First Evidence of Rhombic $(NaCl)_2^-$. Ab Initio Reexamination of the Sodium Chloride Dimer Anion

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Received: May 31, 2002; In Final Form: August 27, 2002

The possibility of electron binding to sodium chloride dimers in the gas-phase was studied at the coupled cluster level with single, double, and noniterative triple excitations using aug-cc-pVDZ+6*s*6*p*4*d* basis sets. It was found that three kinds of anions can be formed—quasi-linear dipole-bound, nearly rhombic quadrupole-bound, and linear solvated-electron anions. In contrast to the earlier results, it was found 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 corresponds to the dipole-bound anion of quasi-linear structure $(NaCl\cdots NaCl)^-$ whose vertical electron binding energy is 12 051 cm^{-1}. It was also found that solvated-electron structure $(ClNa\cdots NaCl)^-$ is considerably higher in energy than the anionic global minimum but its vertical electron detachment energy is significantly larger (i.e., 21 306 cm^{-1}). The nearly rhombic $(NaCl)_2^-$ lies only 0.181 eV above the anionic global minimum but below the global minimum of the neutral species.

1. Introduction

1.1. Binding of an Excess Electron to Sodium Chloride Clusters.

Substantial current interest in binding an excess electron to ionic clusters produced a significant number of manuscripts devoted to such 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 those 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.

Alkali halides are among the most important ionic compounds and therefore their properties have been the subject of many theoretical and experimental studies. Alkali halide clusters with one excess electron, such as Na_nF_{n-1} are said to be "essentially built around the rock-salt lattice, at least for small n[11]". Honea et al. identified two categories:[12,13](1) when $2n - 1$ is the product of three integers ($i \times j \times k$), then the structure is an $i \times j \times k$ cuboid portion of the rock-salt bulk lattice and the excess electron is bound to the *surface* of the cluster—these clusters involve an electron in a so-called *surface state*;(2) when $2n = i \times j \times k$, the structure is a cuboid lattice with one vacancy occupied by the excess electron, as in a bulk *F-center*.

The latter are characterized by larger ionization potentials (IPs) than the former. For example, the calculated IPs are 3.48 for Na_4F_3 (belonging to category (2)) and 1.99 eV for $Na_{14}F_{13}$ (category (1)).[11]

Only a small portion of the research devoted to alkali halides has been dedicated to molecular anions derived from such clusters. In fact, surprisingly, the problem of an extra electron binding to sodium chloride clusters is not yet fully understood. In this study, we focus on the smallest sodium chloride cluster $(NaCl)_2$ and its ability to bind an extra electron.

One is able to find several experimental reports containing the photoelectron and photodetachment spectra of $(NaCl)_2^-$, thus providing the vertical electron detachment energies of the ground and excited anionic states.[3,14,15] Although reliable and informative, the experimental measurements 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.

The number of theoretical papers devoted to $(NaCl)_2^-$ is rather limited. The majority of the theoretical studies were undertaken using molecular dynamics methods and simulated annealing.[3,5,16] Such treatments are based on considering a given cluster ($(NaCl)_2^-$, in this case) to be a collection of sodium cations, chlorine anions, and one excess electron with only the one electron being treated quantum mechanically. The interactions among the ions are modeled using empirical force fields having pairwise long-range Coulomb interactions and repulsive terms, with the parameters chosen to reproduce the bond length in the NaCl monomer and in the bulk solid. The electron−ion potential is modeled in terms of a one-electron pseudopotential.[5] Such a treatment can be applied to small molecular system as $(NaCl)_2^-$, but in the present study we chose to employ correlated ab initio methods. There are two excellent quantum chemistry studies of the anionic sodium chloride dimer by Sunil and Jordan,[1,2] but they both were published in the 1980s and thus the treatment employed (basis sets and electron correlation) had to be relatively low due to the limited computer resources available then.

The lack of recent ab initio data on one of the simplest alkali halide compounds has motivated us to undertake a more thorough study of the possibility of an excess electron binding to $(NaCl)_2$. In this contribution, not only do we present an ab

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10.1021/jp021318b CCC: $22.00

initio reexamination of the anionic sodium chloride dimer but also we show the first theoretical evidence that the rhombic $(NaCl)_2^-$ anion is indeed electronically stable. We believe this contribution is important because there is common opinion that $(NaCl)_2^-$ can exist in only two forms: (i) linear (or quasi-linear) $^-(NaCl\cdots NaCl)$ as a dipole-bound anionic state, and (ii) as a "solvated electron" linear species $ClNa\cdots(-)\cdots NaCl$, with the excess electron trapped between the positive sodium centers. If the existence of the rhombic anion is excluded, one misses the important issue of attaching the excess electron to the global-minimum structure of the neutral parent, which indeed is a rhombus. Moreover, we show that it is the quadrupole potential of the rhombic neutral molecular host that is, in fact, responsible for the excess electron binding in this case.

1.2. Dipole- and Quadrupole-Bound Anions and Solvated Electrons. The binding of electrons to polar molecules has been addressed in many theoretical studies.[17−30] It has been shown that, within the Born−Oppenheimer (BO) approximation, species with a dipole moment greater than 1.625 D possess an infinite number of bound anionic states.[31,32] 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.[17] 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 electron in a dipole-bound state occupies a diffuse orbital localized mainly on the positive side of the dipole.[20] 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 dipole-bound states with electron binding energies much larger than the molecular rotational constants.[33]

The electron binding energy (D) can be estimated on the basis of Koopmans' theorem (KT)[34] 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.[21] In contrast, the role of electron correlation has 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[18,19,21−24] although higher-order correlation effects can also be significant.[21−24,29,35] 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 referred to as *solvated electrons* (SE), has been known since 1864 when they were observed in liquid ammonia.[36] Since then, many systems containing solvated electrons have been studied, such as $(NaCl)_n^-$ (n = 2,3,4),[1,2] $(HF)_n^-$ (n = 2,3),[37] and $[O{=}C(NH_2)_2]^-$.[38]

There are several important differences between SE systems and dipole-bound anions. The former contain an extra electron localized primarily *inside* a cluster of polar molecules whose dipoles are directed toward the excess electron.[39] 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 vertical electron detachment energies (VDE) and to undergo large geometrical rearrangements upon electron detachment because the dipoles directed toward one another are highly unfavorable in the absence of the electron.[1,2,38,39]

Higher multipole moments may also be responsible for an excess electron binding. In particular, the possibility of forming stable anions by molecules with significant quadrupole moments and vanishing dipole moments has attracted both theoretical[40−44] and experimental chemists.[45,46] These molecular anions are similar to dipole-bound anions, however, the generalization of the electrostatic model developed for dipole-bound anions to quadrupole-bound anions (QBS) is not straightforward. The charge distribution in a quadrupole is characterized by eigenvalues of the traceless quadrupole tensor[47]

$$Q_{\alpha,\beta} = \sum_i q_i(3r_i^{\alpha}\, r_i^{\beta} - r_i^2\delta_{\alpha,\beta}) \tag{1}$$

where r_i^{α} is the αth Cartesian coordinate of the charge q_i. For a species with cylindrical symmetry around the z axis, such as the $(NaCl)_2$ rhombus studied here, the nondiagonal elements $Q_{\alpha,\beta}$ vanish and $Q_{x,x} = Q_{y,y} = -0.5\, Q_{z,z}$. Then $Q = Q_{z,z}$ may be used to characterize the quadrupole potential. The Schrödinger equation for an electron in the potential of a cylindrical point quadrupole

$$\left(-\frac{1}{2}\nabla^2 - \frac{Q(3\cos^2\theta - 1)}{4r^3}\right)\phi_{\mathrm{mbe}} = \epsilon\phi_{\mathrm{mbe}} \tag{2}$$

has a bound solution for any nonzero value of Q due to the strong singularity at the origin[48,49] (in eq 2 ϕ_{mbe} describes a multipole-bound electron (mbe) and ϵ is the negative of the excess electron binding energy). We would like to stress that, unlike the dipole case for which the dipole moment (μ) has to exceed 1.625 D for bound states to exist, the quadrupole potential can support bound states for any $Q > 0$ (see discussion given in ref 49). Therefore, any discussion considering the problem of a critical value of Q regarding an excess electron binding seems pointless.

If a "hard core" repulsion is included in the electrostatic model of eq 2, then a bound solution may disappear or may persist if Q is large enough.[45] Therefore, the definition of quadrupole-bound anions cannot be solely based on the magnitude of Q. One needs to take into account the spatial extent of the charge distribution of the neutral molecule as well as the short-range occupied orbital exclusion (ooe) effects. It has been proposed by Gutowski and Skurski[42] to consider an anionic state to be bound as a result of the static interaction with the charge distribution of a neutral system denoted N if the one-particle Schrödinger equation

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{elst}}^{\mathrm{exact}} + V_{\mathrm{ooe-exch}}^{\mathrm{exact}}\right)\phi_{\mathrm{mbe}} = \epsilon\phi_{\mathrm{mbe}} \tag{3}$$

possesses a bound solution. Here, $V_{\mathrm{elst}}^{\mathrm{exact}}$ represents the potential from the exact charge distribution ρ_N^{exact} of N

$$V_{\mathrm{elst}}^{\mathrm{exact}}\phi(1) = \int \frac{\rho_N^{\mathrm{exact}}(2)}{r_{1,2}}\mathrm{d}\tau_2\phi(1), \tag{4}$$

and $V_{\mathrm{ooe-exch}}^{\mathrm{exact}}$ guarantees that the Pauli exclusion principle requirements are not violated by ϕ_{mbe}. Equation 3 applies to any multipole-bound anion and may be reduced to a one-particle Schrödinger equation for a dipole-bound anion or to eq 2 through a truncated multipole expansion of $V_{\mathrm{elst}}^{\mathrm{exact}}$ and neglect of $V_{\mathrm{ooe-exch}}^{\mathrm{exact}}$.

Since, in practical calculations, the $V_{\mathrm{elst}}^{\mathrm{exact}}$ and $V_{\mathrm{ooe-exch}}^{\mathrm{exact}}$ operators are not available, it has been proposed[42] to use a well-known approximation to eq 3 at the Hartree−Fock (HF) self-consistent-field (SCF) level of theory. With ρ_N^{exact} in $V_{\mathrm{elst}}^{\mathrm{exact}}$ replaced by ρ_N^{HF}, and $V_{\mathrm{ooe-exch}}^{\mathrm{exact}}$ replaced by the standard SCF exchange operators, eq 3 becomes equivalent to the KT description of the excess electron binding. In this case ϵ is equal to the energy of the virtual orbital ϕ_{mbe} obtained in the SCF calculation for N. The electron binding energy at the KT level of theory is given by the negative of ϵ and is labeled D^{KT}.

The criterion given by eq 3 is necessary but not sufficient to identify a dipole- or a quadrupole-bound anion (see the discussion in ref 42). There are many systems, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ) or tetracyanoethylene (TCNE), for which there is at least one negative eigenvalue in the SCF spectrum of virtual molecular orbitals, and the related orbital is occupied in the anionic state.[50,51] Although the negative eigenvalue indicates that the excess electron is already bound as a result of the static plus SCF exchange interaction with the charge distribution of the neutral core, the charge distribution of the excess electron may reveal that one is not dealing with the multipole-bound anion. In brief, the charge distribution of N and of the excess electron should not have major regions of large overlap. Moreover, the symmetry of the charge distribution of the excess electron has to be consistent with the electrostatic potential produced by the lowest nonvanishing multipole moment of N. In fact, in the anionic states of TCNQ and TCNE, the excess electron occupies π molecular orbitals dominated by valence 2p atomic orbitals. Hence, the spatial extent of the charge distributions of the excess electron and of N are not different enough to invoke the multipole-binding model.

1.3. $(NaCl)_2^-$. The Current Status. Our goal in this section is to provide the reader with the most recent results that are available in the literature considering the excess electron binding to sodium chloride dimer. As far as the geometrical structures are concerned, there are only two kinds that have been described: (i) a linear (or slightly bent) structure in which the two NaCl monomers are aligned *head-to-tail* as to maximize the polarity of the dimer, and the excess electron is localized mainly outside the molecular framework at the positive end of the molecular dipole (e···Na−Cl···Na−Cl); and (ii) a linear $D_{\infty h}$-symmetry structure in which two NaCl monomers are aligned *head-to-head* and the excess electron is localized mainly inside the cluster, between two sodium atoms (Cl−Na···e···Na−Cl).

Structure (i) is a dipole-bound anion that belongs to the “surface states”, while structure (ii) is the solvated-electron species that serves as a simple model for an F-center.

The experimental value of the vertical electron detachment energy of $(NaCl)_2^-$ has been reported by Bloomfield et al. as 1.55 ± 0.05 eV.[3] This value comes from the photoelectron and photodetachment spectra performed for a variety of stoichiometric cluster anions $(NaCl)_n^-$ (where $n = 2-13$). Earlier, this group reported the value of 1.25 ± 0.01 eV by means of their photodetachment threshold measurements on sodium chloride cluster anions in the plume of laser-vaporized sodium chloride.[14] The experimental VDE = 1.55 eV seems more reliable in the context of simulated annealing results providing 1.58 eV[3] and 1.59 eV.[5] In addition, Yu et al.[5] found that both simulated annealing and local minimization techniques yield a slightly bent *head-to-tail* chain as the minimum energy structure for the anionic $(NaCl)_2^-$ cluster. Local minimization performed by the same group led also to a SE (*head-to-head*) isomer for which they predicted a vertical electron binding energy of 2.88 eV.[5] This structure, however, was found to be higher than the *head-to-tail* global minimum by 0.82 eV. Thus it appears that the experimental data[5] relate to the *head-to-tail* dipole-bound anion.

To the best of our knowledge, the best and most recent ab initio calculations for the sodium chloride dimer anion have been performed by Sunil and Jordan and reported as two separate manuscripts.[1,2] Sunil and Jordan first studied the neutral and anionic form of the sodium chloride dimer by employing the SCF method with 6-31G basis sets augmented on the sodium and chlorine atoms with diffuse *s* and *p* functions, and with *d* functions[1,52] (the resulting basis set was later referred to as the SJ basis set[2] by these authors). There were two geometrically stable anionic structures found, the *head-to-tail* $(NaCl\cdots NaCl)^-$ dipole-bound anion and the “solvated-electron” species (ClNa···(−)···NaCl) with 1.28 and 2.55 eV vertical detachment energies, respectively. In addition, the SE system was predicted to be higher in energy than the dipole-bound anion by 0.51 eV.[1]

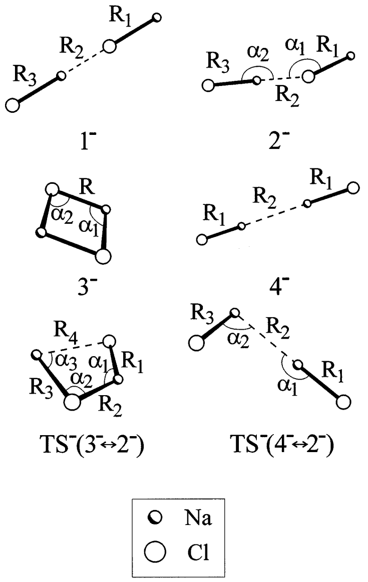

Figure 1. Equilibrium structures corresponding to the anionic minima and transition states studied in this work. The values of the geometrical parameters defined here are given in Table 1.

In their second paper on this subject, Sunil and Jordan not only improved their results by including correlation effects at the MP2 level and replacing the SJ basis with the 6-31+G(2d) basis, but also studied the $(NaCl\cdots NaCl)^- \leftrightarrow$ (ClNa···(−)··· NaCl) interconversion. They obtained VDE values of 1.42 eV (HF/6-31+G(2d)) and 1.46 eV (MP2/6-31+G*) for the dipole-bound $(NaCl\cdots NaCl)^-$ anion, and 2.55 eV (HF/6-31+G(2d)) and 2.87 eV (MP2/6-31+G*) for the solvated electron (ClNa···(−)···NaCl) species.[2] The transition state (TS) connecting these two minima was also found to be capable of supporting a stable anion (with VDE = 0.50 eV, at the MP2/6-31+G* level). The TS’s geometrical structure was found to be planar and L-shaped as shown in the bottom right picture of Figure 1. As obtained at the MP2/6-31+G* level, there is a kinetic barrier of 0.27 eV for the SE → TS → DBS transformation and of 0.78 eV for the reverse process[2].

Both simulated annealing and local minimization techniques predicted the dipole-bound anion to be slightly bent.[5] Sunil and Jordan also found it to be bent when studied with the SJ basis set;[1] however, with the 6-31+G(2d) basis, this anion was linear.[2] These results[1,2] are consistent with the observation of Sunil and Jordan that the Na−Cl−Na bending potential is quite flat (e.g., with the 6-31+G(2d) basis set, there is a bending mode with a frequency of only 5 cm^{-1}).[2]

Sunil and Jordan also examined the possibility of supporting an electronically stable anion by the rhombic cluster. Since the rhombic D_{2h}-symmetry structure is undoubtedly the global minimum on the potential energy surface of the neutral species (as confirmed by many studies[1,2,5,10]), it seemed natural to explore its capability of binding an excess electron. However, their ab initio calculations failed to yield a stable anion for this cyclic dimer.[2]

In this paper, we present an ab initio reexamination of excess electron binding to the sodium chloride dimer providing electron binding energies calculated at the coupled-cluster level with single and double excitations and noniterative triples (CCSD(T)) with correlation-consistent basis sets. In particular, we show that the rhombic D_{2h}-symmetry structure of the neutral supports an electronically stable anion of quadrupole-bound nature.

2. Methods

We first studied the ground-state potential energy surfaces of the neutral and anionic sodium chloride dimers at the second-order Møller−Plesset perturbation theory (MP2)[53] level. Because the methods we used are based on an unrestricted Hartree−Fock (UHF) starting point, it is important to make sure 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 0.7501 in all anion cases. Hence, we are certain that spin contamination is not large enough to significantly affect our findings.

The electron binding energies (D) 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 and the coupled-cluster method with single, double, and noniterative triple excitations (CCSD(T)).[54] In addition, D was analyzed within the perturbation framework designed for dipole-bound anions and solvated electrons described previously by Gutowski and Skurski.[37] It should be pointed out, however, that a recent contribution by Peterson and Gutowski[35] suggests that perturbative rather than full inclusion of triple excitations in the coupled cluster method (i.e., CCSD(T) vs CCSDT) may lead to either underestimation or overestimation of the electron binding energy for some weakly bound systems such as HCN^- or HNC^-.

The simplest theoretical approach to estimate D is based on Koopmans' theorem (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 the electron binding energy, 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

$$\Delta D^{\mathrm{SCF}}_{\mathrm{ind}} = D^{\mathrm{SCF}} - D^{\mathrm{KT}} \tag{5}$$

where

$$D^{\mathrm{SCF}} = E^{\mathrm{SCF}}_{\mathrm{N}} - E^{\mathrm{SCF}}_{\mathrm{A}} \tag{6}$$

and $E^{\mathrm{SCF}}_{\mathrm{N}}$ and $E^{\mathrm{SCF}}_{\mathrm{A}}$ stand for 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 it is approximated here by $\Delta D^{\mathrm{MP2}}_{\mathrm{disp}}$, which takes into account proper permutational symmetry for all electrons in the anion

$$\epsilon^{(02)}_{\mathrm{disp}} \approx \sum_{a\in N}\sum_{r<s} \frac{|\langle \phi_a\phi_{\mathrm{mbe}}||\phi_r\phi_s\rangle|^2}{e_a + e_{\mathrm{mbe}} - e_r - e_s} = -\Delta D^{\mathrm{MP2}}_{\mathrm{disp}} \tag{7}$$

where ϕ_a and ϕ_{mbe} are *spin orbitals* occupied in the unrestricted Hartree−Fock (UHF) anion wave function, ϕ_r and ϕ_s are unoccupied orbitals, and the e's are the corresponding orbital energies. The subscript mbe denotes the multipole bound electron's spin−orbital.

The total MP2 contribution to D defined as

$$\Delta D^{\mathrm{MP2}} = D^{\mathrm{MP2}} - D^{\mathrm{SCF}} \tag{8}$$

is naturally split into dispersion and nondispersion terms

$$\Delta D^{\mathrm{MP}2} = \Delta D^{\mathrm{MP2}}_{\mathrm{disp}} + \Delta D^{\mathrm{MP2}}_{\mathrm{no-disp}} \tag{9}$$

with the latter dominated by the correlation correction to 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

$$\Delta D^{\mathrm{MPn}} = D^{\mathrm{MPn}} - D^{\mathrm{MP}(n-1)} \quad n = 3,4 \tag{10}$$

Finally, the contributions beyond the fourth-order are estimated by subtracting MP4 results from those obtained at the coupled-cluster SD(T) level

$$\Delta D^{\mathrm{CCSD(T)}} = D^{\mathrm{CCSD(T)}} - D^{\mathrm{MP4}} \tag{11}$$

The diffuse character of the orbital describing the loosely bound electron necessitates the use of extra diffuse basis functions having very low exponents.[55] In addition, the basis set chosen to describe the neutral molecular host should be flexible enough to (i) accurately describe the static charge distribution of the neutral, 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[56] supplemented with a 5*s*5*p* set of diffuse functions centered on the terminal sodium atom (for linear (**1**) and bent (**2**) species, see Figure 1), in the middle of the rhombus for species **3**, and between the two sodium atoms in **4**. We checked (for structure **3**) that replacing the 6*s*6*p*4*d* diffuse set centered in the middle of the rhombus with two such sets centered on both sodium atoms instead changes the electron binding energy by less than 5 cm^{-1} at the KT level, which corresponds to 0.02% of D^{KT}. Since introducing two 6*s*6*p*4*d* diffuse sets instead of one leads to serious linear dependencies in the basis set[57] and does not substantially improve our results, we decided to use just one 6*s*6*p*4*d* diffuse set, which also allows to ensure consistency with other results presented in this work.

The evaluation of the electron binding energies was performed with the aug-cc-pVDZ basis set supplemented with a 6*s*6*p*4*d* set of diffuse functions centered as described above. The aug-cc-pVDZ basis set was chosen since we earlier showed its usefulness in describing multipole-bound anions compared to other commonly used one-electron basis sets.[55] The extra diffuse functions do not share exponent values and we used even-tempered[58] six-term *s*, six-term *p*, and four-term *d* basis sets. The geometric progression ratio was equal to 3.2,[59] 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} a.u., for the *s*, *p*, and *d* symmetries, respectively.

We determined that the MP2 electron binding energy of the rhombic anion **3**$^-$ increases by only 0.1 cm^{-1} when the aug-cc-pVDZ+6s6p4d basis set is replaced with the aug-cc-pVDZ+7*s*7*p*5*d* basis set. Since we determined this for the most weakly bound anion considered in this work, we are confident the extra diffuse functions are not necessary to properly reproduce the electron binding energies of any of the sodium chloride dimer anions.

All calculations were performed with the GAUSSIAN98 program[60] on AMD Athlon 950 MHz and Pentium IV 1.7GHz computers, as well as on SGI Origin2000 and Compaq Sierra systems. The three-dimensional plots of molecular orbitals were generated with the MOLDEN program.[61]

3. Results

3.1. Neutral Species. We focused our investigation of the ground-state potential energy surface (PES) of the neutral sodium chloride dimer on finding the structure corresponding to the global minimum. On the basis of our MP2/aug-cc-pVDZ+5*s*5*p* calculations, we confirmed that the rhombic D_{2h}-symmetry structure **3** (see Figure 1) is indeed a minimum and it is the lowest energy structure of the neutral NaCl dimer. The geometry of this rhombus is given in Table 1 together with the corresponding MP2 vibrational frequencies. As shown in Figure 2, the rhombic $(NaCl)_2$ lies 2.073 eV below the energy of two separated monomers, thus its formation is thermodynamically favorable. The Na−Cl distances in **3** are longer than in the NaCl monomer by 0.1694 Å.[62]

Since the dipole moment of **3** vanishes by symmetry, the first nonvanishing multipole moment is the quadrupole (*Q*). Having in mind the ionic character of all $(NaCl)_n$ clusters, one would expect rather significant magnitudes of the *Q* tensor for the rhombic dimer. Indeed, the eigenvalues of the traceless quadrupole moment tensor collected in Table 1 are large (ca. 76.2, 1.4, and −77.6 D × Å). Comparing these values to the eigenvalues of *Q* found previously for $(BeO)_2$ (i.e., 38.9, 1.1, and −39.9 D × Å),[42] and knowing that the beryllium oxide dimer at its rhombic geometry forms an electronically stable anion of quadrupole-bound nature,[40,42] we questioned the earlier reports[1] indicating the instability of rhombic $(NaCl)_2{}^-$.

In addition, we tried to find a local minimum on the neutral PES of the sodium chloride dimer that corresponds to a structure with only one inter-monomer Na^+Cl^- interaction. Such a structure would be either *linear* or *bent*. First, we verified that the linear neutral system of $C_{\infty v}$ symmetry possesses one (degenerate) imaginary frequency corresponding to the soft bending mode. However, if one allows this structure to bend, the algorithm we used does not lead to a minimum on the PES. Instead, it converges to a bent structure of the neutral $(NaCl)_2$, which corresponds to a stationary point but with one very soft (9*i* cm^{-1}) imaginary frequency. Despite many attempts (that included using various basis sets as well as the density functional method with the B3LYP functional), we were not able to find any linear or quasi-linear neutral $(NaCl)_2$ structure that corresponds to a true local minimum on the PES. The observations that others[1] also failed to find such a minimum suggests it is likely that the neutral linear (or bent) sodium chloride dimer indeed is not a minimum but distorts to give the stable rhombic structure. This explanation is confirmed by the observation that the soft imaginary vibration found for the neutral bent dimer corresponds to the ring opening/closing movement, and if one deforms the structure along that mode, then the rhombic structure is achieved.

3.2. Anionic Species. *3.2.1. Geometries and Relative Stabilities.* We first focused on the anions that result from attaching an excess electron to the dipole field of the parent neutral dimers so we started from the linear NaCl···NaCl structure that maximizes the dipole moment and therefore is expected to bind an extra electron relatively strongly. However, the corresponding anion (termed **1**$^-$ in Figure 1) possesses one (degenerate) imaginary frequency of 21*i* cm^{-1} (see Table 1). Therefore, we deformed the **1**$^-$ along the mode corresponding to the imaginary frequency, which resulted in locating the **2**$^-$ minimum (all frequencies real, see Table 1). This *bent* anion **2**$^-$ of C_s symmetry is the global-minimum on the anionic PES (see Figure 2). As shown in Figure 3, the molecular orbital holding the extra electron in **2**$^-$ is localized primarily outside the molecular framework, in the vicinity of the positive site of the molecular dipole, which is typical for dipole-bound anions. As we already discussed in Section 1.3, various theoretical treatments lead to different conclusions about the character of the linear and bent anionic stationary points. However, since the Na−Cl−Na bending potential is quite flat, these two anions should be relatively alike. Indeed, their total electronic energies differ only by 0.011 eV, and, as we discuss in the next section, they have similar electron binding energies.

We verified that the dipole-bound anion **2**$^-$ is the global minimum on the ground-state anionic potential energy surface. An analogous conclusion has been established by others.[1−3,5] According to our finding, **2**$^-$ lies 2.405 eV below the energy of the two isolated neutral NaCl monomers, and 0.332 eV below the energy of the neutral rhombic global minimum **3** (see Figure 2).

Even though the rhombic structure of the neutral $(NaCl)_2$ had been described as not capable of forming a stable anion (see Section 1.3), we decided to verify that, because the large eigenvaluess of the quadrupole moment *Q* (see Table 1) suggested that supporting a stable anionic state might occur. We found that the D_{2h}-symmetry rhombic $(NaCl)_2$ does indeed bind an extra electron to form an electronically stable anion. We term this anion (**3**$^-$) quadrupole-bound because (i) the neutral parent possesses no orbital vacancies, (ii) the lowest nonvanishing multipole moment of the neutral parent is the quadrupole, (iii) the anion is bound at the electrostatic-exchange (i.e., Koopmans') level, where the excess electron occupies an a_g molecular orbital which is localized primarily outside the molecular framework, and (iv) the symmetry of the charge distribution of the excess electron is consistent with the electrostatic potential produced by the quadrupole moment of the neutral $(NaCl)_2$, which results in localizing of the excess electron primarily in the vicinity of both sodium atoms that act as positive poles of molecular quadrupole (see Figure 3). As we discuss in the next section, this anion is much more weakly bound than other anionic species described in this work.

To the best of our knowledge, the existence of electronically stable rhombic $(NaCl)_2{}^-$ has not been described in the literature thus far. This anion lies above the global anionic minimum **2**$^-$ by 0.181 eV, but 0.151 eV below the global minimum for the neutral **3** (see Figure 2). We consider the stability of this anion important information that is needed to have a thorough insight into the process of creation negatively charged sodium chloride dimers.

TABLE 1: The Geometries, Harmonic Vibrational Frequencies for the Neutral and Anionic $(NaCl)_2$ at the MP2 Stationary Points[a]

species/ symmetry	electronic state	geometry[b]	vibrational frequencies[c]	lowest nonvanishing multipol moment for the neutral[d]
1	anion	R_1(Na−Cl) = 2.649	$\nu_{1.2} = 14i\ (\pi)$	$\mu^{SCF} = 22.47$
linear	$^2\Sigma$	R_2(Na•••Cl) = 2.594	$\nu_{3.4} = 70\ (\pi)$	$\mu^{MP2} = 2\ 2.28$
$C_{\infty v}$		R_3(Na−Cl) = 2.521	$\nu_5 = 133\ (\sigma)$	
			$\nu_6 = 229\ (\sigma)$	
			$\nu_7 = 331\ (\sigma)$	
2	anion	R_1(Na−Cl) = 2.648	$\nu_1 = 15\ (a')$	$\mu^{SCF} = 21.62$
bent	$^2A'$	R_2(Na•••Cl) = 2.595	$\nu_2 = 71\ (a'')$	$\mu^{MP2} = 21.29$
C_s		R_3(Na−Cl) = 2.523	$\nu_3 = 71\ (a')$	
		$\alpha_1 = 146.66$	$\nu_4 = 144\ (a')$	
		$\alpha_2 = 177.71$	$\nu_5 = 227\ (a')$	
			$\nu_6 = 330\ (a')$	
3	neutral	R(Na−Cl) = 2.595	$\nu_1 = 92\ (b_{1u})$	$Q_{xx}^{SCF} = -77.64$
rhombic	^1A_g	$\alpha_1 = 101.73$	$\nu_2 = 134\ (a_g)$	$Q_{yy}^{SCF} = 1.43$
D_{2h}		$\alpha_2 = 78.27$	$\nu_3 = 224\ (b_{2u})$	$Q_{zz}^{SCF} = 76.21$
			$\nu_4 = 230\ (b_{1g})$	$Q_{xx}^{MP2} = -76.58$
			$\nu_5 = 255\ (a_g)$	$Q_{yy}^{MP2} = 1.02$
			$\nu_6 = 273\ (b_{3u})$	$Q_{zz}^{MP2} = 75.56$
	anion	R(Na−Cl) = 2.631	$\nu_1 = 244i\ (b_{3u})$[e]	$Q_{xx}^{SCF} = -79.96$
	^2A_g	$\alpha_1 = 101.57$	$\nu_2 = 42\ (b_{1u})$	$Q_{yy}^{SCF} = 1.45$
		$\alpha_2 = 78.43$	$\nu_3 = 124(a_g)$	$Q_{zz}^{SCF} = 78.51$
			$\nu_4 = 213\ (b_{1g})$	$Q_{xx}^{MP2} = -78.81$
			$\nu_5 = 238\ (a_g)$	$Q_{yy}^{MP2} = 1.00$
			$\nu_6 = 246\ (b_{3u})$	$Q_{zz}^{MP2} = 77.81$
$\mathbf{3}_{C2v}$	anion	R_1(Na−Cl) = 2.771	$\nu_1 = 61\ (b_2)$	$\mu^{SCF} = 1.54$
C_{2v}	$^2A_1$	R_2(Na−Cl) = 2.542	$\nu_2 = 126\ (a_1)$	$\mu^{MP2} = 1.50$
		$\alpha_1 = 108.06$	$\nu_3 = 142(a_1)$	
		$\alpha_2 = 78.03$	$\nu_4 = 176\ (b_1)$	
			$\nu_5 = 304\ (a_1)$	
			$\nu_6 = 361\ (b_1)$	
4	anion	R_1(Na−Cl) = 2.527	$\nu_{1.2}=29\ (\pi_u)$	$Q_{xx}^{SCF} = 117.59$
linear	$^2\Sigma_g$	R_2(Na•••Na) = 3.912	$\nu_3=59\ (\sigma_g)$	$Q_{yy}^{SCF} = 117.59$
$D_{\infty h}$			$\nu_{4.5} = 63\ (\pi_g)$	$Q_{zz}^{SCF} = -235.18$
(solvated electron)			$\nu_6 = 278\ (\sigma_u)$	$Q_{xx}^{MP2} = 114.23$
			$\nu_7 = 289\ (\sigma_g)$	$Q_{yy}^{MP2} = 114.23$
				$Q_{zz}^{MP2} = -228.46$
$TS^-(\mathbf{3}^- \leftrightarrow \mathbf{2}^-)$	anion	R_1(Na−Cl) = 2.504	$\nu_1 = 64i\ (a')$	$\mu^{SCF} = 6.21$
C_s	$^2A'$	R_2(Na−Cl) = 2.549	$\nu_2 = 59\ (a'')$	$\mu^{MP2} = 6.11$
		R_3(Na−Cl) = 2.743	$\nu_3 = 104\ (a')$	
		R_4(Na•••Cl) = 3.822	$\nu_4 = 172\ (a')$	
		$\alpha_1=125.63$	$\nu_5 = 234\ (a')$	
		$\alpha_2=84.78$	$\nu_6 = 323\ (a')$	
		$\alpha_3=84.72$		
$TS^-(\mathbf{4}^- \leftrightarrow \mathbf{2}^-)$	anion	R_1(Na−Cl) = 2.521	$\nu_1 = 60i\ (a')$	$\mu^{SCF} = 14.03$
C_s	$^2A'$	R_2(Na•••Na) = 3.600	$\nu_2 = 52\ (a')$	$\mu^{MP2} = 13.77$
		R_3(Na−Cl) = 2.528	$\nu_3 = 53\ (a'')$	
		$\alpha_1 = 179.75$	$\nu_4 = 90\ (a')$	
		$\alpha_2 = 90.44$	$\nu_5 = 277\ (a')$	
			$\nu_6 = 286\ (a')$	

[a] The SCF and MP2 dipole moments ($^\mu$) and eigenvalues of the traceless quadrupole tensor (Q) of the rhombus $(NaCl)_2$ are reported both at the neutral and anionic MP2 stationary points. [b] The bond lengths (R) in Å, valence angles (α) in degrees. See Figure 1 for geometrical parameter definitions. [c] The vibrational frequencies in cm^{-1}. [d] The dipole moments in Debyes and the eigenvalues of the quadrupole moment in Debyes×Å. [e] The zero-point averaged anionic structure is rhombic (see Section 3.2.1).

The vibrational frequencies of $\mathbf{3}^-$ collected in Table 1 indicate that this possesses one imaginary frequency of b_{3u} symmetry. We verified that if one deforms the planar rhombic structure along this mode, one reaches a local minimum that possesses C_{2v} symmetry and is a slightly distorted rhombus (termed $\mathbf{3}_{C2v}$ in Table 1). This is the species that represents a proper local minimum on the ground-state energy surface. Moreover, we found that, when the b_{3u} vibration's zero-point energy is included, the barrier connecting $\mathbf{3}^-$ and the slightly distorted rhombus $\mathbf{3}_{C2v}$ is more than surmounted. Therefore, we conclude that, when averaged over zero-point vibrations, this structure is effectively rhombic and planar (D_{2h}).

The conversion from rhombic $\mathbf{3}^-$ to the lowest-energy anion $\mathbf{2}^-$ can be realized by overcoming a small kinetic barrier of

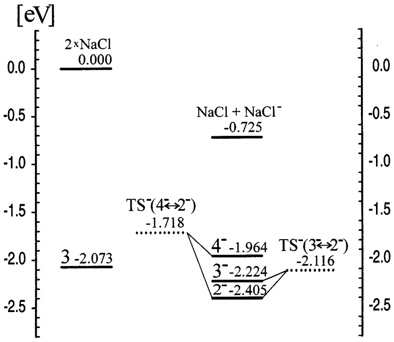

Figure 2. Relative electronic CCSD(T) energies (in eV) of the stationary points: minima (solid line) and selected transition states (dotted line) on the anion (right) and neutral (left) ground-state potential energy surface. The zero of energy is taken to be twice the CCSD(T) energy of the neutral NaCl monomer.

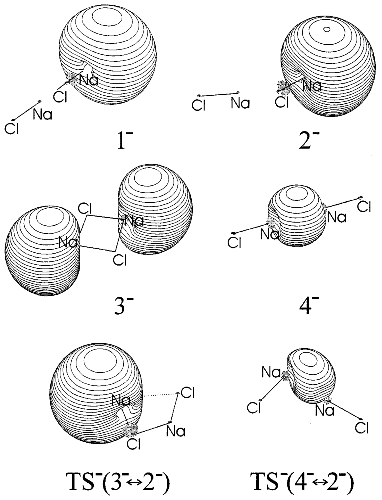

Figure 3. Singly occupied molecular orbital (SOMO) holding the excess electron in the ground electronic states of anions supported by sodium chloride dimers plotted with 0.015 (for **1**$^-$ and **2**$^-$), 0.01 (for **3**$^-$), 0.025 (for **4**$^-$), 0.015 (for TS$^-$(**3**$^-$↔**2**$^-$)), and 0.04 (for TS$^-$(**4**$^-$↔**2**$^-$)) bohr$^{-3/2}$ contour spacing, respectively.

TABLE 2: Components of the Vertical Electron Binding Energies D (in cm^{-1}) of Sodium Chloride Dimer Anions of Dipole-Bound, Quadrupole-Bound, and Solvated-Electron Character Calculated with the aug-cc-pVDZ+6*s*6*p*4*d* Basis Sets

	1$^-$linear $C_{\infty v}$	**2**$^-$bent C_s	**3** rhombic D_{2h} neutral geometry	**3**$^-$ rhombic D_{2h} anionic geometry	**4**$^-$ linear $D_{\infty h}$ solvated electron
D^{KT}	11182	11138	184	244	20069
$\Delta D^{\mathrm{SCF}}_{\mathrm{ind}}$	542	546	22	27	1139
$\Delta D^{\mathrm{MP2}}_{\mathrm{disp}}$	427	437	559	621	519
$\Delta D^{\mathrm{MP2}}_{\mathrm{no-disp}}$	−143	−153	−13	−18	−481
ΔD^{MP3}	26	26	−12	−11	100
ΔD^{MP4}	23	22	118	126	−81
$\Delta D^{\mathrm{CCSD(T)}}$	33	35	303	281	41
Sum	**12090**	**12051**	**1161**	**1270**	**21306**

0.108 eV (872 cm^{-1}),[63] and the corresponding transition state (TS) structure of C_s symmetry, termed TS$^-$(**3**$^-$↔**2**$^-$), is depicted in Figure 1. The geometrical parameters of TS$^-$(**3**$^-$↔**2**$^-$) are collected in Table 1 while its singly occupied molecular orbital is shown in Figure 3. We estimated the vertical electron stability of this anion to be 0.718 eV (5795 cm^{-1}) at the CCSD(T)/aug-cc-pVDZ+6*s*6*p*4*d* level which indicates that the excess electron is not going to auto-detach during **3**$^-$ to **2**$^-$ interconversion via TS$^-$(**3**$^-$↔**2**$^-$).

To complete the picture we also considered the *head-to-head* Cl−Na···e···Na−Cl structure of the sodium chloride dimer, termed **4**$^-$. As explained in Sections 1.1 and 1.3, such a structure is linear and consists of two NaCl monomers oriented inward so their dipole moments cancel, and an extra electron that is trapped between two sodium atoms. Such species are commonly called "solvated electrons" (SE), and can alternatively be viewed as two polar molecules (NaCl in this case) linked by a one-electron σ bond formed by the constructive overlap of the two NaCl monomers' dipole orbitals (see Figure 3).

The SE isomer of $(NaCl)_2{}^-$ has previously been described by Sunil and Jordan[1,2] who predicted it to be thermodynamically unstable with respect to the linear global-minimum of the anion (by 0.51 eV) and estimated its vertical electron detachment energy to be 2.87 eV at the MP2/6-31+G* level. According to our results, the SE structure (labeled **4**$^-$ in this work) is indeed higher in energy (by 0.441 eV) than **2**$^-$; however, it lies 1.239 eV below the sum of the energies of the isolated NaCl and NaCl$^-$ (see Figure 2). Also, **4**$^-$ is slightly (by 0.109 eV) unstable with respect to the global minimum of the neutral species **3**.

The SE anion **4**$^-$ can transform to the lowest energy anion **2**$^-$ but a kinetic barrier of 0.246 eV (1981 cm^{-1})[63] has to be overcome via the corresponding L-shaped transition state structure of C_s symmetry, termed TS$^-$(**4**$^-$↔**2**$^-$) (see Figure 1). The geometrical parameters of TS$^-$(**4**$^-$↔**2**$^-$) are collected in Table 1 while its singly occupied molecular orbital is shown in Figure 3. We estimated the vertical electron stability of this TS to be 2.094 eV (16 892 cm^{-1}) at the CCSD(T)/aug-cc-pVDZ+6*s*6*p*4*d* level which indicates that the excess electron is not going to spontaneously detach during **4**$^-$ to **2**$^-$ conversion via TS$^-$(**4**$^-$↔**2**$^-$). Our results on the **4**$^-$↔**2**$^-$ interconversion are consistent with those obtained by Sunil and Jordan[2] whose estimate of the height of the kinetic barrier for this process was 0.27 eV (see discussion given in ref 2 and Section 1.3 of this manuscript for details).

3.2.2. Vertical Electron Binding Energies. The electron binding energy 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 **1**$^-$, **2**$^-$, **3**$^-$, and **4**$^-$ structures of sodium chloride dimer are presented in Table 2. In each case, excluding the rhombic structure, we provide the results calculated at anionic equilibrium geometry. For the rhombic structure, we provide the electron binding energies calculated at both the neutral and anionic equilibrium geometries. However, to simplify the discussion, we limit it to the electron binding energies obtained for the equilibrium anionic geometries because they correspond to vertical electron detachment energies (VDEs).

In the KT approximation, the electron binding energy results from the electrostatic and exchange interactions of the loosely bound electron with the SCF charge distribution of the neutral molecule. For three anions (of DBS: **1**$^-$ and **2**$^-$, or SE character: **4**$^-$), the D^{KT} values are relatively large: 11 182 cm^{-1} for **1**$^-$, 11 138 cm^{-1} for **2**$^-$, and 20 069 cm^{-1} for **4**$^-$ and are responsible for 92−94% of the total electron binding energies (see Table 2). In the case of **3**$^-$ (quadrupole-bound anion), D^{KT} is much smaller (244 cm^{-1}) and responsible for only 19% 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 $\Delta D^{\mathrm{SCF}}{}_{\mathrm{ind}}$) to be small for all four anions and responsible for only 2−5% of the total D (see Table 2).

The contribution denoted $\Delta D^{\mathrm{MP2}}_{\mathrm{disp}}$ 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 $\mathbf{1}^-$, $\mathbf{2}^-$, and $\mathbf{4}^-$ and 49% (for $\mathbf{3}^-$ of the total D (see Table 2).

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 an effect first appears at the MP2 level and is denoted by $\Delta D^{\mathrm{MP2}}_{\mathrm{no-disp}}$. In all of the cases at hand, MP2 electron correlation effects reduce the lowest nonvanishing moment of the neutral system (see Table 1). Therefore, the value of $\Delta D^{\mathrm{MP2}}_{\mathrm{no-disp}}$ is destabilizing but small, yet the total MP2 contribution to D remains stabilizing due to the dominant role of the dispersion component in each case.

The contributions from ΔD^{MP3} and ΔD^{MP4} are stabilizing but very small (less than 1% of D) for all of our anions except in the quadrupole-bound $\mathbf{3}^-$ for which the ΔD^{MP4} term is 10% of the total value of D. 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 $\mathbf{1}^-$, $\mathbf{2}^-$, and $\mathbf{4}^-$ (less than 1% of D). In the case of $\mathbf{3}^-$, however, the $\Delta D^{\mathrm{CCSD(T)}}$ is large and responsible for 22% of D (see Table 2).

Combining all of these contributions produces our final predictions for the vertical electron detachment energies of 12 090 and 12 051 cm^{-1} for $\mathbf{1}^-$ and $\mathbf{2}^-$, respectively (whose nature we characterize as dipole-bound), 1270 cm^{-1} for $\mathbf{3}^-$ (quadrupole-bound nature), and 21 306 cm^{-1} for $\mathbf{4}^-$ (which is a solvated-electron system).

On the basis of our results, we speculate about what kinds of molecular anions can be created after attaching excess electrons to sodium chloride clusters. Because in a neutral experimental sample, both monomers and dimers of NaCl may be present, 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 to result in forming linear or quasi-linear (bent) thermodynamically stable dipole-bound anions (described in this work as $\mathbf{2}^-$). Alternatively, the $NaCl^-$ anions may form (via colliding with the neutral NaCl) the "solvated-electron" anions $\mathbf{4}^-$. The $\mathbf{4}^-$, being thermodynamically unstable, will eventually convert via L-shaped transition states ($\mathrm{TS}^-(\mathbf{4}^-\leftrightarrow\mathbf{2}^-)$) to the linear (or bent) dipole-bound anions, although a kinetic barrier of 0.246 eV must be overcome. The rhombic anions created by attaching the excess electrons to rhombic neutrals, may also convert to the linear (or bent) $\mathbf{2}^-$ anions via $\mathrm{TS}^-(\mathbf{3}^-\leftrightarrow\mathbf{2}^-)$ transition states, although a small kinetic barrier of 0.108 eV has to be overcome.

4. Summary

The lowest-energy isomer of $(NaCl)_2^-$ is a quasi-linear dipole-bound $(ClNa\cdots ClNa)^-$ whose vertical detachment energy (VDE) is 12 051 cm^{-1}. The quadrupole-bound nearly rhombic isomer of this anion lies 0.18 eV above the dipole-bound anion and has a VDE of 1270 cm^{-1}. Finally, the solvated-electron isomer ClNa(−)NaCl lies 0.44 eV above the dipole-bound anion but has a large VDE of 21 306 cm^{-1}. There are small barriers separating both the rhombic and solvated-electron anions from the dipole-bound species.

Acknowledgment. This work was supported by NSF Grant 9982420 to J. Simons and the Polish State Committee for Scientific Research (KBN) Grant No. DS/8371-4-0137-2 to P. Skurski. The computer time provided by the Center for High Performance Computing at the University of Utah is also gratefully acknowledged.

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(62) The results for the monomer that we used for comparison were calculated by us at the same level of theory to ensure consistency. Hence, the geometries of the neutral and anionic monomer were obtained at the MP2/aug-cc-pVDZ+5*s*5*p* level while the electron binding energy was calculated at the CCSD(T)/aug-cc-pVDZ+6*s*6*p*4*d* level. The resulting bond length is 2.4256 Å (for NaCl) and 2.5594 Å (for $NaCl^-$), while the adiabatic electron affinity is 0.725 eV (5844 cm^{-1}).

(63) The height of the kinetic barrier was calculated at the CCSD(T) level with aug-cc-pVDZ+6*s*6*p*4*d* basis set on the basis of the transition state geometry optimized at the MP2 level with aug-cc-pVDZ+5*s*5*p* basis set.