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In a classical model, some anions exist due to the attraction between an electron and a molecule's dipole moment. When the dipole moment is sufficiently large ($\mu_{crit} > 2.5 \, D$), an electron can be trapped. Can a sufficiently large quadrupole moment produce the same effect? To help answer this question, we can search for molecules with a large quadrupole moment and use predictive, *ab initio*, correlated quantum chemistry methods to assess whether an anion forms and, if it does, to discover its nature. For this purpose, coupled-cluster calculations are reported for the structure and properties of K_nCl_m and $K_nCl_m^-$ ($n,m=0-2$). The KCl_2 superhalogen was found to have an electron affinity of 4.2 eV and is stable towards dissociation by 26 kcal/mol. The $(KCl)_2$ dimer has a rhombic ground state with a large electric quadrupole moment. Rhombic and linear configurations of the $(KCl)_2^-$ anion correspond to stationary states that are nearly degenerate in total energy. The rhombic anion has a single, weakly bound state that could be a ''quadrupole-bound'' state on the basis of a comparison of its characteristics with those of dipole-bound states. Linear $KClKCl^-$ has seven excited states; four of them can be identified as dipole-bound states. KCl and KCl_2 possess rather similar dipole moments and their anions have two excited dipole-bound states each. © *1999 American Institute of Physics.* [S0021-9606(99)31324-6]

I. INTRODUCTION

Whether a bound anion exists or not is a property that can be extracted from the Schrödinger equation, provided that a sufficiently accurate solution is obtainable. However, other than recognizing that a vacancy exists in a molecular shell structure that might suggest the formation of a valence anion, the *conceptual* basis for anion formation frequently appeals to classical models. These can be viewed as arising from a multipole expansion of an effective potential extracted from the Schrödinger equation. On this basis, it has been predicted[1–6] that an electron can be bound by a classical dipole field if the dipole moment exceeds $\mu_{crit} = 1.625 \, D$. Subsequent experimental[7–14] and computational[15–23] studies have proven the existence of such states in *real* polar molecular systems, providing a more realistic estimate of 2.5 D for μ_{crit}. By analogy with the binding of an extra electron by a sufficiently strong dipole field, it is tempting to consider the next term in the multipole expansion, and the possibility of the attachment of an extra electron by a classical quadrupole field of a molecular system. This should be particularly relevant when the system is lacking a permanent dipole moment, and we should be able to assess the critical value of the quadrupole moment required to sustain a quadrupole-bound state.

Jordan and Liebman[24] have considered attachment of an extra electron to a $(BeO)_2$ dimer and concluded that the extra electron is bound in the $(BeO)_2^-$ anion primarily by the quadrupole field of the neutral dimer. However, the value of 0.65 eV, which they have obtained for the binding energy of the electron at the Hartree–Fock (HF) level of theory, is more characteristic for conventional (or valence) states of

anions. Performing calculations on the structure of $(BeO)_2$ and $(BeO)_2^-$ by the coupled-cluster singles and doubles with perturbation triples [CCSD(T)] method, we found the binding energy of the extra electron in $(BeO)_2^-$ to be even larger (about 0.9 eV). Since an extra electron is attached to the positive end of the dipole in dipole-bound anions (see, for example, Refs. 25 and 26, and references therein), one might anticipate a similar attachment to the positive poles of a quadrupole, and the corresponding anion states should be approximately as diffuse as dipole-bound states. However, we have not found any trace of a diffuse bound state in $(BeO)_2^-$, although we have used a basis containing rather diffuse functions (up to the exponent of 0.000 001).

Prasad *et al.*[27,28] have evaluated critical values of the quadrupole moment required for linear symmetric MX_2 systems to sustain a bound anion state. They have applied essentially the same approach as had been used for evaluating critical values of the dipole moment; namely, they have studied the behavior of an electron in permanent charge fields formed by two linear triads of equidistant point charges $(Q, -2Q, Q)$ and $(-Q, 2Q, -Q)$. However, their critical values are too approximate to offer useful guidelines.[29] Presumably, quadrupole fields stronger than those in $(BeO)_2$ are required to sustain a quadrupole-bound anion state. $(BeO)_2$, according to our CCSD(T) computations, has components of $\Theta_{xx} = -13.05$, $\Theta_{yy} = 13.45$, and $\Theta_{zz} = 0.40$.

Since nuclear frames of dimers of oppositely directed, polar diatomic molecules do mimic classic point-charge quadrupoles, we have performed a search of weakly bound anionic states that might be attributed to quadrupole-bound states for a series of $(MX)_2$ dimers.[30] We have found that the

$(KCl)_2$ dimer appears to be a reasonable candidate because the ground-state D_{2h} geometry of the neutral parent dimer does not change significantly upon attachment of an extra electron, and the binding energy of the electron is sufficiently small.

The ground state of a $(KCl)_2^-$ congener, $(NaCl)_2^-$, has been found to be linear,[31,32] and the neutral dimer NaClNaCl possesses a rather large dipole moment of 20.9 D at this linear geometry. Therefore, we have considered linear configurations of the $(KCl)_2$ and $(KCl)_2^-$ dimers as well and estimated the number and symmetries of dipole-bound states of linear KClKCl$^-$, since it was predicted[33] on the basis of Koopmans' theorem that dipole moments in excess of 11 D are required to sustain a dipole-bound state of π-symmetry.

The first dissociation channel of alkali halide dimers is known to correspond to monomers.[34–36] No information is available on dissociation trends in anions of the corresponding dimers; therefore, it is interesting to compare fragmentation patterns of $(KCl)_2$ and $(KCl)_2^-$. To estimate fragmentation energies, we need to compute the ground-state total energies of all constituents entering both systems. Previous geometry optimizations have been performed for K_2Cl (Ref. 37) and KCl_2^- (Ref. 38).

We have recently found triatomic superhalogens MX_2 (LiF_2, $LiCl_2$, NaF_2, and $NaCl_2$) (Ref. 39) to be thermodynamically stable. Because KCl_2 belongs to the same class of superhalogens, it is interesting to consider its thermodynamic stability and estimate its adiabatic electron affinity as well.

First motivated by a search for a quadrupole-bound state of $(KCl)_2^-$, we finally performed the following: CCSD(T) optimizations for all the K_nCl_m and $K_nCl_m^-$ systems ($n,m = 0–2$), calculations of the first-order properties of the neutral species and their adiabatic electron affinities (A_{ad}), determinations of excited states of the $K_nCl_m^-$ anions when such states exist, and estimations of thermodynamic stability in both series.

In the final section, we discuss whether the $(D_{2h}, {}^2A_1)$ state of $(KCl)_2^-$ may be attributed to its quadrupole-bound state.

II. COMPUTATIONAL METHODS

The calculations have been performed with the ACES II suite of programs[40] by the CCSD(T) method[41,42] with the use of Sadlei's POL1 basis[43] especially defined to describe polarizabilities that allow fairly diffuse electronic distributions. This basis consists of $14s10p4d$ and $15s13p4d$ primitive Gaussians contracted to $7s5p2d$ and $9s7p2d$ for Cl and K, respectively.

The adiabatic electron affinity (A_{ad}) of a neutral species is defined as the difference between the ground-state total energies of the species and its anion. Within the Born–Oppenheimer approximation, we evaluate the A_{ad} as

$$A_{ad} = E_{tot}(N, R_e) + Z_N - E_{tot}(A, R_e^-) - Z_A = \Delta E_{el} + \Delta E_{nuc}, \quad (1)$$

where R_e and R_e^- denote the equilibrium geometrical configurations of the neutral species and the anion, respectively.

If an anion possesses stable excited states, we define the binding energies of an extra electron ($A^{(n)}$) in these states by analogy with Eq. (1) relative to the ground states of the corresponding neutral parent species

$$A^{(n)} = E_{tot}(N, R_e) + Z_N - E_{tot}(A, R_e^-(n)) - Z_A$$
$$= \Delta E_{el}^{(n)} + \Delta E_{nuc}^{(n)}. \quad (2)$$

The zero-point vibrational energies in Eqs. (1) and (2) are estimated within the harmonic approximation.

To investigate the ability of $(KCl)_2$, K_2Cl, and KCl_2 to have the low-energy attachment of an extra electron, we have applied the electron-attached, equation-of-motion coupled-cluster (EA-EOMCC) method,[44,45] which treats simultaneously a number of states having one more electron than an initial parent state. The parent state is described at the CCSD level as

$$|\Psi_{CCSD}\rangle = e^{\hat{T}}|\Phi_0\rangle, \quad (3)$$

where $|\Phi_0\rangle$ is a reference Hartree–Fock (HF) wavefunction and $\hat{T} = \hat{T}_1 + \hat{T}_2$ is the cluster operator limited to single and double excitations. The transformed Hamiltonian is defined as

$$\hat{\bar{H}} = e^{-\hat{T}} \hat{H} e^{\hat{T}}, \quad (4)$$

and $\hat{\bar{H}} - E_{CCSD}$ is diagonalized over configurations comprising all one-particle ($1p$) and two-particle-one-hole ($2p1h$) determinants, which correspond to configurations with an extra electron added. Final states are linear combinations

$$\left(\sum_a c_a a^\dagger + \sum_{a,b,j} c_{a,b}^j a^\dagger b^\dagger j \right) e^{\hat{T}}|\Phi_0\rangle, \quad (5)$$

where $a^\dagger, b^\dagger$ denote creation operators for unoccupied orbitals (particles), j is an annihilation operator for orbital j (hole) occupied in the reference Φ_0 state, and c_a and $c_{a,b}^j$ are amplitudes. The eigenvalues obtained from the diagonalization are the vertical attachment energies with respect to the CCSD reference state.

When performing EA-EOMCC computations, we have added a set of diffuse functions in the middle $[(KCl)_2]$ or in the direction of the positive dipole end (K_2Cl, KCl_2, and KClKCl). This set has been used before[33,46] and consists of seven sp-shells (the exponents are 0.001, 0.0005, 0.0001, 0.00005, 0.00001, 0.000005, and 0.000001).

First-order properties of the neutral species have been calculated at both HF and CCSD(T) levels. The electric dipole moment is a first-rank tensor $\mu = \Sigma_i e_i r_{i\alpha}$, and the electric quadrupole moment is a second-rank tensor defined[47] by the equation

$$\Theta_{\alpha\beta} = \frac{1}{2} \sum_i e_i (3 r_{i\alpha} r_{j\beta} - r_i^2 \delta_{\alpha\beta}), \quad (6)$$

where e_i are charges of particles $r_i^2 = x_i^2 + y_i^2 + z_i^2$ ($\mathbf{r}_i$ are the particle's positions at a coordinate system), $\alpha, \beta = x, y, z$, and δ_{ij} is the substitution tensor (Kronecker's symbol) defined as $\delta_{\alpha\beta} = 1$ if $\alpha = \beta$, and zero otherwise.

At the HF level, the electronic components of the electric quadrupole moments are calculated as usual:[48]

TABLE I. Bond lengths (in Å), vibrational frequencies (in cm^{-1}), bond angles (in degrees), and zero-point energies (in kcal/mol) of K_nCl_m, $(n,m = 0-2)$ and their anions computed at the CCSD(T)/POL1 level. Experimental data for diatomic species (Ref. 51) and $(KCl)_2$ (Ref. 52) are in parentheses.

	Cl_2	Cl_2^-	KCl	KCl^-	K_2	K_2^-
R_e	2.06(1.99)	2.643	2.73(2.67)	2.860	3.98(3.91)	4.51
ω_e	529(560)	243	272(281)	213	85(92)	54

Properties	K_2Cl	KCl_2	K_2Cl^-	KCl_2^-	$(KCl)_2$[a]	$(KCl)_2^-$[b]
$R(K-Cl)$	2.88	2.89	2.93	2.90[c]	2.89(2.950(54))	2.85(3.02)
$\angle ClKCl°$	91.8[d]	180.0[d]	54.6	180.0	93.7(96.0(2.4))	97.2(88.9)
Freq.	$\omega(a_1) = 69$	199	$\omega(\pi_u) = 22$	38	$\omega(b_{1u}) = 67$	$\omega(b_{1u}) = 36$
	$\omega(b_1) = 201$	86	$\omega(\sigma_g) = 131$	155	$\omega(a_g) = 96$	$\omega(a_g) = 89$
	$\omega(a_1) = 225$	260	$\omega(\sigma_u) = 224$	235	$\omega(b_{1g}) = 187$	$\omega(b_{2u}) = 177$
					$\omega(b_{2u}) = 202$	$\omega(b_{1g}) = 175$
					$\omega(a_g) = 209$	$\omega(a_g) = 196$
					$\omega(b_{3u}) = 210$	$\omega(b_{3u}) = 196$

[a]The results of calculations at the MBPT(2) level with a larger basis set (Ref. 36): $R(K-Cl) = 2.86$, $\angle ClKCl° = 93.8$. Their frequencies computed at the SCF level are $\omega(b_{1u}) = 74$, $\omega(a_g) = 101$, $\omega(b_{1g}) = 168$, $\omega(b_{2u}) = 171$, $\omega(a_g) = 185$, $\omega(b_{3u}) = 193$.

[b]Linear $KClKCl^-$, MBPT(2)/POL1 results: bond lengths are 2.924, 2.933, 2.849, respectively; frequencies are $\omega(\pi) = 16$ and 30, $\omega(\sigma) = 109$, 207, and 248.

[c]HF results from Ref. 38: $R(K-Cl) = 2.96$, $\omega(\pi_u) = 53$, $\omega(\sigma_g) = 150$, $\omega(\sigma_u) = 235$.

[d]$\angle KClK°$ angle. The results of calculations at the CCSD(T) level with a larger basis set (Ref. 37): $R(K-Cl) = 2.84$, $\angle KClK° = 92.2$. Their frequencies computed at the HF level are $\omega(a_1) = 75$, $\omega(b_1) = 177$, $\omega(a_1) = 189$.

$$\langle \Theta_{\alpha\beta} \rangle = \int \Theta_{\alpha\beta}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}, \tag{7}$$

where ρ is the HF electronic density. At the CCSD(T) level, we use the so-called ''relaxed'' density $D(\mathbf{r}) = \Sigma_{p,q}\psi_p(\mathbf{r}) \times D_{pq}\psi_q^*(\mathbf{r})$, where D_{pq} consists of the one-particle response density and the molecular orbital relaxation part.[49,50] Consequently, Eq. (7) is replaced by the equation

$$\langle \Theta_{\alpha\beta} \rangle = \int \Theta_{\alpha\beta}(\mathbf{r})D(\mathbf{r})d\mathbf{r} = \sum_{p,q} \Theta_{\alpha\beta}^{pq}D_{pq}. \tag{8}$$

Dipole moment components are calculated in the manner similar to Eqs. (7) and (8), and the dipole moment is defined as $(\Sigma_\alpha \mu_\alpha^2)^{1/2}$. Our calculations are performed in the center-of-mass coordinate system.

Fragmentation energies are calculated as the differences in the total energy of fragments formed in a particular decay channel of an initial neutral or charged species M and the total energy of M corrected for the zero-point vibrational energies (Z):

$$D_0(M) = \sum_i [E_{tot}(F_i) + Z_{F_i}] - E_{tot}(M) - Z_M$$

$$= D_e(M) + \Delta Z_{nuc}. \tag{9}$$

III. RESULTS AND DISCUSSIONS

A. Structures and frequencies

Table I presents geometrical parameters and harmonic vibrational frequencies of $(KCl)_2$, $(KCl)_2^-$, and their constituents obtained at the CCSD(T)/POL1 level (see Fig. 1). Comparison with experimental data[51,52] shows that our bond lengths are elongated by ≈ 0.07 Å and, consequently, our

frequencies are lower than the experimental (ω_e) frequencies. Similar trends have been observed in other theoretical studies[34–37] performed with moderately sized spd-basis sets. Larger basis sets containing f-functions are required to obtain geometrical parameters that are close to experimental data at the CCSD(T) level.[36,37]

However, the relative error in our bond lengths compared to experiment are rather small (2% for KCl and 1% for K_2) because the species have rather long bond lengths. Also, one can anticipate approximately the same accuracy for the neutral and negatively charged species, though the POL1 basis has a bias towards anions.[53] Some support for such an expectation arises from the results of self-consistent-field/modified coupled-pair functional (SCF/MCPF) calculations for K_2 and K_2^-.[54] The bond lengths obtained for this pair are 4.16 and 4.69 Å which provide the elongation of 0.53 Å in the K–K bond length, exactly the same as obtained in our computations (see Table I). Our geometrical parameters and harmonic frequencies obtained for K_2Cl, KCl_2^-, and $(KCl)_2$ are in good agreement with the results of previous calculations[36,38] (see footnotes in the Table).

It was found previously[32] that the ground-state configuration of the $NaClNaCl^-$ anion is linear, whereas the optimized geometry of linear NaClNaCl corresponds to a transition state whose global minimum is a rhombus in its ground-state configuration. Since linear NaClNaCl possesses a very large dipole moment of 20.9 D,[31] it was concluded that the $NaClNaCl^-$ anion state is of a dipole-bound nature. By analogy, we have performed optimizations and frequency calculations for linear KClKCl and $KClKCl^-$ at the many-body perturbation theory [MBPT(2)] level. The neutral linear structure has an imaginary π-frequency and corresponds to a transition state, whereas the linear $KClKCl^-$ anion corre-

TABLE II. Total energies (E_{tot}, in hartrees) and zero-point vibrational energies (Z, kcal/mol), of K_nCl_m ($n,m=0-2$) and their anions together with adiabatic electron affinities of K_nCl_m computed according to Eq. (2) (A_{ad}, in eV) obtained at the CCSD(T)/POL1 level. Experimental values of the A_{ad} are given in parentheses.

Species	E_{tot}	Z	Species	E_{tot}	Z	A_{ad}
$(KCl)_2$	−2118.250 479	1.39	$(KCl)_2^-$	−2118.253 877	1.15	0.095
KClKCl	−2118.209 147	TS	KClKCl$^-$	−2118.252 271	0.94	0.049
K_2Cl	−1658.397 114	0.71	K_2Cl^-	−1658.424 256	0.57	0.745
KCl_2	−1518.785 903	0.92	KCl_2^-	−1518.940 600	0.66	4.220
KCl	−1059.087 503	0.39	KCl^-	−1059.109 429	0.30	0.601(0.582)[a]
K_2	−1198.571 703	0.12	K_2^-	−1198.589 569	0.08	0.488(0.493)[b]
Cl_2	−919.390 925	0.76	Cl_2^-	−919.484 667	0.75	2.551(2.44±0.1)[c]
K	−599.277 408	⋯	K^-	−599.294 706	⋯	0.471(0.501)[d]
Cl	−459.657 287	⋯	Cl^-	−459.782 813	⋯	3.416(3.617)[d]
K^+	−599.120 364	⋯	Cl^+	−459.196 914	⋯	⋯

[a]See Ref. 66.
[b]See Ref. 67.
[c]See references and discussions in Ref. 68.
[d]See Ref. 65.

sponds to a stationary point at the potential energy surface of $(KCl)_2^-$ similar to NaClNaCl$^-$.

At the MBPT(2) optimized geometry of KClKCl$^-$, we have calculated CCSD(T) total energies of the neutral dimer and its anion. KClKCl$^-$ was found to be slightly higher in total energy than the rhombic ground-state $(KCl)_2^-$ (see Table II). At this linear configuration, the vertical detachment energy of an extra electron is 1.22 eV; that is, it is close to the values of 1.25±0.01 and 1.30 eV obtained for related clusters $(NaCl)_2^-$ (Ref. 55) and $(KI)_2^-$ (Ref. 56), respectively, in photodetachment experiments.

B. First-order properties

Electric dipole and quadrupole moments of the neutral K_nCl_m species calculated with HF [see Eq. (7)] and relaxed [see Eq. (8)] density matrices are presented in Table III. The only available experimental data, the dipole moment of KCl (Ref. 57) of 10.27 D, compare reasonably well with our value of 10.76 D obtained at the CCSD(T)/POL1 level. The increase is due to the optimum geometry of KCl being 0.06 Å too long in the POL basis. The superhalogen KCl_2 possesses a dipole moment that is smaller by only 1 D than the dipole moment of the KCl monomer, and the largest dipole

moment is linear KClKCl. Obviously, all three species are able to form both ground and excited dipole-bound states, since μ_{crit} for formation of the second excited dipole-bound state was predicted to be 4.5 D by Garrett[58,59] and 10 D by Wallis *et al.*[60] Electric quadrupole moments of K, K^-, and Cl^- vanish, because electric quadrupole moments of atomic S-states are zero according to symmetry rules.[61]

Diffuse basis functions[62] are important for a correct reproduction of first-order properties, and the POL1 basis contains rather diffuse functions. Thus, the CCSD(T)/POL1 approach appears to provide rather accurate estimates for components of the electric quadrupole moments, as judged by the results of our calculations on Cl with a significantly larger (but less diffuse) basis set, namely, Dunning's cc-aug-PV5Z ($[21s13p5d4f3g2h]$ contracted to $[8s7p5d4f3g2h]$).[63] The CCSD(T)/cc-aug-PV5Z electric quadrupole moment of Cl is 1.52 a.u.,[64] which is in reasonably good agreement with the CCSD(T)/POL1 value of 1.72 a.u. (see Table III).

Both K_2Cl and $(KCl)_2$ possess electric quadrupole moments that are larger than those of many $(MX)_2$ dimers formed by alkali halide monomers.[30] Because $(KCl)_2$ has no permanent dipole moment, attachment of an extra electron to

TABLE III. Electric dipole (μ) and quadrupole (Θ) moments of $(KCl)_2$ and its constituents. Dipole moments are in debyes and quadrupole moments are in atomic units [1 a.u.=ea_0^2=1.345 035×10^{-26} e.s.u. (or esu×cm²)].

Level	Property	Cl	Cl_2	KCl	K_2	KCl_2	K_2Cl	$(KCl)_2$	$(KCl)_2$[a]	KClKCl[b]
HF	μ	0.0	0.0	10.97	0.0	9.89	0.33	0.0	0.0	25.22
	Θ_{xx}	−0.90	−1.37	−0.29	−9.29	−8.42	−3.33	−36.98	−38.21	−1.222
	Θ_{yy}	1.79	−1.37	−0.29	−9.29	−1.79	30.91	37.366	38.07	−1.22
	Θ_{zz}	−0.90	2.75	0.58	18.58	10.21	−27.57	−0.38	0.14	2.44
CCSD(T)	μ	0.0	0.0	10.76[c]	0.0	9.68	1.66	0.0	0.0	24.93
	Θ_{xx}	−0.86	−1.35	−0.39	−7.19	−8.37	−4.38	−36.29	−37.58	−1.40
	Θ_{yy}	1.72	−1.35	−0.39	−7.19	−1.88	27.18	36.83	37.59	−1.40
	Θ_{zz}	−0.86	2.71	0.78	14.38	10.26	−22.79	−0.55	−0.02	2.80

[a]Computed at the equilibrium D_{2h} geometry of the anion.
[b]Properties are computed at the equilibrium geometry of linear KClKCl$^-$.
[c]Experimental value is 10.27 (Ref. 57).

TABLE IV. Fragmentation energies (in eV) of $(KCl)_2$, $(KCl)_2^-$, and their constituents. Experimental values are given in parentheses.

	Neutrals			Anions	
Channel		D_0	Channel		D_0
$(KCl)_2$	$\rightarrow 2KCl$	$2.00(1.97)^a$	$(KCl)_2^-$	$\rightarrow KCl_2^- + K$	0.95
	$\rightarrow KCl_2 + K$	5.07		$\rightarrow KCl + KCl^-$	1.52
	$\rightarrow KCl_2^- + K^+$	5.13		$\rightarrow K_2Cl^- + Cl$	4.66
	$\rightarrow K_2Cl + Cl$	5.31		$\rightarrow KCl_2 + Cl^-$	1.99
	$\rightarrow K_2 + Cl_2$	7.81		$\rightarrow K_2 + Cl_2^-$	5.36
K_2Cl	$\rightarrow KCl + K$	$0.86(0.95 \pm 0.26)^b$	K_2Cl^-	$\rightarrow KCl^- + K$	1.02
	$\rightarrow KCl^- + K^+$	4.54		$\rightarrow KCl + K^-$	1.14
	$\rightarrow K_2 + Cl$	$4.55(4.81 \pm 0.26)^b$		$\rightarrow K_2 + Cl^-$	1.88
				$\rightarrow K_2^- + Cl$	4.81
KCl_2	$\rightarrow KCl + Cl$	1.12	KCl_2^-	$\rightarrow KCl + Cl^-$	1.90
	$\rightarrow K + Cl_2$	3.19		$\rightarrow KCl^- + Cl$	4.72
	$\rightarrow Cl_2^- + K^+$	4.91		$\rightarrow K + Cl_2^-$	4.86
				$\rightarrow K^- + Cl_2$	6.94
KCl	$\rightarrow K + Cl$	$4.14(4.35)^c$	KCl^-	$\rightarrow K + Cl^-$	1.33
	$\rightarrow K^+ + Cl^-$	5.00		$\rightarrow K^- + Cl$	4.27
K_2	$\rightarrow 2K$	$0.45(0.514)^c$	K_2^-	$\rightarrow K + K^-$	$0.47(0.51)^d$
	$\rightarrow K^+ + K^-$	4.26			
Cl_2	$\rightarrow 2Cl$	$2.05(2.48)^c$	Cl_2^-	$\rightarrow Cl + Cl^-$	$1.18(1.26 \pm 0.01)^e$
	$\rightarrow Cl^+ + Cl^-$	13.71			

[a]See Ref. 72.
[b]See Ref. 73.
[c]See Ref. 51.
[d]See Ref. 74.
[e]See Ref. 75.

the $(KCl)_2$ dimer could be due to its electric quadrupole field. Note that the in-plane components of the $(KCl)_2$ electric quadrupole moment are nearly equal in absolute magnitude at the equilibrium D_{2h} geometry of the $(KCl)_2^-$ anion.

C. Adiabatic electron affinity

Adiabatic electron affinities calculated according to Eq. (1) are presented in the last column of Table II together with experimental data available for atoms[65] and diatomic species.[66–68] Our values compare fairly well with experiment, having exhibited the largest discrepancy of 0.2 eV for the EA of Cl. In the latter case, an inclusion of higher harmonics beyond fs are required for the computed EA values to reach experiment.[64]

As expected, KCl_2 possesses an A_{ad} that is higher than the EA of Cl, making KCl_2 a superhalogen. KCl_2 has the lowest A_{ad} in the series $LiF_2(5.45\,eV)$, $LiCl_2(4.97\,eV)$, $NaF_2(5.12\,eV)$, $NaCl_2(4.69\,eV)$,[39] and $KCl_2(4.22\,eV)$. In the corresponding anion series, KCl_2^- has the lowest vertical detachment energy of 5.43 eV, a value that is in good agreement with Scheller and Cederbaum's[38] value of 5.37 eV obtained by the Green-function method.

The K_2Cl trimer has an A_{ad} that is slightly higher than the A_{ad}s of K_2 and KCl and essentially lower than that of KCl_2. The difference between K_2Cl and KCl_2, which stipulates such a significant difference in their A_{ad}s, consists of a different character of their half-filled highest occupied MO (HOMO) which should be filled with an extra electron to form the corresponding anions. In K_2Cl, the HOMO has a_1 symmetry and has antibonding character; the Mulliken charge distribution is $Cl^- K_2^+$. In KCl_2, the HOMO is non-

bonding (of the b_2 type) and consists of Cl's π orbitals; the charge distribution corresponds to $K^+Cl_2^-$. An extra electron in KCl_2^- fills the ligand molecular orbital localized on the chlorine atoms, which possess a high electronegativity. Attachment of an extra electron to K_2Cl or KCl_2 leads to a strong distortion of their geometries resulting in the linear shape of both K_2Cl^- and KCl_2^- anions (with formal charge distributions KCl^-K and $Cl^{-0.5}KCl^{-0.5}$, respectively). Thus, the extra electron in KCl_2^- is delocalized over electronegative ligands, which is one of the essential attributes of a superhalogen.[69,70]

The A_{ad} of the $(KCl)_2$ dimer, obtained at the CCSD(T)/POL1 level as the difference between the total energies of the equilibrium D_{2h} configurations of the anion and its neutral parent, is 0.095 eV. Such a value is intermediate between typical binding energies of an extra electron in dipole-bound states (of 1–20 meV scale))[14] and weak valence-binding energies (e.g., 0.3 eV in LiH).[71] We shall address below whether the D_{2h} state of $(KCl)_2^-$ can be considered as a quadrupole-bound state.

D. Thermodynamic stability of K_nCl_m and $K_nCl_m^-$

To estimate thermodynamic stability of both series, we have estimated fragmentation energies of all low-energy channels in K_nCl_m and $K_nCl_m^-$. Keeping in mind a rather high value of the KCl_2 A_{ad}, we have also computed fragmentation energies for channels leading to formation of the K^+ cation. Our fragmentation energies, computed according to Eq. (9), are presented in Table IV and compared to ex-

perimental data.[51,72–75] Comparison shows rather good agreement, with the largest deviation being for the ''notorious'' Cl_2 of 0.43 eV (10 kcal/mol).

The CCSD(T)/POL1 dimerization energy of $(KCl)_2$ is in nice agreement with experiment. However, it is relatively independent of the level of computations, because even at the restricted HF level, it was calculated[35] to be 1.85 eV (versus experiment 1.97 eV).[72] Interestingly, dissociation channels $KCl_2 + K$ and $KCl_2^- + K^+$ have nearly the same energies, due, in part, to the small ionization potential of K and very high electronegativity of KCl_2. The value of 5.13 eV for the $KCl_2^- + K^+$ channel is even slightly larger than the energy of dissociation KCl to $K^+ + Cl^-$. This allows an alternative way of considering alkali halide crystals as $[MX_2]^- M^+$ salts instead of $X^- M^+$ ones. Some support to this conjecture is given by the results of Weiss *et al.*[76] in their *ab initio* study of Na_nCl_n and Na_nCl_{n-1}, $n \leq 4$ clusters. They have found that the most stable is tetrahedral Na_4Cl_4, which is of the NaCl-bulk lattice type, whereas odd-n Na_3Cl_3 is less stable and geometrically fragile.

The trimers K_2Cl and KCl_2 are rather weakly bound, and they are somewhat less stable than their corresponding anions. The more stable character of K_2Cl^- and KCl_2^- is related to the fact that they have larger A_{ad}s than KCl and Cl. Our computed fragmentation energies of K_2Cl are in agreement with experimental data[73] within experimental error bars.

The $(KCl)_2^-$ anion is less stable than its neutral parent dimer, and the first fragmentation channel corresponds to the formation of K, which requires about 20 kcal/mol. Therefore, attachment of an electron to the $(KCl)_2$ dimer greatly facilitates the abstraction of a K atom. Thus, a conceivable method for water solvation of KCl crystals could tentatively be related to attachment of an extra electron to surface defects, which could result in an easy abstraction of K atoms from surface layers.

E. Excited dipole-bound states

To calculate binding energies of an extra electron in excited weakly bound anion states, we have employed the EA-EOMCC method (see Sec. II). The POL1 basis was augmented by diffuse sp-functions, which allows one to describe rather diffuse electron distributions. This approach has been applied previously to a series of polar diatomic molecules,[33] and the results of our calculations are in excellent agreement with the results obtained with the use of ''infinite'' numerical basis sets.[77,78]

As expected, K_2^-, $(KCl)_2^-$, and K_2Cl^- have no diffuse excited states (see Table V). That means that the electric quadrupole moments in K_2 and K_2Cl as well as the dipole moment in K_2Cl are not large enough to support quadrupole-bound or dipole-bound states in the corresponding anions. The vertical attachment energies of K_2 and K_2Cl are only slightly lower than their adiabatic EAs, whereas a drastic difference between the A_{ad} and the E_{va} of KCl_2 is observed (see Table II).

The EA-EOMCC vertical attachment energy of an extra electron from $(KCl)_2^-$ is 0.09 eV, which is close to the A_{ad} of 0.095 eV of $(KCl)_2$, obtained at the CCSD(T)/POL1 level.

TABLE V. Vertical electron attachment energies (E_{va}) of K_2, KCl, KCl_2, K_2Cl, $(KCl)_2$, and KClKCl (at the anion geometry) computed with the EA-EOMCC method together with their dipole moments. Dipole moments are in debyes, energies are in eV.

		K_2	$(KCl)_2$	K_2Cl	KCl_2	KCl	KClKCl
DM		0.0	0.0	1.66	9.68	10.76	24.93
E_{va}	1st	0.40	0.09	0.56	1.33	0.57	1.22
	2nd			0.48	0.53	0.03	0.27[a]
	3rd				0.02	1×10^{-3}	0.27[a]
	4th				7×10^{-4}		0.20[b]

[a]π-states.
[b]E_{va}s of the less bound four states are 0.04, 0.01, 2×10^{-3}, 2×10^{-4}.

No other diffuse state was found for the $(KCl)_2^-$ anion at the neutral equilibrium D_{2h} geometry.

KCl and KCl_2 possess rather similar dipole moments and extra electrons in their anion states have similar binding energies. The latter are slightly larger in KCl^-, which is consistent with a larger dipole moment of KCl. The magnitude of binding energies of an extra electron in excited states of KCl^- are similar to those calculated previously[33] for $NaCl^-$, whose neutral precursor has the dipole moment of 8.97 D.

Linear KClKCl possesses a large dipole moment of 25 D at the anion linear geometry. As expected, the linear anion possesses a rather large number of excited states. The second excited state has π-symmetry; all other excited and ground states are of the σ-type. The second, third, and fourth anion states can be attributed to valence-excited states since the extra electron is bound rather strongly in these states; that is, the corresponding electron distributions are not diffuse. Four upper states possess typically dipole-bound characteristics: low binding energies and diffuse distributions of the extra electron. All eight anionic states can be considered as corresponding to different channels of the $(KCl)_2^-$ dissociation, namely, those presented in Table IV added to $KCl_2 + K^-$ and $K_2^- + Cl_2$. The π-channel could be tentatively attributed to the symmetric $KCl + KCl^-$ channel.
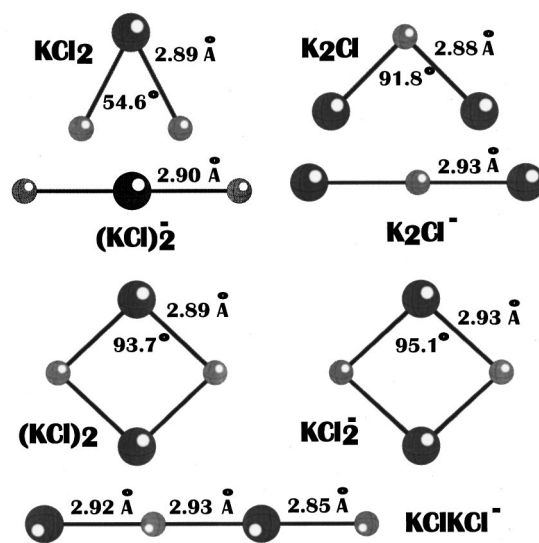

FIG. 1. Ground-state geometrical configurations of KCl_2, K_2Cl, $(KCl)_2$, their anions, and $KClKCl^-$.

F. Quadrupole-bound state of $(KCl)_2^-$

There is consensus about the nature of the dipole-bound states of anions as a state characterized by a rather diffuse distribution of an extra electron. The most important characteristic of such states is that they are formed by polar molecules possessing sufficiently large dipole moments. One can assert almost certainly that a molecular system will attach an extra electron if its dipole moment exceeds 2.5 D. The second important characteristic of the anion dipole-bound states is that their equilibrium geometrical configurations are essentially the same as those of their neutral precursors (say, the bond length increments are 0.01 Å or so).[17,18] Third, even at the HF level, one could see the appearance of dipole-bound states as corresponding to small negative eigenvalues of the neutral lowest unoccupied MO (LUMO) or the anion HOMO provided that sufficiently diffuse functions are included in the basis set. This reflects the relative smallness of correlation contributions to the binding energies of dipole-bound electrons because of their spatial difference from the rest of the electrons.

By analogy, one could expect approximately the same characteristics for anticipated quadrupole-bond states that might be formed by systems lacking a permanent dipole moment but possessing a large quadrupole field. However, the electric quadrupole moment is a second-rank tensor contrary to the electric dipole moment. It could mean that critical values of the quadrupole components will strongly depend on the topology of the nuclear framework. For example, Prasad *et al.*[27,28] have obtained a difference of an order-of-magnitude for critical values of the electric quadrupole moment required for linear symmetric point charges $(Q, -2Q, Q)$ and $(-Q, 2Q, -Q)$ to provide an electron moving in the field of these triads with a positive binding energy.

Let us consider the structure of $(KCl)_2^-$ in some detail. Attachment of an extra electron to $(KCl)_2$ leads to increasing the K–K distance by ≈ 0.1 Å, whereas the Cl–Cl distance remains practically intact. This results in elongation of the K–Cl bound length by 0.03 Å, or 1%, which is only slightly larger than in the case of dipole-induced binding, and in some increase of the quadrupole moment of the neutral dimer at the anion geometry (see Table III). The Mulliken charge distribution in the neutral dimer is $(K^+Cl^-)_2$, whereas in the anion, it is $(K^{+0.5}Cl^-)_2$. Thus, the extra electron is attached to the two positive ends of the quadrupole formed by the nuclear frame of the dimer. Obviously, an analysis of the anion HOMO composition will lead to the same conclusion. The value of a classic quadrupole moment calculated according to its definition as $2Q_K * Z_1^2 - 2Q_{Cl} * Z_2^2$, where Z_1 and Z_2 are the distances of Ks and Cls from the center of mass, equals $+13.1$ a.u., which is rather large (compare, e.g., to 1.7 a.u. in CS_2).[29]

The LUMO eigenvalue of the neutral $(KCl)_2$ dimer is positive in calculations with the POL1 basis but becomes negative and small in absolute value when diffuse basis functions are added to the basis. This is the indication that the extra electron has a diffuse distribution, although less diffuse than in typical dipole-bound states.

That such similarities exist between the characteristics of

$(KCl)_2^-$ and typical dipole-bound anions suggests the conclusion that the extra electron in $(KCl)_2^-$ may be said to be *quadrupole-bound*. We will address the critical values of the electric quadrupole moment required to sustain quadrupole-bound states in anions of neutral systems with linear, rhombic, and some other topologies in a forthcoming paper.[30]

IV. CONCLUSION

Our CCSD(T) study on the structure of K_nCl_m and $K_nCl_m^-$ ($n,m = 0-2$) has revealed several interesting features, which can be briefly summarized as follows.

(i) KCl_2 is a superhalogen and possesses an adiabatic electron affinity of 4.2 eV, which exceeds the electron affinity of Cl by 0.6 eV. As a consequence, the ionic KCl crystals can be described as $K^+[KCl_2]^-$ instead of the usual K^+Cl^-. The same description is valid for other MX alkali halides, since their MX_2 units are superhalogens as well.

(ii) The $(KCl)_2^-$ anion is thermodynamically less stable than the neutral dimer $(KCl)_2$. This could enhance solvation rates of KCl crystals in the presence of an electron (charge) transfer process.

(iii) The rhombic ground-state $(KCl)_2$ dimer forms two anionic states upon attachment of an extra electron: rhombic and linear. The rhombic $(KCl)_2^-$ anion is shown to be quadrupole-bound, and the linear anion is shown to possess a number of excited dipole-bound states, because the neutral KClKCl dimer possesses a large dipole moment of 25 D at the anion geometry. Linear KClKCl corresponds to a transition state on the potential energy surface.

(iv) KCl_2 is stable towards dissociation by 26 kcal/mol; both K_2Cl^- and KCl_2^- anions are thermodynamically more stable than their neutral parents.

[1] E. Fermi and E. Teller, Phys. Rev. **72**, 406 (1947).
[2] M. H. Mittelman and V. P. Myerscough, Phys. Lett. **23**, 545 (1966).
[3] J. E. Turner and K. Fox, Phys. Lett. **23**, 547 (1966).
[4] W. R. Garrett, Chem. Phys. Lett. **5**, 393 (1970).
[5] O. H. Crawford, Mol. Phys. **20**, 585 (1971).
[6] L. E. Turner, Am. J. Phys. **45**, 758 (1977).
[7] S. F. Wong and G. Schulz, Phys. Rev. Lett. **33**, 134 (1974).
[8] K. Rohr and F. Linder, J. Phys. B **9**, 2521 (1976).
[9] R. D. Mead, K. R. Lykke, W. C. Lineberger, J. Marks, and J. I. Brauman, J. Chem. Phys. **81**, 4883 (1984).
[10] J. Marks, J. I. Brauman, R. D. Mead, K. R. Lykke, and W. C. Lineberger, J. Chem. Phys. **88**, 6785 (1988).
[11] T. Andersen, K. R. Lykke, D. M. Neumark, and W. C. Lineberger, J. Chem. Phys. **86**, 1858 (1987).
[12] K. R. Lykke, D. M. Neumark, T. Andersen, V. J. Trapa, and W. C. Lineberger, J. Chem. Phys. **87**, 6842 (1987).
[13] C. Defrançois, H. Abdoul-Carime, N. Khelifa, and J. P. Schermann, Phys. Rev. Lett. **73**, 2436 (1994).

[14] C. Desfrançois, H. Abdoul-Carime, and J. P. Schermann, Int. J. Mod. Phys. B **10**, 1339 (1996).

[15] K. D. Jordan and P. D. Burrow, Acc. Chem. Res. **11**, 341 (1978).

[16] J. Simons and K. D. Jordan, Chem. Rev. **87**, 535 (1987).

[17] G. L. Gutsev and L. Adamowicz, J. Phys. Chem. **99**, 13412 (1995).

[18] G. L. Gutsev, A. L. Sobolewski, and L. Adamowicz, Chem. Phys. **196**, 1 (1995).

[19] G. L. Gutsev and L. Adamowicz, Chem. Phys. Lett. **246**, 245 (1995).

[20] G. L. Gutsev and R. J. Bartlett, J. Chem. Phys. **105**, 8785 (1996).

[21] M. Gutowski, P. Skurski, A. I. Boldyrev, J. Simons, and K. D. Jordan, Phys. Rev. A **54**, 1906 (1996).

[22] M. Gutowski, K. D. Jordan, P. Skurski, J. Phys. Chem. **102**, 2624 (1998).

[23] G. L. Gutsev, P. Jena, and R. J. Bartlett, Phys. Rev. A **58**, 4792 (1998).

[24] K. D. Jordan and J. F. Liebman, Chem. Phys. Lett. **62**, 143 (1979).

[25] K. D. Jordan and W. Luken, J. Chem. Phys. **64**, 2760 (1976).

[26] N. A. Oyler and L. Adamowicz, Chem. Phys. Lett. **219**, 223 (1994).

[27] M. V. N. A. Prasad, R. F. Wallis, and R. Herman, Phys. Rev. B **40**, 5924 (1989).

[28] M. V. N. A. Prasad, R. F. Wallis, and R. Herman, Solid State Commun. **77**, 973 (1991).

[29] G. L. Gutsev, R. J. Bartlett, and R. N. Compton, J. Chem. Phys. **108**, 6756 (1998).

[30] G. L. Gutsev, P. Jena, and R. J. Bartlett (unpublished).

[31] K. K. Sunil and K. D. Jordan, J. Phys. Chem. **91**, 1710 (1987).

[32] K. K. Sunil and K. D. Jordan, Chem. Phys. Lett. **164**, 509 (1989).

[33] G. L. Gutsev, M. Nooijen, and R. J. Bartlett, Chem. Phys. Lett. **276**, 13 (1997).

[34] R. P. Dickey, D. Maurice, R. J. Cave, and R. Mawhorter, J. Chem. Phys. **98**, 2182 (1993).

[35] J. Modisette, L. Lou, and P. Norlander, J. Chem. Phys. **101**, 8903 (1994).

[36] C. Ochsenfeld and R. Ahlrichs, Ber. Bunsenges. Phys. Chem. **98**, 34 (1994).

[37] C. Ochsenfeld and R. Ahlrichs, J. Chem. Phys. **101**, 5977 (1994).

[38] M. K. Scheller and L. S. Cederbaum, J. Chem. Phys. **99**, 441 (1993).

[39] G. L. Gutsev, R. J. Bartlett, A. I. Boldyrev, and J. Simons, J. Chem. Phys. **107**, 3867 (1997).

[40] ACES II is a program product of the Quantum Theory Project, University of Florida. J. F. Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W. J. Lauderdale, S. R. Gwaltney, S. Beck, A. Balkova, D. E. Bernholdt, K.-K. Baeck, P. Rozyczko, H. Sekino, C. Huber, and R. J. Bartlett. Integral packages included are VMOL (J. Almlöf and P. R. Taylor), VPROPS (P. R. Taylor), and ABACUS (H. J. Helgaker, Aa. Jensen, P. Jørgensen, and P. R. Taylor).

[41] M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, J. Chem. Phys. **83**, 4041 (1985).

[42] R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, Chem. Phys. Lett. **165**, 513 (1990).

[43] A. J. Sadlej, Theor. Chim. Acta **81**, 339 (1992).

[44] H. Sekino and R. J. Bartlett, Int. J. Quantum Chem., Symp. **18**, 255 (1994).

[45] M. Nooijen and R. J. Bartlett, J. Chem. Phys. **102**, 3629 (1995).

[46] G. L. Gutsev, M. Nooijen, and R. J. Bartlett, Phys. Rev. A **57**, 1646 (1998).

[47] A. D. Buckingham, Q. Rev., Chem. Soc. **13**, 183 (1959).

[48] R. J. Bartlett and J. F. Stanton, Rev. Comp. Chem. **5**, 65 (1994).

[49] R. J. Bartlett, in *Modern Electronic Structure Theory, Part I*, edited by D. A. Yarkony (World Scientific, Singapore, 1995) p. 1047.

[50] M. Medved, M. Urban, and J. Noga, Theor. Chem. Acc. **98**, 75 (1997).

[51] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand-Reinhold, New York, 1979).

[52] R. J. Mawhorter, M. Fink, and J. G. Hartley, J. Chem. Phys. **83**, 4418 (1985).

[53] G. L. Gutsev and R. J. Bartlett, Chem. Phys. Lett. **265**, 12 (1997).

[54] H. Partridge and C. W. Bauschlicher, Jr., Theor. Chim. Acta **83**, 201 (1992).

[55] Y. A. Yang, C. W. S. Conover, and L. A. Bloomfield, Chem. Phys. Lett. **158**, 279 (1989).

[56] Y. A. Yang, L. A. Bloomfield, C. Jin, L. S. Wang and R. E. Smalley, J. Chem. Phys. **96**, 2453 (1992).

[57] *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide (CRC, Boca Raton, FL, 1994).

[58] W. R. Garrett, J. Chem. Phys. **73**, 5721 (1980).

[59] W. R. Garrett, J. Chem. Phys. **77**, 3666 (1982).

[60] R. F. Wallis, R. Herman, and H. W. Milnes, J. Mol. Spectrosc. **4**, 51 (1960).

[61] S. C. Ceraulo and R. S. Berry, Phys. Rev. A **44**, 4145 (1991).

[62] A. J. Sadlei, J. Chem. Phys. **96**, 2048 (1992).

[63] D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **98**, 1358 (1993).

[64] G. L. Gutsev, P. Jena, and R. J. Bartlett, Chem. Phys. Lett. **291**, 547 (1998).

[65] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **14**, 731 (1985).

[66] T. M. Miller, D. G. Leopold, K. K. Murray, and W. C. Lineberger, J. Chem. Phys. **85**, 2368 (1986).

[67] K. M. McHugh, J. G. Eaton, G. H. Lee, H. M. Sarkas, L. H. Kidder, J. T. Snodgrass, M. R. Manaaa, and K. H. Bowen, J. Chem. Phys. **91**, 3792 (1989).

[68] G. L. Gutsev, Chem. Phys. **156**, 427 (1991).

[69] G. L. Gutsev and A. I. Boldyrev, Chem. Phys. **56**, 277 (1981).

[70] G. L. Gutsev and A. I. Boldyrev, Adv. Chem. Phys. **61**, 169 (1985).

[71] H. W. Sarkas, J. H. Hendricks, S. T. Arnold, and K. H. Bowen, J. Chem. Phys. **100**, 1884 (1994).

[72] G. M. Rothberg, J. Chem. Phys. **34**, 2069 (1961).

[73] M. M. Kappes, P. Radi, M. Schär, and E. Schumacher, Chem. Phys. Lett. **113**, 243 (1985).

[74] T. V. R. Rao and S. V. J. Lakshman, J. Quant. Spectrosc. Radiat. Transf. **11**, 1157 (1971).

[75] W. A. Chupka, J. Berkowitz, and D. Gutman, J. Chem. Phys. **55**, 2724 (1971).

[76] P. Weiss, C. Ochsenfeld, R. Ahlrichs, and M. M. Kappes, J. Chem. Phys. **97**, 2553 (1992).

[77] L. Adamowicz and R. J. Bartlett, J. Chem. Phys. **83**, 6268 (1985).

[78] L. Adamowicz and R. J. Bartlett, J. Chem. Phys. **88**, 313 (1988).