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Negative Ion Formation in Sodium Chloride Trimer—An ab Initio Study

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The possibility of an excess electron binding to a sodium chloride trimer in the gas phase was studied at the coupled-cluster level of theory with single, double, and noniterative triple excitations with the six-term s, six-term p, and four-term d (aug-cc-pVDZ+6s6p4d) basis sets. It was found that two types of anions can be formed: dipole-bound anions and solvated-electron (SE) species. The global minimum on the ground-state anionic potential energy surface corresponded to the Λ-shaped anionic structure, the vertical electron binding energy of which was 7858 cm^{-1}. It was also found that the energy of SE structures, which are locally geometrically stable yet thermodynamically unstable, was considerably higher than that of dipole-bound anions. However, their vertical electron detachment energies were significantly larger (i.e., 26 906 and 34 052 cm^{-1}).

1. Introduction

1.1. Preceding Studies. This is the second paper in which we describe our efforts to study an excess electron binding to sodium chloride (NaCl) clusters. The importance of binding an extra electron to ionic clusters manifests itself by the significant number of manuscripts devoted to this phenomenon over the past two decades.**[1−10]** The study of such clusters can provide valuable information about the connection between the properties of the isolated atoms, molecules, or ions and the properties of the bulk material. In addition, clusters with excess electrons exhibit diverse electron binding motifs, especially as the cluster sizes increase. For example, an excess electron can fill the vacancy of a missing anion in $A_n^+B_{n-1}^-$ to form a so-called F-center. Alternatively, the relatively large surface-to-volume ratios of small clusters makes it likely that an extra electron may form a surface state.

The simplest NaCl cluster (NaCl dimer) has attracted the largest number of scientists; therefore, one is able to find several experimental reports containing the photoelectron and photodetachment spectra of $(NaCl)_2^-$ that provide the vertical electron detachment energies (VDEs) of the ground and excited anionic states.[3,11,12] The experimental measurements, although reliable and informative, cannot determine the geometrical structure of the anion or neutral species. In contrast, theoretical treatments, especially ab initio methods, are able to provide precise information about the origin of the electron binding by describing the potential responsible for it.

In our preceding paper,[13] we reported ab initio results on the anionic NaCl *dimer*. It was found that three types of anions could be formed: quasi-linear dipole-bound anions, a rhombic quadrupole-bound anion, and linear solvated-electron (SE) anions. In contrast to the earlier results, we showed that the rhombic neutral dimer (which is the neutral global minimum) does bind an excess electron to form an electronically stable anion of quadrupole nature. The global minimum on the ground-state anionic potential energy surface (PES) corresponds to the dipole-bound anion of quasi-linear structure ($(NaCl\cdots NaCl)^-$), the vertical electron binding energy of which is 12 051 cm^{-1} (1.494 eV). It was also found that the energy of the SE structure $(ClNa\cdots NaCl)^-$ is considerably higher than that of the anionic global minimum, but the VDE of the former is significantly larger (i.e., 21 306 cm^{-1} [2.642 eV]). The almost rhombic $(NaCl)_2^-$ lies only 0.181 eV above the anionic global minimum but is below the global minimum of the neutral species.[13]

On the basis of our results, we also speculated about what types of molecular anions can be created after attaching excess electrons to NaCl clusters. In a neutral experimental sample, both monomers and dimers of NaCl may be present; therefore, one can expect that the excess electron can attach either to the monomer, to form $NaCl^-$, or to the rhombic dimer, thus forming quadrupole-bound rhombic $(NaCl)_2^-$. It is likely that such negatively charged monomers may subsequently collide with neutral NaCl molecules, resulting in the formation of linear or quasi-linear (bent) thermodynamically stable dipole-bound anions. Alternatively, the $NaCl^-$ anions may form (via collision with the neutral NaCl) "SE" anions that are thermodynamically unstable and may eventually convert via L-shaped transition states to the linear (or bent) dipole-bound anions, although a kinetic barrier of 0.246 eV must be overcome.[13] The rhombic anions, created by attaching the excess electrons to rhombic neutrals, may also convert to the linear (or bent) anions via transition states, although a small kinetic barrier of 0.108 eV must be overcome.[13]

In the present work, we have focused our attention on the NaCl trimer and its ability to bind an excess electron. We consider our effort as the next step toward understanding the possible formation of electronically stable anions based on the NaCl clusters. To the best of our knowledge, this phenomenon has not been extensively studied thus far. In particular, we were able to find only theoretical results considering $(NaCl)_3^-$ that were published by Sunil and Jordan in 1987, however, which described only the D_{3h}-symmetry SE species.[1] In comparison to the NaCl dimer, $(NaCl)_3$ is more challenging, because various interaction networks in $(NaCl)_3$ lead to a variety of different clusters, each of which may bind an extra electron. Therefore, we considered several neutral structures, corresponding to local minima on the neutral ground-state PES. Moreover, we studied the anionic PES, searching for structures that are specific for

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the anion (i.e., those which do not correspond to the stationary points on the neutral PES).

1.2. Dipole-Bound Anions and Solvated Electrons. In the preceding paper (devoted to NaCl dimers),[13] we gave a detailed discussion that involved dipole-bound and quadrupole-bound anions, and SEs, and we explained how to distinguish one from another. Therefore, we now limit our description of these species by indicating only the qualitative differences among them.

The binding of electrons to polar molecules has been addressed in many theoretical studies.[14−27] It has been shown that, within the Born−Oppenheimer (BO) approximation, species with a dipole moment of >1.625 D possess an infinite number of bound anionic states.[28,29] However, a more-practical critical value, to experimentally observe a dipole-bound state (DBS) of anion bound by at least 1 cm^{-1}, was found to be slightly larger (ca. 2.5 D).[14] In fact, this "practical" value depends strongly on the size and chemical structure of a molecule (i.e., the number and type of inner-shell and valence orbitals). Jordan and Luken demonstrated that the loosely bound DBS electron occupies a diffuse orbital localized mainly on the positive side of the dipole.[17] This finding has been confirmed in many more-recent studies. The role of non-BO coupling has been studied by Garrett, who concluded that such couplings are negligible for DBSs with electron binding energies much larger than the molecular rotational constants.[30]

The electron binding energy (D) can be estimated on the basis of Koopmans' theorem (KT),[31] as well as at other levels of theory. The orbital relaxation effects, which are neglected in the KT approximation, have been found to be quite small for a variety of dipole-bound anionic states.[18] In contrast, the role of electron correlation has been proven to be very significant. In fact, in many cases, the electron binding energy of a dipole-bound anion is dominated by the contribution from electron correlation. In particular, the dispersion interaction of the excess electron with the electrons of the neutral parent molecule proved to be crucial for the stability of the dipole-bound anion,[15,16,18−21] although higher-order correlation effects can also be significant.[18−21,26,32]

An excess electron may be trapped inside a molecular cluster, instead of being attached to the dipole moment of the neutral cluster. The existence of such species, very often called SEs, has been known since 1864, when they were observed in liquid ammonia.[33] Since then, many systems that contain SEs have been studied, such as $(\text{HF})_n^-$ ($n = 2, 3$)[34,35] and $[\text{O}{=}\text{C}(\text{NH}_2)_2]_2^-$.[36] Moreover, it has recently been suggested (for [ClNa···(−)···NaCl]) that the SE species can alternatively be viewed as several polar molecules linked by a one-electron σ bond formed by the constructive overlap of a few monomers' dipole orbitals (each of which comes from one polar monomer).[13]

There are several important differences between SE systems and dipole-bound anions. Anions of the former type contain an extra electron localized primarily *inside* a cluster of polar molecules whose dipoles are directed toward the excess electron.[37] In the latter, an excess electron is localized *outside* the molecular framework and the dipoles are aligned constructively. SE systems are known to usually possess relatively large VDEs and undergo large geometrical rearrangements upon electron detachment, because the dipoles directed toward one another are highly unfavorable in the absence of the electron.[1,2,36,37]

2. Methods

We first studied the ground-state PESs of the neutral and anionic NaCl trimers at the second-order Møller−Plesset perturbation theory (MP2)[38] level. Because the methods we used are based on an unrestricted Hartree−Fock (UHF) starting point, it is important to ensure that little, if any, artificial spin contamination enters into the final wave functions. We computed the expectation value $\langle S^2 \rangle$ for species studied in this work and found values of 0.7500 or 0.7502 in all anion cases. Hence, we are certain that spin contamination is not large enough to affect our findings significantly.

The D values were calculated using a supermolecular approach (i.e., by subtracting the energies of the anion from those of the neutral). This approach requires the use of size-extensive methods, for which we have employed Møller−Plesset perturbation theory up to the fourth order (MPn ($n = 2, 3, 4$)) and the coupled-cluster method with single, double, and noniterative triple (CCSD(T)) excitations.[39] In addition, the value of D was analyzed within the perturbation framework designed for dipole-bound anions and SEs described previously by Gutowski and Skurski.[21]

The simplest theoretical approach to estimate D is based on KT. The KT binding energy (D^{KT}) is the negative of the energy of the relevant unfilled orbital obtained from a Hartree−Fock self-consistent field (SCF) calculation on the neutral molecule. This is a static approximation to D, which neglects both orbital relaxation and electron correlation effects. These effects were taken into account by performing SCF and CCSD(T) calculations for the neutral and the anion.

The polarization of the neutral host (N) by the excess electron, and the effect of back-polarization, are taken into account when the SCF calculation is performed for the anion (A), and the accompanying induction effects on D are given by

$$\Delta D^{\text{SCF}}_{\text{ind}} = D^{\text{SCF}} - D^{\text{KT}} \qquad (1)$$

where

$$D^{\text{SCF}} = E^{\text{SCF}}_{\text{N}} - E^{\text{SCF}}_{\text{A}} \qquad (2)$$

and $E^{\text{SCF}}_{\text{N}}$ and $E^{\text{SCF}}_{\text{A}}$ represent the SCF energies of the neutral and the anion, respectively.

The dispersion interaction between the loosely bound electron and N was extracted from the MP2 contribution to D. The dispersion term is a second-order correction, with respect to the fluctuation−interaction operator, and is approximated here by $\Delta D^{\text{MP2}}_{\text{disp}}$, which takes into account proper permutational symmetry for all electrons in the anion:

$$\epsilon^{(02)}_{\text{disp}} \approx \sum_{a\in \text{N}} \sum_{r<s} \frac{|\langle \phi_a \phi_{\text{mbe}} || \phi_r \phi_s \rangle|^2}{e_a + e_{\text{mbe}} - e_r - e_s} = -\Delta D^{\text{MP2}}_{\text{disp}} \qquad (3)$$

where ϕ_a and ϕ_{mbe} are spin orbitals occupied in the UHF anion wave function, ϕ_r and ϕ_s are unoccupied orbitals, and the e terms are the corresponding orbital energies. The subscript mbe denotes the multipole (dipole in this case)-bound electron's spin orbital.

The total MP2 contribution to D, defined as

$$\Delta D^{\text{MP2}} = D^{\text{MP2}} - D^{\text{SCF}} \qquad (4)$$

is naturally split into dispersion and nondispersion terms:

$$\Delta D^{\text{MP2}} = \Delta D^{\text{MP2}}_{\text{disp}} + \Delta D^{\text{MP2}}_{\text{no-disp}} \qquad (5)$$

The latter term is dominated by the correlation correction to

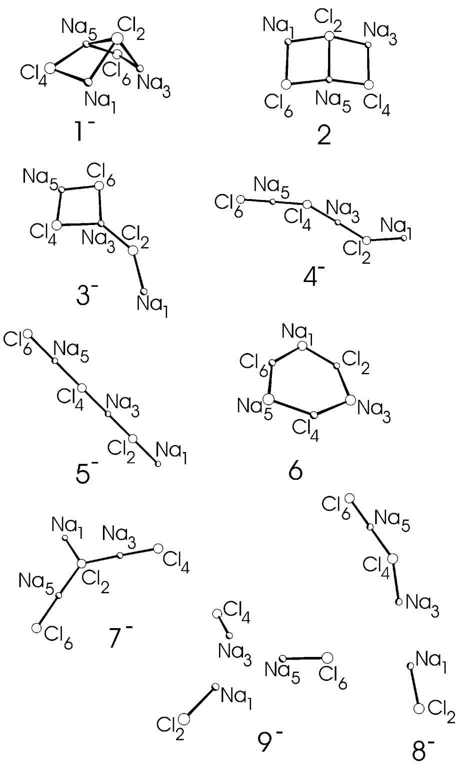

Figure 1. Equilibrium structures corresponding to the anionic minima studied in this work. For **6**, the neutral equilibrium structure is shown, because the corresponding anion is not stable.

the static Coulomb interaction between the loosely bound electron and the charge distribution of N.

The higher-order MP contributions to D are defined as

$$\Delta D^{\mathrm{MP}n} = D^{\mathrm{MP}n} - D^{\mathrm{MP}(n-1)} \qquad (\text{for } n = 3, 4) \tag{6}$$

Finally, the contributions beyond the fourth order are estimated by subtracting MP4 results from those obtained at the CCSD(T) level.

$$\Delta D^{\mathrm{CCSD(T)}} = D^{\mathrm{CCSD(T)}} - D^{\mathrm{MP4}} \tag{7}$$

The diffuse character of the orbital describing the loosely bound electron necessitates the use of extra diffuse basis functions that have very low exponents.[40] In addition, the basis set chosen to describe the neutral molecular host should be flexible enough to (i) describe the static charge distribution of the neutral accurately and (ii) allow for polarization and dispersion stabilization of the anion, upon electron attachment. The geometry optimization calculations and the vibrational frequency calculations were performed with the aug-cc-pVDZ basis set,[41] supplemented with a six-term s, six-term p, and four-term d (6s6p4d) basis set of diffuse functions centered on the terminal Na atom (for linear (**5** and **5**$^-$), zigzag (**4**$^-$), kite-shaped (**3**$^-$), and Y-shaped (**7**$^-$) species; see Figure 1), in the center of the ring for species **6**, and between the two or three Na atoms in **8**$^-$ and **9**$^-$, respectively. In the case of Λ-shaped (**1**$^-$) and arrow-shaped (**2** and **2**$^-$) species, the additional 6s6p4d set of diffuse functions was centered on an atom localized on the positive end of the molecular dipole (i.e., $\mathrm{Cl}_{(2)}$ for both Λ-shaped and arrow-shaped systems; see Figure 1).

Evaluation of the D values was performed with the aug-cc-pVDZ+6s6p4d basis set, centered as described previously. The aug-cc-pVDZ basis set was chosen because we earlier showed its usefulness in describing multipole-bound anions, compared to the usefulness of other commonly used, one-electron basis sets.[40] The extra diffuse functions do not share exponent values, and we used even-tempered,[42] six-term s, six-term p, and four-term d (6s6p4d) basis sets. The geometric progression ratio was equal to 3.2,[43] and, for each symmetry, we started to build up the exponents of the extra diffuse functions, from the lowest exponent of the same symmetry included in aug-cc-pVDZ basis set designed for sodium. As a consequence, we achieved the lowest exponents of 6.7520884×10^{-6}, 5.8952718×10^{-6}, and 4.4631956×10^{-4} au for the s, p, and d symmetries, respectively.

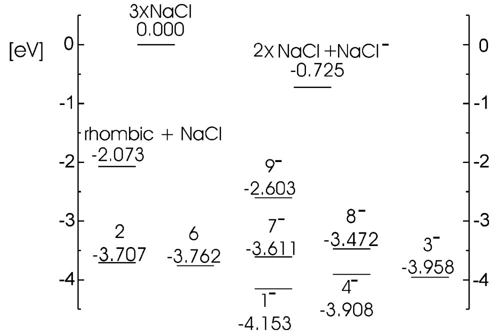

Figure 2. Relative electronic CCSD(T) energies (in eV) of the minima on the anion (right) and neutral (left) ground-state potential energy surface. The zero of energy is taken to be triple the CCSD(T) energy of the neutral NaCl monomer.

All calculations were performed with the Gaussian 98 program[44] on AMD Athlon 950 MHz and Pentium IV 2.0 GHz computers, as well as on SGI and Compaq Sierra numerical servers. The three-dimensional plots of molecular orbitals were generated with the MOLDEN program.[45]

3. Results

3.1. Neutral Species. We focused our investigation of the ground-state PES of the neutral NaCl trimer on finding the structure corresponding to the global minimum. On the basis of our MP2/aug-cc-pVDZ+6s6p4d calculations, we found that the cyclic D_{3h}-symmetry structure **6** (see Figure 1) is a minimum, and it is the lowest-energy structure of the neutral NaCl trimer. The geometry of this cyclic trimer is given in Table 1S, together with the corresponding MP2 vibrational frequencies. (See Supporting Information.) As shown in Figure 2, the cyclic $(\mathrm{NaCl})_3$ lies 3.762 eV below the energy of three separated monomers and 1.689 eV below the energy of rhombic $(\mathrm{NaCl})_2$ and the monomer; thus, its formation is thermodynamically favorable. The Na−Cl distances in **6** are longer than those in the NaCl monomer (by 0.1501 Å[46]) and shorter than those in the rhombic dimer (by 0.0193 Å).

The dipole moment of **6** vanishes by symmetry; therefore, the first nonvanishing multipole moment is the quadrupole (Q). Recalling the ionic character of all $(\mathrm{NaCl})_n$ clusters, one would expect rather-significant magnitudes of the Q tensor for the cyclic trimer. However, in the case of **6**, the eigenvalues of the traceless quadrupole moment tensor collected in Table 1S are small (ca. 7.4, −3.7, and −3.7 D·Å). Comparing these values to the eigenvalues of Q found previously for $(\mathrm{NaCl})_2$ (i.e., 76.2, 1.4, and −77.6 D·Å),[13] and knowing that the NaCl dimer in its rhombic geometry forms a very weakly bound (ca. 190 cm^{-1} at the KT level of theory) anion of quadrupole-bound nature, we suspect that the formation of an electronically stable anion by the cyclic $(\mathrm{NaCl})_3$ is not likely. We confirmed this assumption by employing very diffuse basis sets and verifying that the corresponding anion is not bound at the electrostatic-exchange (i.e., KT) level.

In addition, we searched for other (local) minima on the neutral PES of the trimer. We found that the arrow-shaped (**2**) neutral trimer is such a local minimum-energy structure (see Figure 1); it lies only 0.055 eV above the energy of the cyclic neutral (**6**) structure but 3.707 eV below the energy of three separated monomers and 1.634 eV below the energy of rhombic $(NaCl)_2$ and the monomer (see Figure 2). The cyclic global minimum on the neutral PES is not capable of forming a stable anion; therefore, it is likely that the excess electron can initially attach to the arrow-shaped trimer **2**, as we discuss later.

It should also be noted that unconstrained geometry optimization of the pseudolinear (i.e., zigzag) neutral NaCl trimer did not result in the location of any local minimum corresponding to such a pseudolinear structure. Instead, it collapses to the cyclic structure **6**, which is assumed to be the global minimum on the PES of the neutral species. Therefore, we conclude that the zigzag pseudolinear structure of the neutral trimer is not geometrically stable.

Several other structures we examined were found to be geometrically unstable, such as the linear $C_{\infty v}$-symmetry structure **5**, the Y-shaped molecule (whose initial geometry was assumed to be similar to that of the $\mathbf{7}^-$ anion), and the kite-shaped structure (analogous to that of the $\mathbf{3}^-$ anion); however, they correspond to the stationary points (with one or more imaginary frequencies) on the PES of the neutral trimer.

This led us to the conclusion that there are, in fact, only two structures of the neutral $(NaCl)_3$ that correspond to the global (cyclic D_{3h}-symmetry structure **6**) and local (arrow-shaped system **2**) minima. We verified that **6** does not form an electronically stable anion, whereas **2** seems important when excess electron attachment is considered.

3.2. Anionic Species. *3.2.1. Geometries and Relative Stabilities.* We first examined the possibility of supporting an electronically stable anion by the cyclic cluster **6**. The cyclic D_{3h}-symmetry structure **6** is the global minimum on the PES of the neutral species; therefore, it seemed natural to explore its capability of binding an excess electron. Despite many attempts that included the use of more and more diffuse basis functions, our ab initio calculation failed to yield a stable anion for this cyclic trimer. In particular, the anion is not bound at the electrostatic-exchange (i.e., KT) level, which suggests that the neutral cyclic trimer **6** is not capable of forming an electronically stable anion.

Next, we performed an extensive search of the ground-state PES of the anion to find the structure corresponding to the global minimum. We found that the unusual Λ-shaped structure $\mathbf{1}^-$ (see Figure 1) is geometrically stable and is the lowest-energy structure of the anionic NaCl trimer. As such, this structure is thermodynamically stable, because the energy effect of any conceivable process (i.e., isomerization or fragmentation) involving it as a substrate is positive. The structure $\mathbf{1}^-$ consists of two NaCl monomers oriented in the same direction and one monomer oriented in the opposite direction (see Figure 1 and Table 1S, where the geometrical parameters for $\mathbf{1}^-$ are defined and listed, respectively). The Λ-shape structure is a dipole-bound anion, because of the significant dipole moment of its neutral parent (10.1 D; see Table 1S). We also show that the singly occupied molecular orbital (SOMO) holding the excess electron in $\mathbf{1}^-$ is localized primarily outside the molecular framework, in the vicinity of the positive end of the molecular dipole (see Figure 3). Although the D value calculated for $\mathbf{1}^-$ (7858 cm^{-1}) is smaller than that for other anions based on the NaCl trimer, the thermodynamical stability of $\mathbf{1}^-$ results from the relatively high number of the inter-monomer Na^+Cl^- interactions. To the best of our knowledge, the existence of an electronically stable Λ-shaped anionic trimer has not been described in the literature thus far.

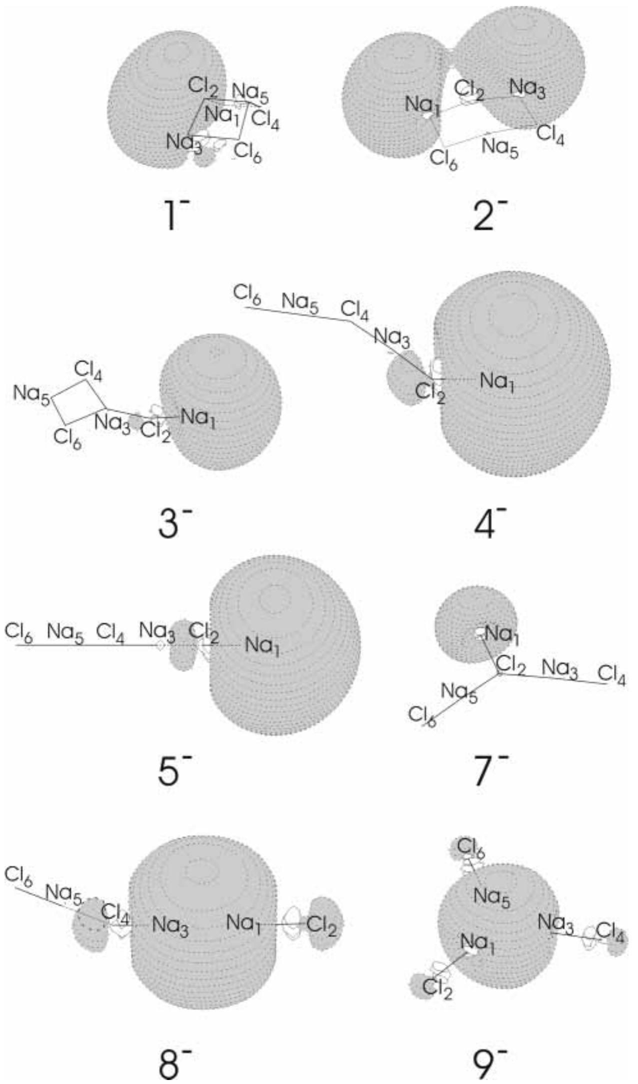

Figure 3. Singly occupied molecular orbitals (SOMOs) holding the excess electron in the ground electronic states of anions supported by NaCl trimers.

According to our CCSD(T) results, $\mathbf{1}^-$ lies 4.153 eV below the energy of three isolated neutral monomers, 0.391 eV below the energy of the neutral cyclic global minimum **6**, and 1.355 eV below the energy of rhombic $(NaCl)_2$ and $NaCl^-$ (see Figure 2).

In addition, we considered other anionic structures that result from the attachment of an excess electron to the dipole field of the neutral trimer. We found that the kite-shaped ($\mathbf{3}^-$), zigzag ($\mathbf{4}^-$), and Y-shaped ($\mathbf{7}^-$) structures are electronically stable and correspond to local minima on the anionic PES. The geometrical parameters defining the $\mathbf{3}^-$, $\mathbf{4}^-$, and $\mathbf{7}^-$ anions are collected in Table 1S, whereas the corresponding structures are depicted in Figure 1.

The dipole-bound anion $\mathbf{3}^-$ lies only 0.195 eV above the global anionic minimum $\mathbf{1}^-$ and 0.196 eV below the global minimum for the neutral **6** (see Figure 2), despite its relatively small D value (9779 cm^{-1}, see Table 1). Therefore, we conclude that the significant number of inter-monomer Na^+Cl^- interactions is responsible for the relatively low total energy of $\mathbf{3}^-$ (see Figures 1 and 2).

The zigzag anion $\mathbf{4}^-$ is thermodynamically unstable (by 0.245 eV), with respect to the global minimum $\mathbf{1}^-$ (see Figure 2). This

TABLE 1: Components of the Vertical Electron Binding Energies *D* (in cm^{-1}) of NaCl Trimer Anions of Dipole-Bound and Solvated-Electron Character, Calculated with the aug-cc-pVDZ+6s6p4d Basis Sets

	$\mathbf{1}^-$	**2**	$\mathbf{2}^-$	$\mathbf{3}^-$	$\mathbf{4}^-$	**5**	$\mathbf{5}^-$	$\mathbf{7}^-$	$\mathbf{8}^-$	$\mathbf{9}^-$
D^{KT}	6036	985	1514	8821	13550	12299	13493	16757	25615	32627
ΔD_{ind}^{SCF}	913	113	151	568	580	558	569	725	1155	1621
ΔD_{disp}^{MP2}	1078	749	850	424	475	487	451	590	491	610
$\Delta D_{no-disp}^{MP2}$	−360	−43	−67	−124	−142	−92	−118	−226	−413	−834
ΔD^{MP3}	34	−12	−10	23	23	17	19	33	85	185
ΔD^{MP4}	68	138	140	33	33	47	36	18	−62	−213
$\Delta D^{CCSD(T)}$	89	243	203	34	41	43	38	51	35	56
sum	7858	2173	2781	9779	14560	13359	14488	17948	26906	34052

result seems surprising, in comparison with the previous findings in which zigzag structures such as the $(NaCl)_2^-$ dimer[13] or $(HF)_3^-$ trimer[34] were found to correspond to the global minima on the anionic PESs of the NaCl dimer and HF trimer, respectively. Even though the energy of $\mathbf{4}^-$ is greater than that of $\mathbf{1}^-$, it is less than that of the lowest neutral structure, by 0.146 eV (see Figure 2).

The large *D* value (17 948 cm^{-1}; see Table 1) of the Y-shaped C_{2v}-symmetry anion ($\mathbf{7}^-$) results from the large dipole moment (21.46 D) of its neutral parent (see Table 1S). However, the presence of only two stabilizing inter-monomer Na^+Cl^- interactions causes a relatively high total energy of this species. The $\mathbf{7}^-$ anion is thermodynamically unstable (by 0.542 eV), with respect to $\mathbf{1}^-$; however, it lies 2.886 eV below the sum of the energies of two isolated NaCl and one $NaCl^-$ species (see Figure 2). Also, the energy of $\mathbf{7}^-$ is slightly greater (by 0.151 eV) than that of the global minimum of the neutral species **6**.

The SOMO orbitals holding excess electrons in the kite-shaped ($\mathbf{3}^-$), zigzag ($\mathbf{4}^-$), and Y-shaped ($\mathbf{7}^-$) anions are depicted in Figure 3. It seems clear that, for each anion, the extra electron is localized primarily outside the cluster, at the positive end of the molecular dipole.

For completeness, in Table 1S, we also present the linear C_{2v}-symmetry structure (**5**) that maximizes the dipole moment and, therefore, is expected to bind an extra electron relatively strongly. However, the corresponding anion possesses two (degenerate) imaginary frequencies and lies 0.259 eV above the energy of $\mathbf{1}^-$. When deformed along the negative modes, the linear $\mathbf{5}^-$ anion bends to achieve the local minimum energy structure $\mathbf{4}^-$ (zigzag).

The excess electron can also be trapped between two or three local dipoles, and we consider two structures of this type (SE structures): (i) the so-called "2+1" bent structure ($\mathbf{8}^-$) and (ii) the triangular D_{3h}-symmetry structure ($\mathbf{9}^-$). Although the neutral trimers in these configurations are geometrically unstable, the presence of the excess electron stabilizes such minima on the anionic PES to render them locally geometrically stable. Our SE systems possess large VDEs (26 906 and 34 052 cm^{-1} for structures $\mathbf{8}^-$ and $\mathbf{9}^-$, respectively; see Table 1), which makes their detection possible in photoelectron spectra. The SE structures are thermodynamically unstable (by 0.681 and 1.550 eV for $\mathbf{8}^-$ and $\mathbf{9}^-$, respectively), with respect to the global minimum $\mathbf{1}^-$ (see Figure 2). Also, the energies of $\mathbf{8}^-$ and $\mathbf{9}^-$ are greater (by 0.290 and 1.159 eV for $\mathbf{8}^-$ and $\mathbf{9}^-$, respectively) than that of the global minimum of the neutral (**6**). The energy of $\mathbf{8}^-$ is less than that of $\mathbf{9}^-$, by 0.869 eV, because of the presence of one stabilizing inter-monomer Na^+Cl^- interaction. We want to stress that the concept of the possible importance of such structures of the polar trimers (i.e., so-called "2+1" structure) has been suggested by Gutowski and co-workers, who examined an analogous structure for $(HF)_3^-$.[35] The D_{3h}-symmetry structure ($\mathbf{9}^-$) is geometrically stable only in the presence of the excess electron, because the orientation of the local dipoles toward one another is highly unfavorable and transformation to the lowest-energy structure requires large geometrical rearrangement. The existence of $\mathbf{9}^-$ has been previously predicted by Sunil and Jordan, who found it to be unstable (by 0.5 eV) to dissociation to $(NaCl)_2 + NaCl^-$ but bound (by 2.29 eV), with respect to $3NaCl + e^-$; they also estimated its VDE to be 3.77 eV at the SCF level with the 6-31G basis sets (augmented with s and p diffuse functions on Na atoms and d-symmetry diffuse functions on the Cl atoms).[1]

3.2.2. Vertical Electron Binding Energies. The value of *D* was partitioned into incremental contributions, calculated at "successive" levels of theory (KT, SCF, MP*n* ($n = 2, 3, 4$), and CCSD(T)), as discussed in section 2, and the results for the optimal $\mathbf{1}^-$, **2**, $\mathbf{2}^-$, $\mathbf{3}^-$, $\mathbf{4}^-$, **5**, $\mathbf{5}^-$, $\mathbf{7}^-$, $\mathbf{8}^-$, and $\mathbf{9}^-$ structures are presented in Table 1. In each case, we provide the results calculated at the anionic equilibrium geometry. For the linear (**5**) and arrow-shaped (**2**) structures, we provide the *D* values calculated at both the neutral and anionic equilibrium geometries. However, for the sake of simplicity, we limit the discussion to the *D* values obtained for the equilibrium anionic geometries, because they correspond to VDEs.

In the KT approximation, *D* results from the electrostatic and exchange interactions of the loosely bound electron with the SCF charge distribution of the neutral molecule. For seven anions (of DBS character ($\mathbf{1}^-$, $\mathbf{3}^-$, $\mathbf{4}^-$, $\mathbf{5}^-$, and $\mathbf{7}^-$) or SE character ($\mathbf{8}^-$, $\mathbf{9}^-$)) considered in this work, the D^{KT} values are relatively large: 6036 cm^{-1} for $\mathbf{1}^-$, 8821 cm^{-1} for $\mathbf{3}^-$, 13 550 cm^{-1} for $\mathbf{4}^-$, 13 493 cm^{-1} for $\mathbf{5}^-$, 16 757 cm^{-1} for $\mathbf{7}^-$, 25 615 cm^{-1} for $\mathbf{8}^-$, and 32 627 cm^{-1} for $\mathbf{9}^-$; these D^{KT} values are responsible for 77%−96% of the total value of *D* (see Table 1). In the case of $\mathbf{2}^-$, D^{KT} is much smaller (1514 cm^{-1}) and is responsible for 54% of the total value of *D*.

The SCF binding energies include orbital relaxation and, thus, take into account static polarization of the neutral molecule by the extra electron and the secondary effect of back-polarization. We found these contributions (which can be interpreted as orbital relaxation corrections to D^{KT}, denoted as ΔD_{ind}^{SCF}) to be responsible for 4%−12% of the total value of *D* (see Table 1).

The contribution denoted as ΔD_{disp}^{MP2} results from dynamical correlation between the loosely bound electron and the electrons of the neutral molecule. This stabilization is caused by quantum mechanical charge fluctuations and is responsible for ca. 2%−4% (for $\mathbf{3}^-$, $\mathbf{4}^-$, $\mathbf{5}^-$, $\mathbf{7}^-$, $\mathbf{8}^-$, and $\mathbf{9}^-$), 14% (for $\mathbf{1}^-$), and 31% (for $\mathbf{2}^-$) of the total value of *D* (see Table 1).

In addition to the dispersion interaction, other electron correlation factors may also affect the charge distribution (and multipole moments) of the neutral molecule and, thus, its electrostatic interaction with the extra electron. Such effects first appear at the MP2 level and are denoted $\Delta D_{no-disp}^{MP2}$. In all the cases at hand, MP2 electron correlation effects slightly reduce the lowest nonvanishing moment of the neutral system (see

Table 1S). Therefore, the value of $\Delta D^{\mathrm{MP2}}_{\mathrm{no-disp}}$ is destabilizing but small, yet the total MP2 contribution to D remains stabilizing, because of the dominant role of the dispersion component in each case except **9**$^-$, where this contribution is destabilizing (-224 cm^{-1}).

The contributions from ΔD^{MP3} and ΔD^{MP4} are usually stabilizing but very small (<1% of the total value of D, except in **2**$^-$, for which the ΔD^{MP4} term is 5% of the total value of D) for all anions. Higher-order correlation effects, calculated here as $\Delta D^{\mathrm{CCSD(T)}}$ (the difference between CCSD(T) and MP4 binding energies), are stabilizing in all cases but relatively unimportant for all our anions (ca. 1% of the total value of D, except in **2**$^-$, for which the $\Delta D^{\mathrm{CCSD(T)}}$ term is 7% of the total value of D) (see Table 1).

Combining all these contributions produces our final predictions for the VDEs: 7858, 2781, 9779, 14 560, 14 488, and 17 948 cm^{-1} for **1**$^-$, **2**$^-$, **3**$^-$, **4**$^-$, **5**$^-$, and **7**$^-$, respectively (whose nature we characterize as DBS), and 26 906 and 34 052 cm^{-1} for **8**$^-$ and **9**$^-$, respectively (which are SE systems).

4. Summary

We studied the possibility of an excess electron binding to the NaCl trimer in the gas phase. On the basis of our ab initio coupled-cluster method with single, double, and noniterative triple calculations with aug-cc-pVDZ+6s6p4d basis sets, we concluded the following:

(1) NaCl trimers are capable of forming electronically stable anions of either dipole-bound or solvated-electron nature.

(2) The lowest-energy isomer of $(\mathrm{NaCl})_3^-$ is a Λ-shaped dipole-bound anion, the vertical electron detachment energy (VDE) of which is 7858 cm^{-1}.

(3) The energy of solvated-electron structures are greater than those of dipole-bound anions; however, the VDEs of the former are significantly larger.

(4) The lowest-energy isomer of the neutral NaCl trimer is the cyclic D_{3h}-symmetry species, and it does not form an electronically stable anion.

(5) The number of local minima is larger for the anionic species than for the neutral NaCl trimer, because of the possible formation of solvated-electron species (that can be viewed alternatively as polar monomers linked by a one-electron σ bond) and also because new minima on the potential energy surface may develop, as a consequence of the binding of an excess electron.

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Supporting Information Available: Table 1S containing the geometries and harmonic vibrational frequencies for the neutral and anionic $(\mathrm{NaCl})_3$ at the MP2 stationary points and the corresponding lowest nonvanishing multipole moments for the neutral species. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) The results for the monomer that we used for comparison were calculated by us at the same level of theory to ensure consistency. The resulted bond length is 2.4256 Å (for NaCl) and 2.5594 Å (for NaCl$^-$), whereas the adiabatic electron affinity is 0.725 eV (5844 cm^{-1}).