structure of liquid ammonia.[39] In this model the N–H and H–H distances are 1.6243 and 1.0124 Å, respectively. The charge distribution of the ammonia molecule is described by three charges ($0.462e$) on the hydrogen atoms and one charge ($-1.386e$) located on the C_3 molecular axis at 0.156 Å away from the nitrogen atom and toward the hydrogen atoms. The dipole moment of the interaction model is 1.50 D (Ref. 38) very close to a recent experimental[40] gas phase value (1.56 D). By using the present reparametrized functional and the geometry of the model, we obtain $\mu=1.62$ D (DFT/aug-cc-pVDZ), in good agreement with the experiment. For comparison, we have also made a MP2/aug-cc-pVDZ calculation obtaining the dipole moment as 1.57 D.

MD of liquid ammonia was carried out using the MOLDY program[41] in the *NVE* ensemble at the experimental density $d=0.73$ g/cm^3, with $N=216$ ammonia molecules. The average temperature was $T=197.2$ K, and a time step of 0.25 fs was used. After 250 ps of equilibration, 50 configurations (2.5 ps spaced) were selected for the subsequent QM calculations.

For predicting the electronic properties of liquid ammonia, supermolecular structures including explicitly a number n of ammonia molecules ($n=1$, 2, 5, 8, 10, and 14) were selected. These supermolecular structures include a central ammonia molecule and the $n-1$ closest neighbors, and when $n=14$ the system corresponds to the first coordination shell of liquid ammonia obtained from the N–N radial distribution function. Surface effects on these finite aggregates were minimized by embedding the clusters in the charge distribution of all the remaining ammonia molecules within a sphere of 10.14 Å radius (half of the simulation box size). Hence, three procedures are used. In the first, we use the gas-phase free optimized clusters. In the second, we use aggregates obtained from the liquid simulation without considering correction to the surface effects. Finally, in the third we embed these aggregates in the atomic charges of the remaining ammonia molecules, thus minimizing surface effects. These situations are illustrated in Figs. 1 and 2. The embedding charge distribution corresponds to the charges of the ammonia interaction model used in the simulation.

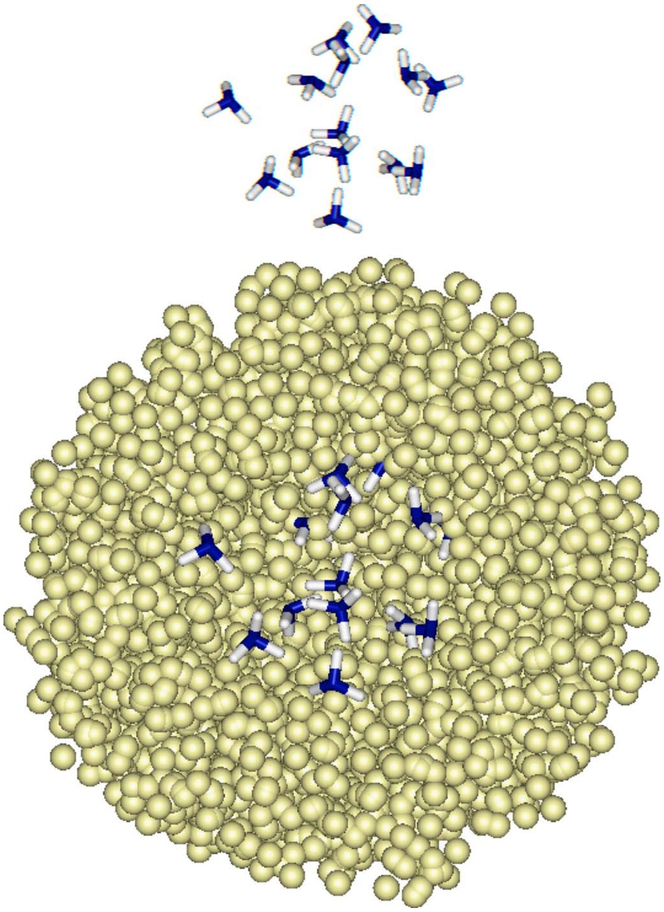

FIG. 2. (Color online) Supermolecular structure showing one aggregate composed of 14 ammonia molecules nonembedded (top) and embedded (bottom) in the electrostatic field of the charges of the remaining ammonia molecules in the liquid.

The evaluation of the average in-solution dipole moment of ammonia was carried out by using the charges obtained from a Merz-Kollman electrostatic fitting.[42,43] Two procedures are used to estimate the dipole moment of the ammonia monomer in the liquid situation (embedded aggregates). In the first, we use the Merz-Kollman distribution to obtain the individual atomic charges of all ammonia molecules and therefrom the average individual dipole moment is calculated using these charges. The final result is an average over all molecules in the 50 sampled configurations. This procedure has been proposed and successfully used before.[44] In the second, we use an iterative procedure, also described before[45] that equilibrates the dipole moment of the solute in the environment of the electrostatic field of the solvent. The results of these two procedures to estimate the average dipole moment were compared, and as we will see they lead essentially to the same result.

TABLE I. Orbital binding energies and electron affinities (eV) for MP2/aug-cc-pVDZ optimized structures of ammonia clusters. Bracketed values are ΔE calculations.

		Orbital	HF	P3	MPW1PW91		CCSD(T)	Expt.
					α=0.30	α=0.75		
NH_3	C_{3v}	$4a_1$	−0.97	−0.77	−0.52[−0.71]	0.29[−0.62]	[−0.75]	
		$3a_1$	11.69	10.65	10.67[10.66]	7.78[10.87]	[10.77]	10.85[a]
		$1e_1$	17.00	16.26	15.93	12.93		15.8[a]
		$2a_1$	31.04	29.23	28.79	23.90		27.76[a]
		$1a_1$	423.24		410.89	391.64		405.6[b]
$(NH_3)_2$	C_s	$9a'$	−0.86	−0.64	−0.39[−0.58]	0.44[−0.45]	[−0.59]	
		$8a'$	11.03	9.91	10.03[9.89]	7.16[9.75]	[10.01]	
		$7a'$	12.02	10.85	11.01	8.14		
		$6a'$	16.36	15.55	15.28	12.26		
		$2a''$	16.37	15.44	15.31	12.32		
		$1a''$	17.27	16.44	16.21	13.21		
		$5a'$	17.30	16.45	16.23	13.22		
$(NH_3)_3$	C_{3h}	$5a'$	−0.94	−0.69	−0.49[−0.66]	0.32[−0.48]	[−0.63]	
		$4a'$	11.08	9.86	10.14[10.32]	7.32[9.33]	[9.98]	
		$4e'$	11.55	10.29	10.56	7.69		
		$3e'$	16.37	15.32	15.30	12.29		
		$1e''$	16.61	15.69	15.57	12.58		
		$1a''$	16.71	15.81	15.67	12.68		
		$3a'$	17.23	16.17	16.12	13.03		
$(NH_3)_4$	C_{4h}	$5a_g$	−0.91	−0.67	−0.48[−0.64]	0.31[−0.44]	[−0.60]	
		$4a_g$	10.77	9.50	9.84 (10.04)	7.05[8.84]	[9.62]	
		$4e_u$	11.28	9.99	10.31	7.47		
		$4b_g$	11.76	10.46	10.76	7.87		
		$3b_g$	16.24	15.13	15.16	12.14		
		$1b_u$	16.41	15.47	15.38	12.41		
		$1e_g$	16.47	15.37	15.39	12.48		
		$1a_u$	16.49	15.55	15.53	12.55		
		$3e_u$	16.57	15.63	15.46	12.35		
		$3a_g$	16.81	15.72	15.71	12.65		
$(NH_3)_5$	C_1	$26a$	−0.87	−0.61	−0.43[−0.60]	0.38[−0.39]	[−0.54]	
		$25a$	10.72	9.43	9.79[10.01]	7.00[10.91]	[9.55]	
		$24a$	11.08	9.78	10.12	7.30		
		$23a$	11.084	9.783	10.13	7.31		
		$22a$	11.63	10.31	10.63	7.76		
		$21a$	11.68	10.37	10.68	7.81		
		$20a$	16.22	15.09	15.14	12.13		
		$19a$	16.33	15.22	15.25	12.22		
		$18a$	16.39	15.43	15.36	12.37		
		$17a$	16.41	15.431	15.37	12.38		
		$16a$	16.46	15.49	15.42	12.39		
		$15a$	16.47	15.50	15.424	12.41		

[a] Reference 46.

[b] Reference 47.

III. RESULTS AND DISCUSSION

A. Electron binding energies and vertical electron affinities of gas-phase ammonia clusters

Reparametrized DFT and CCSD(T) electron binding energies (EBEs) for the free ammonia clusters shown in Fig. 1 are reported in Table I. For comparison, Hartree-Fock and standard MPW1PW91 (α=0.75) DFT results are also reported. EBEs are overestimated by Hartree-Fock calculations and underestimated by the standard DFT method. For the ammonia monomer, the calculated results for the $3a_1$ orbital from P3 (10.65 eV), reparametrized (α=0.30) DFT (10.67 eV), CCSD(T) (10.77 eV), and experiment[46] (10.85 eV) are in good agreement with one another. It is interesting to note that the first ionization energy corresponding to $3a_1$ obtained with the reparametrized DFT result is the same whether it is calculated as the orbital energy (with opposite sign) or as the corresponding total energy difference. This is an interesting feature that is satisfied by the exact DFT, although as our result for the $4a_1$ virtual orbital suggests (see Table I), this is not verified for the vertical electron affinity. The DFT result for the $1e_1$ degenerate level (15.93 eV) is also in good agreement with the experimental result (15.8 eV) of Banna and Shirley.[46] These authors also report the $2a_1$ electron binding energy as 27.76 eV, which is below the DFT and P3 predictions by 1.0 and 1.5 eV, respectively. The reparametrized DFT approach estimates the $1a_1$ core-electron binding energy as 410.9 eV, which is 5.3 eV above the experimental value (405.6 eV),[47] although it coincides with the core-electron binding energy of the atomic nitrogen (410.9 eV).

For the ammonia dimer the DFT result was parametrized so that the $8a'$ EBE (10.03 eV) is numerically the same as the CCSD(T) prediction ($\Delta E = 10.01$ eV). In general, a good agreement is observed between P3, DFT, and CCSD(T) calculations for the first EBE of the clusters. The first vertical ionization energy of the ammonia clusters decreases from 10.77 eV (NH_3) to 9.55 eV $(NH_3)_5$. Similar trends are observed for the P3 and reparametrized DFT calculations.

VEAs of small ammonia clusters are also reported in Table I. They are negative and not very dependent on the cluster size. ΔE results for the vertical electron affinities based on the reparametrized DFT and CCSD(T) are in good agreement with P3 predictions. Reparametrized DFT results for the LUMO energies are only approximately 0.10–0.20 eV above the ΔE from CCSD(T). Our results indicate that, in general, EBE and VEA for the ammonia clusters using the reparametrized functional are in good agreement with both GF and CCSD(T) calculations. This agreement may be considered as an indication that the present DFT reparametrization can provide reliable results for larger aggregates.

B. Electronic polarization of liquid ammonia

One interesting feature characterizing the electronic properties of water is the significant increase of the dipole moment of the water molecule from the gas (1.856 D) to the liquid phase (~2.60 D) (see Ref. 17). This increase is related to the electronic polarization and the cooperative effects induced by hydrogen bonding. Since hydrogen bonding is also important in ammonia it should be expected that the dipole moment of liquid ammonia is considerably increased in comparison with the gas phase value. The electronic polarization of liquid systems has been considered in several studies before.[17,48–51] Table II reports dipole moment calculations using supermolecular structures extracted from the liquid simulation using a different number (n) of explicit ammonia molecules. For each n the calculations were performed in the presence (embedded) and absence (nonembedded) of embedding charges (see Fig. 2). It should be observed that by including the polarization field of embedding charges, surface effects are minimized and the results should correspond more closely to the liquid phase. We will first discuss the calculation of the average dipole moment μ of each ammonia molecule (or monomer) in a cluster of size n. The results for μ are reported in Table II (results for nonembedded clusters are shown in parentheses) and were evaluated using 50 configurations from the MD simulation. They were also averaged over the n molecules of the cluster. In the presence of the embedding charges, the ammonia average dipole moment is not very dependent on the number n of molecules explicitly included in the QM calculations, and it changes from $\mu = 2.01 \pm 0.08$ D ($n=1$) to $\mu = 2.05 \pm 0.09$ D ($n=14$). If this last value is taken as an estimate of the in-liquid ammonia dipole moment, we conclude that it is increased by ~0.43 D relative to the isolated gas phase value (1.62 D). An alternative procedure to obtain the dipole moment of liquid ammonia is by using an iterative procedure,[45] and it will be used next for comparison. First a simulation is performed with the original Impey-Klein parameters.[38] Using statistically uncorrelated configurations extracted from the simulation, an average dipole moment and the atomic charges are obtained using the MP2/aug-cc-pVDZ calculations of one central ammonia surrounded by the atomic charges of all the others. From these, new atomic charges are obtained using a Merz-Kollman electrostatic fitting and these are updated in the Coulomb part of the Impey-Klein potential to perform a new simulation and the dipole moment is obtained again. The procedure is then iterated until convergence.[45] These results are shown in Fig. 3. In this figure every calculated result (black circle) represents an average value. The final converged result of 2.02 ± 0.10 D is in excellent agreement with the previous di-

TABLE II. Average dipole moment (D) obtained using 50 configurations composed of n ammonia molecules. μ is the average dipole moment of the ammonia monomer in the clusters. μ_T is the average total dipole moment of the cluster. These quantities were calculated using embedded and nonembedded clusters (in parentheses). Except where noted all calculations were made using MPW1PW91/aug-cc-pVDZ with $\alpha = 0.30$ in Eq. (1).

n	μ	μ_T
1	$2.01 \pm 0.08 (1.62)$	$2.01 \pm 0.08 (1.62)$
2	$2.00 \pm 0.16 (1.74 \pm 0.15)$	$2.90 \pm 0.81 (2.52 \pm 0.72)$
5	$2.01 \pm 0.13 (1.77 \pm 0.14)$	$4.61 \pm 1.72 (4.04 \pm 1.50)$
8	$2.02 \pm 0.11 (1.80 \pm 0.10)$	$5.19 \pm 2.23 (4.77 \pm 1.98)$
10	$2.04 \pm 0.11 (1.83 \pm 0.10)$	$6.16 \pm 2.49 (5.43 \pm 2.20)$
14	$2.05 \pm 0.09 (1.85 \pm 0.09)$	$7.57 \pm 3.00 (6.66 \pm 2.64)$
Iterative[a]	2.02 ± 0.10	

[a] Iterative procedure using MP2/aug-cc-pVDZ (see Fig. 3).

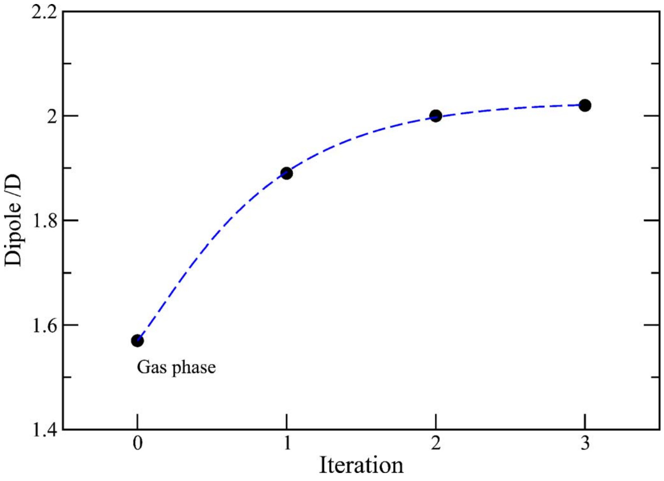

FIG. 3. (Color online) Calculated (MP2/aug-cc-pVDZ) in-solution average dipole moment of the ammonia monomer with respect to the number of iterations.

pole moment of $\mu=2.05\pm0.09$ D obtained from the electrostatic map of the aggregates with electrostatic embedding. Therefore, our results indicate that polarization effects in liquid ammonia contribute to increase its dipole moment by ~27% in comparison with the gas phase value. This is a significant change although less important than the ~40% increase of the water dipole moment.[17,50] The present result for the average dipole moment of liquid ammonia is 0.23 D above the result reported by Deng *et al.* (1.82 D),[13] which was based on a molecular dynamics simulation (at $T=260$ K) for a model of liquid ammonia that takes into account the dipole polarizability of the nitrogen atom. The difference between the present estimate for the average dipole moment of liquid ammonia, which is based on two different theoretical approaches, and the results of Deng *et al.*[13] is possibly related to limitations of their polarizable model (it is not clear how the gas phase polarizability of the nitrogen atom can be used in solution) or to the different thermodynamic conditions (our simulation was carried out at $T=197.2$ K).

In comparison with the embedded clusters, results for the average dipole moment in nonembedded clusters exhibit some dependence on the size n, and μ increases from 1.62 D ($n=1$) to 1.85 ± 0.09 D ($n=14$). This size dependence is possibly related to surface effects that are, in principle, minimized in the embedded systems, where the polarizing charges are a simplified representation of the polarization effects of the outer molecules of the liquid environment.

Table II also reports the average total dipole moment of the aggregate (μ_T). They are dependent on the size and for the embedded situation they increase from $\mu_T=2.01\pm0.08$ D for $n=1$ to $\mu_T=7.57\pm3.0$ D for $n=14$. This property is characterized by significant fluctuations reflecting the modifications of the structure and charge distribution of the ammonia hydrogen bonding network. Significant fluctuations are also observed in nonembedded clusters although smaller μ_T values are predicted due to the absence of the polarizing field of the embedding charges.

C. The density of states of liquid ammonia

The electronic DOS of ammonia clusters ($n=5$, 8, 10, and 14) calculated using the reparametrized DFT/aug-cc-pVDZ calculations are shown in Fig. 4, where the symmetry labels of the isolated ammonia molecule are used to define the orbital energy bands in the aggregates. The core ($1a_1$) DOS is not very dependent on the cluster size. For embedded clusters and $n=14$, fitting to a Gaussian distribution leads to a maximum at -410.6 eV and full width at half maximum (FWHM) of 0.87 eV. In comparison with embedded clusters, the $1a_1$ DOS of nonembedded clusters are only slightly shifted to lower values. The DOS corresponding to the $2a_1$, $1e_1$, and $3a_1$ valence bands are weakly dependent on the number n of ammonia molecules for $n\geqslant5$. Only the edge of the $3a_1$ band is slightly shifted to the right (lower energies) as n increases. A more significant change concerns the presence of the embedding charges and the $4a_1$ virtual band. In comparison, with embedded clusters, the $4a_1$ virtual band in the nonembedded case is shifted to the left (higher energies), possibly reflecting the energetic stabilization of the virtual orbitals of the ammonia molecules closer to the cluster surface.

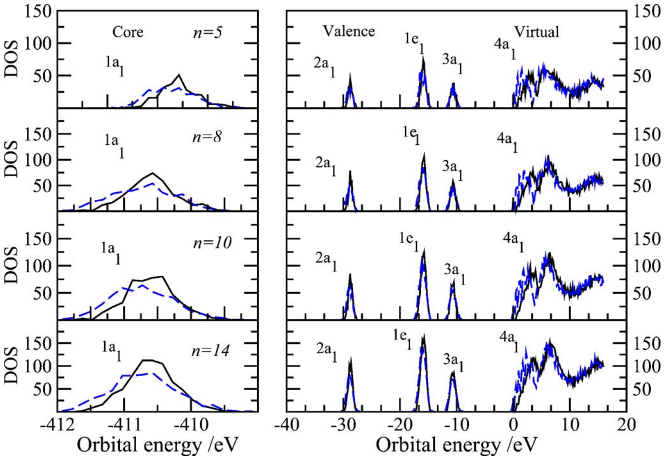

FIG. 4. (Color online) Electronic density of states (DOS) of ammonia clusters ($n=5$, 8, 10, and 14) in the presence (solid line) and absence (dashed line) of embedding charges.

D. Electron binding energies and vertical electron affinity of liquid ammonia

The average EBE of the $3a_1$ orbital (HOMO) and VEA of ammonia clusters are reported in Table III (results in parentheses are for nonembedded clusters). The $3a_1$ EBE is seen to depend on the size n and for embedded clusters it decreases from 10.72 ± 0.39 eV ($n=1$) to 9.88 ± 0.20 eV ($n=14$). The dependence of the $3a_1$ EBE with n can be well represented by a linear relation $a+b/n$ leading to an extrapolated vertical binding energy for liquid ammonia of 9.74 ± 0.73 eV (see Table III). For nonembedded clusters, the $3a_1$ EBE decreases from 10.67 eV ($n=1$) to 9.69 ± 0.52 eV ($n=14$), and the extrapolated value is 9.47 ± 0.52 eV. In contrast with the dependence of the valence band edge (HOMO) with the cluster size, the average value of the $3a_1$ energy band (~10.64 eV) is essentially the same for all the clusters. These averages were estimated by fitting a Gaussian distribution to the calculated DOS and the corresponding half widths (0.96–1.10 eV) are also reported in Table III. For nonembedded clusters the DOS maxima are slightly shifted toward higher energies and their half widths are in the 1.25–1.36 eV range. In comparison with embedded clusters, the only noticeable difference is the increase in the bandwidth. The broader electronic energy bands in the nonembedded clusters can be understood by the larger energy fluctuations in a less homogenous system due to the existence of the surface effects.

The average VEAs for ammonia aggregates of different sizes are also reported in Table III. For the embedded case, the VEAs are strongly dependent on the size and changes from -1.45 ± 0.27 eV ($n=1$) to -0.69 ± 0.18 eV($n=14$). The presence of embedding charges minimizes surface effects and the excess electron should be stabilized via internal states. Average VEAs are negative, indicating that vertical electron attachment to neutral ammonia clusters, where an excess electron is internally stabilized by interactions with

TABLE III. Average ionization potentials and vertical electron affinities (eV) obtained using 50 configurations composed of n ammonia molecules. Values in parentheses are for nonembedded clusters. All calculations were made using MPW1PW91/aug-cc-pVDZ with $\alpha=0.30$ in Eq. (1).

n	$3a_1$[a]	$3a_1$[b]	$4a_1$
1	10.72±0.39(10.67)		−1.45±0.27(−0.52)
2	10.32±0.33(10.19±0.24)		−1.28±0.24(−0.36±0.04)
5	10.09±0.30(10.00±0.26)	10.64[0.96](10.64[1.25])	−1.02±0.20(−0.15±0.09)
8	9.99±0.27(9.88±0.23)	10.64[0.98](10.63[1.29])	−0.88±0.20(−0.06±0.10)
10	9.94±0.25(9.79±0.27)	10.65[1.01](10.69[1.29])	−0.82±0.20(−0.02±0.12)
14	9.88±0.20(9.69±0.25)	10.64[1.10](10.67[1.36])	−0.69±0.18(0.04±0.13)
…			
∞[c]	9.74±0.73(9.47±0.52)		−0.49±0.53(0.16±0.22)

[a] Average value of the HOMO.

[b] Average value of the $3a_1$ energy band calculated by fitting a Gaussian distribution to the electronic density of states (DOS). Bracketed values are half widths (FWHM) of the Gaussian distributions.

[c] Extrapolated using the expression $a+b/n$.

the hydrogen bond network, is not observed in small aggregates. An early quantum path-integral molecular dynamics (PIMD) study of $(NH_3)^-_n$ clusters indicated that for $n<32$ internal states are not found.[52] Direct comparison with our results is not possible because they simulated the anion, and the reorganization of the hydrogen bond network thus included in this PIMD study was not made here. It should be expected that the stabilization of an excess electron in liquid ammonia involves a significant reorganization of HB network. This is not possible for a vertical attachment process. However, the negative values of the VEA obtained here for the small neutral $(NH_3)_n$ clusters embedded in a charge distribution representing the liquid environment keep some similarity with the PIMD findings in the sense that the formation of a cavity where an excess electron is energetically stabilized is not favored in small clusters. If an extrapolation procedure for VEA is adopted, the result for embedded clusters (−0.49±0.53 eV) indicates that no *vertical* electron attachment via internal state is observed in liquid ammonia for the present model and thermodynamic conditions.

The nonembedded clusters are more amenable to comparison with situations where the excess electron is stabilized via surface states. The VEAs of the nonembedded ammonia clusters are seen to be even more dependent on the cluster size n. However, in comparison with the embedded clusters important differences can be noted. Significantly higher VEAs are predicted for the small nonembedded clusters. For example, when $n=2$ the $4a_1$ VEAs are −0.36±0.04 eV (nonembedded) and −1.28±0.24 eV (embedded aggregate). Moreover, it can be noted that the VEA of the nonembedded case becomes positive for $n>10$. The electron affinity of hydrogen bonding systems is possibly related to the presence of free or dangling hydrogen atoms. Therefore, positive VEA in nonembedded clusters could be related to the presence of free hydrogen atoms at the outer surface. These results are in the line with the prediction of Barnett *et al.*[52] that small $(NH_3)^-_n$ clusters can stabilize an excess electron via surface states, although the electrons are weakly bounded in a diffuse state. However, it should be observed that in our case, the available surfaces are not really equivalent to the free cluster situation since our nonembedded structures were extracted from the liquid phase simulation, and the orientation at the outer surface thus reflects the organization of the hydrogen bond network of the bulk phase. On the other hand, our main interest is to investigate the energetics of vertical electron attachment to liquid ammonia and to compare our predictions with the corresponding experimental property. The average lowest unoccupied molecular orbital (LUMO) energy can be compared with the location of the bottom of the conduction band of ammonia (V_0) (Ref. 53) or, equivalently, the average VEA can be compared with $-V_0$. Making an extrapolation to the bulk value, the VEA for nonembedded clusters (0.16±0.22 eV) is in good agreement with the vertical electron affinity of liquid ammonia ($-V_0=0.2$ eV).[53]

Finally, another issue worth considering concerns the relationship between the average values of the first IP and the VEA with the total dipole moment μ_T of the clusters. IP and VEA versus μ_T for ammonia clusters of different sizes are represented in Figs. 5 and 6, respectively. A very good correlation with the average total dipole moment (μ_T) can be observed for both properties. It is known that the electron attachment to polar clusters is dependent on the total electric-multipole moments of the aggregate.[54,55] However, the

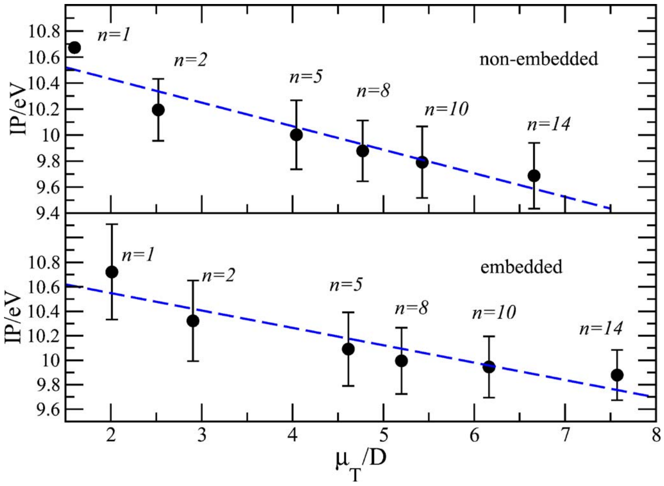

FIG. 5. (Color online) Average vertical ionization potential (IP in eV) vs average total dipole (μ_T in D) of ammonia clusters. The dashed lines are a fitting to the raw data with correlation coefficients $r=0.947$ (nonembedded clusters) and $r=0.925$ (embedded clusters).

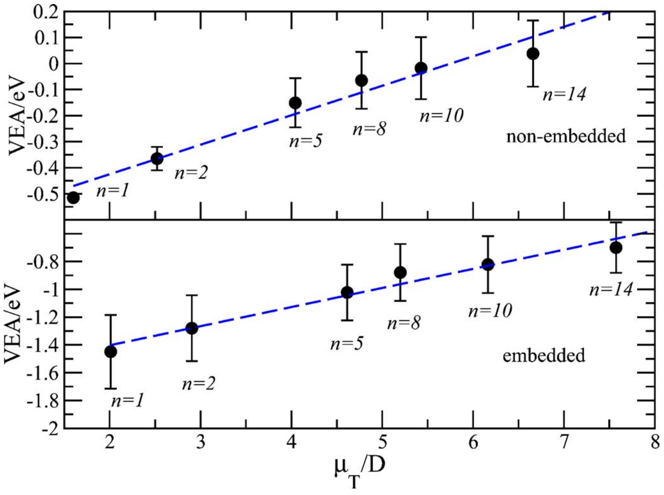

FIG. 6. (Color online) Average vertical electron affinity (EA in eV) vs average total dipole (μ_T in D) of ammonia clusters. The dashed lines are a fitting to the raw data with correlation coefficients $r=0.977$ (nonembedded clusters) and $r=0.983$ (embedded clusters).

present results indicate that the first ionization potential is also correlated with μ_T. Both correlations illustrate the relationship between the hydrogen bond network charge fluctuations and the electronic properties of the aggregates.

IV. CONCLUSIONS

Sequential molecular dynamics/DFT calculations of the electronic properties of liquid ammonia are reported. The DFT calculations are made on structures generated for the liquid phase by molecular dynamics and are based on a reparametrization of the MPW1PW91 exchange-correlation functional that reproduces the electron binding energies of the ammonia dimer. Average properties in the liquid phase were estimated by using 50 configurations from the MD calculations. For each configuration, DFT calculations for ammonia clusters with $n=1$, 2, 5, 8, 10, and 14 were made in the presence and absence of embedding charges representing the liquid environment. We predict that in comparison with the gas phase value, the dipole moment of the ammonia molecule is increased by approximately 27%. This value is obtained in two different ways. In one we use the aggregates embedded in the electrostatic field of the remaining ammonia molecules. In the other we use an iterative procedure to obtain the in-solution dipole moment. Our prediction for the average dipole moment of liquid ammonia (2.05 ± 0.09 D) is 0.23 D above the value reported by Deng *et al.*,[13] which relies on an interaction model for liquid ammonia that includes the dipole polarizability of the nitrogen atom. The average electronic density of states of ammonia clusters has also been calculated. For the embedded model, the DOS maxima are not very dependent on the cluster size. By analyzing the size dependence of the HOMO average energy (edge of the $3a_1$ band) in embedded clusters, we predict that the vertical ionization potential of liquid ammonia (9.74 ± 0.73 eV) is approximately, 1 eV below the gas phase value for the isolated molecule.

Results for the energetics of vertical attachment of an excess electron to neutral ammonia clusters indicate that internally stabilized states are not found in small clusters. On the other hand, our results indicate that the vertical attachment energy of an excess electron in nonembedded ammonia clusters becomes possible for a threshold size value of approximately ten ammonia molecules. The extrapolated VEA of nonembedded clusters estimated from the average LUMO energies (0.16 ± 0.22 eV) is in good agreement with the experimental value for the location of the conduction band edge of liquid ammonia ($-V_0=0.2$ eV). This work provides evidence that both the ionization potential and vertical electron affinity correlate with the total dipole moment of the aggregates. The total dipole moment of ammonia clusters at $T=179.2$ K exhibits significant fluctuations, and the correlations illustrate the dependence of the electronic properties of ammonia on the local order of the hydrogen bond network.

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