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Search for “quadrupole-bound” anions. I.

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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 ($\mu_{\text{crit}} \geq 2.5\, \text{D}$), 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 $\text{K}_n\text{Cl}_m$ and $\text{K}_n\text{Cl}^-_m\,(n,m = 0-2)$. The $\text{KCl}_2$ superhalogen was found to have an electron affinity of 4.2 eV and is stable towards dissociation by 26 kcal/mol. The $(\text{KCl})_2$ dimer has a rhombic ground state with a large electric quadrupole moment. Rhombic and linear configurations of the $(\text{KCl})_2^-$ 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 $\text{KClKCl}^-$ has seven excited states; four of them can be identified as dipole-bound states. $\text{KCl}$ and $\text{KCl}_2$ 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 $\mu_{\text{crit}} = 1.625\, \text{D}$. 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 $\mu_{\text{crit}}$. 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 $(\text{BeO})_2$ dimer and concluded that the extra electron is bound in the $(\text{BeO})_2^-$ 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 $(\text{BeO})_2$ and $(\text{BeO})_2^-$ by the coupled-cluster singles and doubles with perturbation triples [CCSD(T)] method, we found the binding energy of the extra electron in $(\text{BeO})_2^-$ 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 $(\text{BeO})_2^-$, 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 $\text{MX}_2$ 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 $(Q_2Q_2)$ and $(-2Q_2Q_2)$. However, their critical values are too approximate to offer useful guidelines.$^{29}$ Presumably, quadrupole fields stronger than those in $(\text{BeO})_2$ are required to sustain a quadrupole-bound anion state. $(\text{BeO})_2^-$, 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 $(\text{MX})_2$ 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, 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 KCI KCl⁻, since it was predicted 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. 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 K₂Cl (Ref. 37) and KCl₂ (Ref. 38).

We have recently found triatomic superhalogens MX₂ (LiF₂, LiCl₂, NaF₂, and NaCl₂) (Ref. 39) to be thermodynamically stable. Because KCl₂ 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 KₙClₘ and KₙCl⁻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 KₙClₘ 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 by the CCSD(T) method with the use of Sadlej’s POL1 basis 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

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

where $R_e$ and $R_e^-$ denote the geometrical equilibrium 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

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

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

To investigate the ability of (KCl)₂, K₂Cl, and KCl₂ to have the low-energy attachment of an extra electron, we have applied the electron-attached, equation-of-motion coupled-cluster (EA-EOMCC) method, 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

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

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

and $\hat{H} - E_{CCSD}$ 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

$$\left(\sum_a c_{a\beta}^{\dagger} + \sum_{a,b,j} c_{a,j}^{\dagger} b_{b,j}^\dagger\right)e^\hat{T}|\Phi_0\rangle,$$ (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 $|\Phi_0\rangle$ state, and $c_{a\beta}$ and $c_{a,j}^{\dagger}$ 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 of (KCl)₂ or in the direction of the positive dipole end (K₂Cl, KCl₂, and KClKCl). This set has been used before and consists of seven sp-shells (the exponents are 0.001, 0.0005, 0.0001, 0.00005, 0.000001, 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 $\mu = \sum_i e_i r_{ia}$, and the electric quadrupole moment is a second-rank tensor defined by the equation

$$\Theta_{\alpha\beta} = \frac{1}{2} \sum_i e_i(3r_{ia}^2r_{\beta a} - r_{\alpha a}^2\delta_{\alpha\beta}),$$ (6)

where $e_i$ are charges of particles $r_{ia}^2 = x_i^2 + y_i^2 + z_i^2$ ($r_i$ are the particle’s positions at a coordinate system), $\alpha, \beta = x, y, z$, and $\delta_{\alpha\beta}$ 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.
Comparison with experimental data\textsuperscript{51,52} shows that our bond constituents obtained at the CCSD(T)/POL1 level. Experimental data for diatomic species (Ref. 51) and (KCl\textsubscript{2}) (Ref. 52) are in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>Cl\textsubscript{2}</th>
<th>Cl\textsubscript{2}\textsuperscript{−}</th>
<th>KCl</th>
<th>KCl\textsuperscript{−}</th>
<th>K\textsubscript{2}</th>
<th>K\textsubscript{2}\textsuperscript{−}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_\perp$</td>
<td>2.061(1.99)</td>
<td>2.643</td>
<td>2.73 (2.67)</td>
<td>2.860</td>
<td>3.98 (3.91)</td>
<td>4.51</td>
</tr>
<tr>
<td>$\omega_\perp$</td>
<td>529 (560)</td>
<td>243</td>
<td>272 (281)</td>
<td>213</td>
<td>85 (92)</td>
<td>54</td>
</tr>
</tbody>
</table>

Properties  
- K\textsubscript{2}Cl | KCl\textsubscript{2} | KCl\textsuperscript{−} | (KCl\textsubscript{2})\textsuperscript{−} | (KCl\textsubscript{2})\textsuperscript{−} | (KCl\textsubscript{2})\textsuperscript{−}  
- $R(\text{K–Cl})$ | 2.88 | 2.29 | 2.93 | 2.90\textsuperscript{51} | 2.89 (2.95 (54)) | 2.85 (3.02)  
- $\angle \text{ClKCl}$ | 91.8\textsuperscript{4} | 180.0\textsuperscript{1} | 54.6 | 180.0 | 93.7 (96.0 (24)) | 97.2 (88.9)  
- $\omega (\text{a}_1^\perp)$ | 69 | 199 | 22 | 38 | 74 | 101 | 168 | 185 | 193  
- $\omega (\text{b}_1^\perp)$ | 201 | 86 | 131 | 155 | 966 | 96 | 96 | 96  
- $\omega (\text{a}_2)$ | 225 | 260 | 224 | 235 | 187 | 177 | 177 | 177  
- $\omega (\text{b}_2)$ | 202 | 175 | 175 | 177 | 177 | 177 | 177 | 177  
- $\omega (\text{a}_3)$ | 209 | 196 | 196 | 196 | 196 | 196 | 196 | 196  
- $\omega (\text{b}_3)$ | 210 | 196 | 196 | 196 | 196 | 196 | 196 | 196  

\textsuperscript{4}The results of calculations at the MBPT(2) level with a larger basis set (Ref. 36): $R(\text{K–Cl})$ = 2.86, $\angle \text{ClKCl}$ = 92.8. Their frequencies computed at the SCF level are $\omega (\text{b}_1^\perp)$ = 74, $\omega (\text{a}_2)$ = 101, $\omega (\text{b}_2)$ = 168, $\omega (\text{b}_3)$ = 171, $\omega (\text{a}_3)$ = 185, $\omega (\text{b}_3)$ = 193.  
\textsuperscript{5}Linear KKCl\textsuperscript{+}, MBPT(2)/POL1 results: bond lengths are 2.924, 2.933, 2.849, respectively; frequencies are $\omega (\text{a}_2)$ = 16 and 30, $\omega (\text{b}_2)$ = 109, 207, and 248.  
\textsuperscript{6}HF results from Ref. 38: $R(\text{K–Cl})$ = 2.96, $\omega (\text{a}_1)$ = 53, $\omega (\text{a}_2)$ = 150, $\omega (\text{b}_2)$ = 235.  
\textsuperscript{7}$\angle \text{KClK}$\textsuperscript{−} angle. The results of calculations at the CCSD(T) level with a larger basis set (Ref. 37): $R(\text{K–Cl})$ = 2.84, $\angle \text{KClK}$\textsuperscript{−} = 92.2. Their frequencies computed at the HF level are $\omega (\text{a}_1)$ = 75, $\omega (\text{b}_1)$ = 177, $\omega (\text{a}_2)$ = 189.

\[ \langle \Theta_{\alpha\beta} \rangle = \int \Theta_{\alpha\beta}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}, \quad (7) \]

where $\rho$ is the HF electronic density. At the CCSD(T) level, we use the so-called “relaxed” density $D(\mathbf{r}) = \sum_{\rho,q} \psi \psi^\dagger (\mathbf{r}) \times D_{pq}(\mathbf{r})$, where $D_{pq}$ consists of the one-particle response density and the molecular orbital relaxation part.\textsuperscript{49,50}

Consequently, Eq. (7) is replaced by the equation

\[ \langle \Theta_{\alpha\beta} \rangle = \int \Theta_{\alpha\beta}(\mathbf{r}) D(\mathbf{r}) d\mathbf{r} = \sum_{\rho,q} \Theta_{\alpha\beta} D_{pq}. \quad (8) \]

Dipole moment components are calculated in the manner similar to Eqs. (7) and (8), and the dipole moment is defined as $(\sum_{\rho} \mu_{\rho} \psi^\dagger(\mathbf{r}))^1/2$. 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 ($Z$):

\[ D_0(M) = \sum_{\rho} \left[ E_{\text{tot}}(F_{\rho}) + Z_{F_{\rho}} \right] - E_{\text{tot}}(M) - Z_M = D_s(M) + \Delta Z_{\text{inc}}. \quad (9) \]

**III. RESULTS AND DISCUSSIONS**

**A. Structures and frequencies**

Table I presents geometrical parameters and harmonic vibrational frequencies of (KCl\textsubscript{2}), (KCl\textsubscript{2}\textsuperscript{−}), and their constituents obtained at the CCSD(T)/POL1 level (see Fig. 1). Comparison with experimental data\textsuperscript{51,52} shows that our bond lengths are elongated by $\approx 0.07$ Å and, consequently, our frequencies are lower than the experimental ($\omega_\perp$) frequencies. Similar trends have been observed in other theoretical studies\textsuperscript{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.\textsuperscript{36,37}

However, the relative error in our bond lengths compared to experiment are rather small (2% for KCl and 1% for K\textsubscript{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.\textsuperscript{53} Some support for such an expectation arises from the results of self-consistent-field/modified coupled-pair functional (SCF/MCPF) calculations for K\textsubscript{2} and K\textsubscript{2}\textsuperscript{−}.\textsuperscript{34} 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\textsubscript{2}Cl, KCl\textsubscript{2}, and (KCl\textsubscript{2})\textsuperscript{−} are in good agreement with the results of previous calculations\textsuperscript{36,38} (see footnotes in the Table).

It was found previously\textsuperscript{32} that the ground-state configuration of the NaC1NaCl\textsuperscript{−} anion is linear, whereas the optimized geometry of linear NaC1NaCl corresponds to a transition state whose global minimum is a rhombus in its ground-state configuration. Since linear NaC1NaCl possesses a very large dipole moment of 20.9 D,\textsuperscript{31} it was concluded that the NaC1NaCl\textsuperscript{−} anion state is of a dipole-bound nature. By analogy, we have performed optimizations and frequency calculations for linear KClKCl and KClKCl\textsuperscript{−} at the many-body perturbation theory [MBPT(2)] level. The neutral linear structure has an imaginary $\pi$-frequency and corresponds to a transition state, whereas the linear KClKCl\textsuperscript{−} anion corre-
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sponds to a stationary point at the potential energy surface of \((\text{KCl})_2\) similar to NaClNaCl. 

At the MBPT(2) optimized geometry of KCKICl\(^{−}\), we have calculated CCSD(T) total energies of the neutral dimer and its anion. KCKICl\(^−\) 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 (K)\(_2\) (Ref. 56), respectively, in photodetachment experiments.

**B. First-order properties**

Electric dipole and quadrupole moments of the neutral \(\text{K}_2\text{Cl}_m\) 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 KCKICl. Obviously, all three species are able to form both ground and excited dipole-bound states, since \(\mu_{\text{eff}}\) for formation of the second excited dipole-bound state was predicted to be 4.5 D by Garrett\(^{86,85}\) and 10 D by Wallis et al.\(^{61}\) Electric quadrupole moments of K, K\(^{−}\), and Cl\(^{−}\) vanish, because electric quadrupole moments of atomic 5-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\(_2\)Cl 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 (\(\mu\)) and quadrupole (\(\Theta\)) moments of (KCl)\(_2\) and its constituents. Dipole moments are in debyes and quadrupole moments are in atomic units \([1 \text{ a.u.} = e\alpha_0^2 = 1.345 \times 10^{-26} \text{ e.s.u.} \times \text{cm}^2]\). |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Level       | Property    | Cl          | Cl\(_2\)     | KCl         | K\(_2\)     | KCKICl      | (KCl)\(_2\) | (KCl)\(_2\)  | KCIKCl\(^{−}\) |
| HF          | \(\mu\)     | 0.0         | 0.0          | 10.97       | 0.0         | 9.89        | 0.33        | 0.0         | 0.0         | 25.22       |
|             | \(\Theta_{11}\) | -0.90       | -1.37        | -0.29       | -9.29       | -8.42       | -3.33       | -36.98      | -38.21      | -1.222      |
|             | \(\Theta_{22}\) | 1.79        | 1.37         | 0.29        | -9.29       | 1.79        | 30.91       | 37.366      | 38.07       | -1.222      |
|             | \(\Theta_{33}\) | -0.90       | 2.75         | 0.58        | 18.58       | 10.21       | -27.57      | -0.38       | 0.14        | 2.44        |
| CCSD(T)     | \(\mu\)     | 0.0         | 0.0          | 10.76\(^a\) | 0.0         | 9.68        | 1.66        | 0.0         | 0.0         | 24.93       |
|             | \(\Theta_{11}\) | -0.86       | -1.35        | -0.39       | -7.19       | -8.37       | -4.38       | -36.29      | -37.58      | -1.40       |
|             | \(\Theta_{22}\) | 1.72        | -1.35        | -0.39       | -7.19       | -1.88       | 27.18       | 36.83       | 37.59       | -1.40       |
|             | \(\Theta_{33}\) | -0.86       | 2.71         | 0.78        | 14.38       | 10.26       | -22.79      | -0.55       | -0.02       | 2.80        |

\(^a\)Computed at the equilibrium \(D_{3h}\) geometry of the anion.

\(^b\)Properties are computed at the equilibrium geometry of linear KCKICl\(^−\).

\(^c\)Experimental value is 10.27 (Ref. 57).
the (KCl)\textsubscript{2} dimer could be due to its electric quadrupole field. Note that the in-plane components of the (KCl)\textsubscript{2} electric quadrupole moment are nearly equal in absolute magnitude at the equilibrium \(D_{2h}\) geometry of the (KCl)\textsubscript{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\textsuperscript{65} and diatomic species.\textsuperscript{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 \(fs\) is required for the computed EA values to reach experiment.\textsuperscript{64}

As expected, KCl\textsubscript{2} possesses an \(A_{\text{ad}}\) that is higher than the EA of Cl, making KCl\textsubscript{2} a superhalogen. KCl\textsubscript{2} has the lowest \(A_{\text{ad}}\) in the series LiF\textsubscript{2}(5.45 eV), LiCl\textsubscript{2}(4.97 eV), NaF\textsubscript{2}(5.12 eV), NaCl\textsubscript{2}(4.69 eV),\textsuperscript{39} and KCl\textsubscript{2}(4.22 eV). In the corresponding anion series, KCl\textsubscript{2} has the lowest vertical detachment energy of 5.43 eV, a value that is in good agreement with Scheller and Cedermum's\textsuperscript{38} value of 5.37 eV obtained by the Green-function method.

The K\textsubscript{2}Cl trimer has an \(A_{\text{ad}}\) that is slightly higher than the \(A_{\text{ad}}\) of K\textsubscript{2} and KCl and essentially lower than that of KCl\textsubscript{2}. The difference between K\textsubscript{2}Cl and KCl\textsubscript{2}, which stipulates such a significant difference in their \(A_{\text{ad}}\), 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\textsubscript{2}Cl, the HOMO has \(a_{1}\) symmetry and has antibonding character; the Mulliken charge distribution is Cl\textsuperscript{–}K\textsuperscript{+}. In KCl\textsubscript{2}, the HOMO is non-bonding (of the \(b_{2}\) type) and consists of Cl's \(\pi\) orbitals; the charge distribution corresponds to K\textsuperscript{+}Cl\textsuperscript{2−}. An extra electron in KCl\textsubscript{2} fills the ligand molecular orbital localized on the chlorine atoms, which possess a high electronegativity. Attachment of an extra electron to K\textsubscript{2}Cl or KCl\textsubscript{2} leads to a strong distortion of their geometries resulting in the linear shape of both KCl\textsubscript{2−} and KCl\textsubscript{2−} anions (with formal charge distributions KCl\textsuperscript{−}K and Cl\textsuperscript{−}KCl\textsuperscript{−}K, respectively). Thus, the extra electron in KCl\textsubscript{2−} is delocalized over electronegative ligands, which is one of the essential attributes of a superhalogen.\textsuperscript{59,70}

The \(A_{\text{ad}}\) of the (KCl)\textsubscript{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)\textsuperscript{14} and weak valence-binding energies (e.g., 0.3 eV in LiH).\textsuperscript{71} We shall address below whether the \(D_{2h}\) state of (KCl)\textsubscript{2} can be considered as a quadrupole-bound state.

### D. Thermodynamic stability of K\textsubscript{n}Cl\textsubscript{m} and K\textsubscript{n}Cl\textsubscript{m−}

To estimate thermodynamic stability of both series, we have estimated fragmentation energies of all low-energy channels in K\textsubscript{n}Cl\textsubscript{m} and K\textsubscript{n}Cl\textsubscript{m−}. Keeping in mind a rather high value of the KCl\textsubscript{2−} \(A_{\text{ad}}\), we have also computed fragmentation energies for channels leading to formation of the K\textsuperscript{+} cation. Our fragmentation energies, computed according to Eq. (9), are presented in Table IV and compared to experimen-

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**Table IV.** Fragmentation energies (in eV) of (KCl)\textsubscript{2}, (KCl)\textsubscript{2−}, and their constituents. Experimental values are given in parentheses.

<table>
<thead>
<tr>
<th>Channel</th>
<th>(D_0) (eV)</th>
<th>Channel</th>
<th>(D_0) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(KCl)\textsubscript{2}</td>
<td>KCl (D_0)</td>
<td>(KCl)\textsubscript{2−}</td>
<td>KCl (D_0)</td>
</tr>
<tr>
<td>→ 2KCl</td>
<td>2.00(1.97)\textsuperscript{a}</td>
<td>→ KCl (D_0)</td>
<td>0.95</td>
</tr>
<tr>
<td>→ KCl\textsuperscript{−}+K</td>
<td>5.07</td>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}+Cl</td>
<td>1.52</td>
</tr>
<tr>
<td>→ K\textsuperscript{+}Cl+K</td>
<td>5.13</td>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}+Cl</td>
<td>4.66</td>
</tr>
<tr>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}+Cl</td>
<td>5.31</td>
<td>→ KCl\textsuperscript{2−}+Cl</td>
<td>1.99</td>
</tr>
<tr>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}+Cl</td>
<td>7.81</td>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}+Cl</td>
<td>5.36</td>
</tr>
<tr>
<td>K\textsuperscript{2}Cl</td>
<td>KCl\textsuperscript{−}+K</td>
<td>0.86(0.95±0.26)\textsuperscript{b}</td>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}+K</td>
</tr>
<tr>
<td>→ KCl\textsuperscript{−}+K</td>
<td>4.54</td>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}+K</td>
<td>1.14</td>
</tr>
<tr>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}+K</td>
<td>4.55(4.81±0.26)\textsuperscript{b}</td>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}+K</td>
<td>1.88</td>
</tr>
<tr>
<td>KCl</td>
<td>KCl\textsuperscript{−}+Cl</td>
<td>1.12</td>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}+Cl</td>
</tr>
<tr>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}+Cl</td>
<td>3.19</td>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}+Cl</td>
<td>4.72</td>
</tr>
<tr>
<td>→ Cl\textsuperscript{−}+K</td>
<td>4.91</td>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}+Cl</td>
<td>4.86</td>
</tr>
<tr>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}+Cl</td>
<td>0.514 \textsuperscript{c}</td>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}+Cl</td>
<td>6.94</td>
</tr>
<tr>
<td>K\textsuperscript{2}</td>
<td>K\textsuperscript{+}Cl</td>
<td>4.14(4.35)\textsuperscript{d}</td>
<td>→ K\textsuperscript{+}Cl...</td>
</tr>
<tr>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}</td>
<td>5.00</td>
<td>→ K\textsuperscript{+}Cl</td>
<td>4.27</td>
</tr>
<tr>
<td>→ K\textsuperscript{+}Cl\textsuperscript{−}</td>
<td>0.45(0.514)\textsuperscript{d}</td>
<td>→ K\textsuperscript{+}Cl</td>
<td>0.47(0.51)\textsuperscript{d}</td>
</tr>
<tr>
<td>Cl\textsuperscript{2}</td>
<td>2Cl</td>
<td>2.05(2.48)\textsuperscript{e}</td>
<td>→ Cl\textsuperscript{−}+Cl</td>
</tr>
<tr>
<td>→ Cl\textsuperscript{−}+Cl</td>
<td>13.71</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(\textsuperscript{a}\text{See Ref. 72.}\)
\(\textsuperscript{b}\text{See Ref. 73.}\)
\(\textsuperscript{c}\text{See Ref. 51.}\)
\(\textsuperscript{d}\text{See Ref. 74.}\)
\(\textsuperscript{e}\text{See Ref. 75.}\)
experimential data.\textsuperscript{51,72–75} Comparison shows rather good agreement, with the largest deviation being for the “notorius” Cl\textsubscript{2} of 0.43 eV (10 kcal/mol).

The CCSD(T)/POL1 dimerization energy of (KCl)\textsubscript{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\textsuperscript{33} to be 1.85 eV (versus experiment 1.97 eV).\textsuperscript{72} Interestingly, dissociation channels KCl\textsubscript{2} + K and KCl\textsubscript{2} + K\textsuperscript{+} have nearly the same energies, due, in part, to the small ionization potential of K and very high electronegativity of KCl. The value of 5.13 eV for the KCl\textsubscript{2} + K\textsuperscript{+} channel is even slightly larger than the energy of dissociation KCl to K\textsuperscript{+} + Cl\textsuperscript{−}. This allows an alternative way of considering alkali halide crystals as [MX\textsubscript{2}]\textsuperscript{−}M\textsuperscript{+} salts instead of X\textsuperscript{−}M\textsuperscript{+} ones. Some support to this conjecture is given by the results of Weiss et al.\textsuperscript{76} in their \textit{ab initio} study of Na\textsubscript{n}Cl\textsubscript{n} and Na\textsubscript{n}Cl\textsubscript{n−1}, n = 4 clusters. They have found that the most stable is tetrahedral Na\textsubscript{4}Cl\textsubscript{4}, which is of the NaCl-bulk lattice type, whereas odd-n Na\textsubscript{n}Cl\textsubscript{3} is less stable and geometrically fragile.

The trimers K\textsubscript{2}Cl and KCl\textsubscript{2} are rather weakly bound, and they are somewhat less stable than their corresponding anions. The more stable character of K\textsubscript{2}Cl\textsuperscript{−} and KCl\textsubscript{2}\textsuperscript{−} is related to the fact that they have larger A\textsubscript{ad}s than KCl and Cl\textsubscript{2}. Our computed fragmentation energies of K\textsubscript{2}Cl are in agreement with experimental data\textsuperscript{31} within experimental error bars.

The (KCl)\textsubscript{2} anion is less stable than its neutral parent dimer, and the first fragment configuration corresponds to the formation of K, which requires about 20 kcal/mol. Therefore, attachment of an electron to the (KCl)\textsubscript{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.

\section*{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 \textit{sp}-functions, which allows one to describe rather diffuse electron distributions. This approach has been applied previously to a series of polar diatomic molecules\textsuperscript{33} and the results of our calculations are in excellent agreement with the results obtained with the use of “infinitely” numerical basis sets.\textsuperscript{77,78}

As expected, K\textsubscript{2}\textsuperscript{−}, (KCl)\textsubscript{2}\textsuperscript{−}, and K\textsubscript{2}Cl\textsuperscript{−} have no diffuse excited states (see Table V). That means that the electric quadrupole moments in K\textsubscript{2} and K\textsubscript{2}Cl as well as the dipole moment in KCl are not large enough to support quadrupole-bound or dipole-bound states in the corresponding anions. The vertical attachment energies of K\textsubscript{2} and K\textsubscript{2}Cl are only slightly lower than their adiabatic EAs, whereas a drastic difference between the A\textsubscript{ad} and the E\textsubscript{va} of KCl\textsubscript{2} is observed (see Table II).

The EA-EOMCC vertical attachment energy of an extra electron from (KCl)\textsubscript{2} is 0.09 eV, which is close to the A\textsubscript{ad} of 0.095 eV of (KCl)\textsubscript{2}, obtained at the CCSD(T)/POL1 level.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
 & K\textsubscript{2} & (KCl)\textsubscript{2} & K\textsubscript{2}Cl & KCl & KCl\textsubscript{2} \\
\hline
DM & 0.0 & 0.0 & 1.66 & 9.68 & 10.76 & 24.93 \\
\hline
E\textsubscript{va} & 1st & 0.40 & 0.09 & 0.56 & 1.33 & 0.57 & 1.22 \\
2nd & 0.48 & 0.53 & 0.03 & 0.27a & 0.27a \\
3rd & 0.02 & 1 \times 10\textsuperscript{−3} & 0.27a \\
4th & 7 \times 10\textsuperscript{−4} & 0.20b \\
\hline
\end{tabular}
\caption{Vertical electron attachment energies (E\textsubscript{va}) of K\textsubscript{2}, KCl, KCl\textsubscript{2}, KCl, and KCl\textsubscript{2} at the neutral equilibrium D\textsubscript{2h} geometry.}
\end{table}

No other diffuse state was found for the (KCl)\textsubscript{2} anion at the neutral equilibrium D\textsubscript{2h} geometry.

KCl and KCl\textsubscript{2} possess rather similar dipole moments and extra electrons in their anion states have similar binding energies. The latter are slightly larger in KCl\textsuperscript{−}, which is consistent with a larger dipole moment of KCl. The magnitude of binding energies of an extra electron in excited states of KCl\textsuperscript{−} are similar to those calculated previously\textsuperscript{33} for NaCl\textsuperscript{−}, whose neutral precursor has the dipole moment of 8.97 D.

Linear KCl\textsubscript{2} 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 \pi-symmetry; all other excited and ground states are of the \sigma-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 typical 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)\textsubscript{2} dissociation, namely, those presented in Table IV added to KCl\textsubscript{2}+K\textsuperscript{+} and K\textsubscript{2}+Cl\textsubscript{2}. The \pi-channel could be tentatively attributed to the symmetric KCl+KCl\textsuperscript{−} channel.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{Ground-state geometrical configurations of KCl\textsubscript{2}, K\textsubscript{2}Cl, (KCl)\textsubscript{2}, their anions, and KCl\textsubscript{2}.}
\end{figure}
F. Quadrupole-bound state of \((\text{KCl})_2\)

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 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-bound 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 \((\text{KCl})_2^-\) in some detail. Attachment of an extra electron to \((\text{KCl})_2^-\) leads to increasing the K–K distance by \(\approx 0.1\) 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 smaller than in typical dipole-bound states, because their spatial difference from the rest of the electrons.

Thus, the extra electron is attached to the two positive ends of the 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.

The Mulliken charge distribution in the neutral dimer is \((\text{K}^+\text{Cl}^-)_2\), whereas in the anion, it is \((\text{K}^{1+0.5}\text{Cl}^-)_2\). This 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 \(2Q_xZ_1^2 - 2Q_yZ_1Z_2\), 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 \(\text{CS}_2\)).

The LUMO eigenvalue of the neutral \((\text{KCl})_2^-\) 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 \((\text{KCl})_2^-\) and typical dipole-bound anions suggests the conclusion that the extra electron in \((\text{KCl})_2^-\) 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 \(\text{K}_n\text{Cl}_m\) and \(\text{K}_n\text{Cl}_m^-(n,m=0–2)\) has revealed several interesting features, which can be briefly summarized as follows.

(i) \(\text{KCl}_2^-\) 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 \(\text{K}^+\text{[KCl]_2}^-\) instead of the usual \(\text{K}^+\text{Cl}^-\). The same description is valid for other MX alkali halides, since their MX\(_2^-\) units are superhalogens as well.

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

(iii) The rhombic ground-state \((\text{KCl})_2^-\) dimer forms two anionic states upon attachment of an extra electron: rhombic and linear. The rhombic \((\text{KCl})_2^-\) 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 KCIKCl dimer possesses a large dipole moment of 25 D at the anion geometry. Linear KCIKCI corresponds to a transition state on the potential energy surface.

(iv) \(\text{KCl}_2^-\) is stable towards dissociation by 26 kcal/mol; both \(\text{K}_2\text{Cl}^-\) and \(\text{KCl}_2^-\) anions are thermodynamically more stable than their neutral parents.

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