Reactions of ultracold alkali-metal dimers

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We investigate the energetics of reactions involving pairs of alkali-metal dimers. Atom exchange reactions to form homonuclear dimers are energetically allowed for some but not all of the heteronuclear dimers. We carry out high-level electronic structure calculations on the potential energy surfaces of all the heteronuclear alkali-metal trimers and show that trimer formation reactions are always energetically forbidden for low-lying singlet states of the dimers. The results have important implications for the stability of quantum gases of alkali-metal dimers.

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Before proceeding to the trimer formation reactions, we briefly consider atom exchange reactions analogous to (1) for the heteronuclear dimers formed from the alkali metals Li, Na, K, Rb, and Cs. All the homonuclear and heteronuclear dimers except LiRh have been studied in detail by high-resolution spectroscopy, and dissociation energies $D_e$ accurate to $\pm 1$ cm$^{-1}$ or better have been extracted as listed in Table I. The energy changes for the atom exchange reactions can therefore be calculated directly from experiment, and are summarized in Table II. The values given are taken from dissociation energies $D_e$ measured to the dimer equilibrium geometries and so are subject to small corrections for the differences in zero-point energy between reactants and products. These corrections can be up to $+25$ cm$^{-1}$ for LiX systems but are less than $\pm 2$ cm$^{-1}$ for the remainder. It may therefore be concluded that all the heteronuclear Li dimers and KrB will be subject to reactive trap loss, but all the remainder should be stable with respect to atom exchange collisions in their ground rovibronic state.

Trimer formation reactions cannot be considered in a similar way because an experimental binding energy is available only for Li$_3$ [27] and not for any of the heteronuclear trimers. We have therefore carried out electronic structure calculations for all the homonuclear and heteronuclear alkali-metal trimers, using the multireference average-quadratic coupled-cluster method (AQCC). All calculations used the MOLPRO package [28]. The alkali-metal atoms were described in a single-electron model and the core-valence interaction was taken into account using an effective core potential (ECP) with a core polarization potential (CPP). We used the ECPxSDF family of core potentials, developed by the Stuttgart group [29,30], with core polarization potentials based on those of Müller and Meyer [31]. We obtained modified values of the Müller-Meyer cutoff parameter (0.95 for Li, 0.82 for Na, 0.36 for K, 0.265 for Rb, and 0.24 for Cs) that reproduce the experimental bond lengths of the ground-state homonuclear alkali-metal dimers at the same level of theory. We used the uncontracted $sp$ basis sets designed for ECPxSDF core potentials [29,30], augmented by additional $s$, $p$, $d$, and $f$ functions [32]. With these polarization potentials and basis sets, we reproduced the single binding energies for homonuclear alkali-metal dimers with an accuracy better than 1% for Li$_2$, Na$_2$, Rb$_2$, and 2% for K$_2$ and Cs$_2$. The binding energies for the heteronuclear dimers are as good as for the homonuclear dimers, except for LiCs, for which the error in the binding energy was $+2.5\%$.

To understand the doublet states of heteronuclear alkali-metal trimers, it is useful first to consider the homonuclear systems. The important molecular orbitals are those formed...
from the outermost $s$ orbitals on each atom. At an equilateral triangular configuration ($D_{3h}$ symmetry), the two highest occupied molecular orbitals of a homonuclear trimer have $a_1$ and $e$ symmetry. The lowest doublet state has configuration $a_1^2e^1$. It is therefore orbitally degenerate, with $^2E$ symmetry, and is subject to a Jahn-Teller distortion to an isoisosceles geometry ($C_{3v}$) that splits the $e$ orbitals into $a_1$ and $b_2$ components: the $b_2$ orbital has a node between the two equivalent atoms. The equilibrium structures of the homonuclear trimers all have $C_{3v}$ geometries with ground states of $^2B_2$ symmetry.

For a heteronuclear trimer $X_2Y$, the symmetry is always $C_{2v}$ or $C_1$. For $C_{2v}$ geometries, the upper $a_1$ orbital and the $b_2$ orbital are close together in energy and the minimum (restricted to $C_{2v}$) may be on either the $^2A_1$ surface or the $^2B_2$ surface. We have therefore calculated the energy for all the heteronuclear trimers in both $^2A_1$ and $^2B_2$ states for $C_{2v}$ geometries. Typical results are shown for Rb$_2$Cs in the top panel of Fig. 1. The geometry is specified by a bond length $r = r_{X,Y} = r_{X',Y}$ and the angle $\theta$ between the two $XY$ bonds. It may be seen that the two surfaces intersect at an angle near $\theta = 50^\circ$: since the two states have the same symmetry at $C_1$ geometries, they actually intersect only at $C_{2v}$ geometries, producing a seam of conical intersections there. An alternative representation of the results, for all the Rb$X$ systems, is shown in the bottom panel of the figure: in this case $r$ has been optimized to find the energy minimum for each value of $\theta$, producing intersecting potential curves rather than two-dimensional surfaces. The minima on the two surfaces are usually close together in energy (always within 1000 cm$^{-1}$, but often within 200 cm$^{-1}$). However, the $^2B_2$ minimum is below the $^2A_1$ minimum for all the trimers except the seven heteronuclear $X_2Na$ and Cs$_2X$ species; for Rb$_2$Cs, shown in Fig. 1, the $^2B_2$ minimum is near $\theta = 63^\circ$.

The equilibrium geometries and energies for both states are provided as supplemental material [33].

For heteronuclear trimers there is the additional possibility of distortion to a lower-symmetry $C_s$ (scalarene) geometry. We have therefore explored whether such distortions lower the trimer energies. At $C_s$ geometries the valence orbitals formed from atomic $s$ orbitals are all of $a'$ symmetry, so both low-lying states have $^2A'$ symmetry and can mix. Nevertheless, in most cases it is clear whether the singly occupied orbital has bonding character ($a_1$-like) or antibonding character ($b_2$-like) between the two like atoms. For Cs$_2$Li, where the $^2A_1$ state was already below the $^2B_2$ state, distortion does not lower the energy and the equilibrium geometry has $C_{2v}$ symmetry. However, for all the other systems the geometry corresponding to the $^2A_1$ minimum is in fact a saddle point on the full three-dimensional surface: for Li$_2Na$, K$_2Na$, Rb$_2Na$, Cs$_2Na$, Cs$_2K$, and Cs$_2$Rb, this simply deepens the minimum. For Li$_2$K, Li$_2$Rb, Rb$_2$K, K$_2$Cs, Rb$_2$Na, the distortion produces a $^2A'$ state whose absolute minimum (of $C_s$ symmetry) is lower in energy than the $^2B_2$ state (which always retains an equilibrium geometry of $C_{2v}$ symmetry). However, for Li$_2$Cs, Na$_2$Li, Na$_2$K, Na$_2$Rb, Na$_2$Cs, K$_2$Li, Rb$_2$Li, Rb$_2$K, and Rb$_2$Cs the energy gained by distortion is not enough and the $^2B_2$ state of $C_{2v}$ geometry remains the absolute minimum.

Table III summarizes the trimer atomization energies, equilibrium geometries, and the energy change for the trimer formation reactions for all the alkali-metal trimers from Li to Cs. It may be seen that all the trimer formation reactions (from singlet dimers) are substantially endoergic. Trimer formation

### Table I. Dissociation energies $D_e$ (in cm$^{-1}$) for alkali-metal dimers. The quantities in parentheses are uncertainties in the final digit(s).

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>8516.768(8)$^a$</td>
<td>7105.5(1.0)$^b$</td>
<td>6216.886(100)$^c$</td>
<td>5946(100)$^d$</td>
<td>5875.542(5)$^e$</td>
</tr>
<tr>
<td>Na</td>
<td>6022.0286(53)$^f$</td>
<td>5273.62(10)$^g$</td>
<td>5030.502(10)$^h$</td>
<td>4954.237(100)$^i$</td>
<td>4069.208(40)$^j$</td>
</tr>
<tr>
<td>K</td>
<td>4450.906(50)$^j$</td>
<td>4217.815(10)$^k$</td>
<td>3993.47(18)$^l$</td>
<td>3836.14(50)$^m$</td>
<td>3649.695(2)$^n$</td>
</tr>
<tr>
<td>Rb</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td></td>
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$^a$Reference [13].
$^b$Reference [14].
$^c$Reference [15].
$^d$The binding energy for LiRb is not available from experiment, so this value is calculated using the AQCC method described in this paper.
$^e$Reference [16].
$^f$Reference [17].
$^g$Reference [18].
$^h$Reference [19].
$^i$Reference [20].
$^j$Reference [21].
$^k$Reference [22].
$^l$Reference [23].
$^m$Reference [24].
$^n$Reference [25].
$^o$Reference [26].

### Table II. Energy changes $\Delta E_2$ for the reactions $2XY \rightarrow X_2 + Y_2$ (in cm$^{-1}$). The quantities in parentheses are uncertainties in the final digit(s).

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>−328(2)</td>
<td>−533.9(3)</td>
<td>−618(200)</td>
<td>−415.38(2)</td>
</tr>
<tr>
<td>Na</td>
<td>74.3(3)</td>
<td>45.5(5)</td>
<td>236.75(20)</td>
<td>37.81(13)</td>
</tr>
<tr>
<td>K</td>
<td>−8.7(9)</td>
<td>29.1(1.5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Curves for the bond angle \( \theta \) as a function of the RbCs bond length. Entries for alkali-metal atoms and singlet dimers are thus likely to be correct to \( \pm 5\% \). However, trimers may of course still be formed from dimers formed in singlet states near the bottom of the potential well. This contrasts with the situation for reactions involving spin-pair states of alkali-metal atoms and triplet dimers, which have been used to predict them. The use of high-level electronic structure calculations, as in the present work, is essential to obtain reliable conclusions.

Our atomization energies for homonuclear systems may be compared with 13,436 cm\(^{-1}\) for Li\(_3\) from multireference configuration interaction (MRCI) calculations [41], and 5437.1 cm\(^{-1}\) for Cs\(_3\) from full configuration interaction (CI) calculations [42]. Our values for trimers containing Li, Na, and K also agree well (within 1000 cm\(^{-1}\)) with early CI work by Pavolini and Spiegelmann [43]. In all cases the calculations used effective core potentials similar to those in the present work.

The present results for trimer energies may be rationalized using a very simple model. In the simplest form of Hückel theory, considering only one \( s \) orbital on each atom, with a bond integral \( \beta \), a homonuclear dimer in a singlet state has binding energy \( 2|\beta| \). An equilateral trimer has binding energy \( 3|\beta| \), while a linear trimer has binding energy \( 2\sqrt{2}|\beta| \). An atom transfer reaction such as (2) is therefore endoergic by \( |\beta| \), while a linear trimer has binding energy \( 2\sqrt{2}|\beta| \). This is quite different from the result predicted by pairwise additivity. However, simple orbital-based models of chemical bonding must be treated with caution for the alkali metals, because they have low-lying \( p \) orbitals that often make important contributions to bonding.

Pair-pair states can also be important. Thus, while Hückel theory can be used to rationalize the results of the present work, it could not have been used to predict them. The use of high-level electronic structure calculations, as in the present work, is essential to obtain reliable conclusions.
ACKNOWLEDGMENTS

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[32] s functions with exponents 0.010159 for Li, 0.009202 for Na, 0.009433 for K, 0.007182 for Rb, 0.007778 for Cs, p functions with exponents 0.007058 for Li, 0.005306 for Na, 0.004558 for K, 0.004459 for Rb, 0.004186 for Cs, d functions with exponents 0.39 and 0.13 for Li, 0.3 and 0.1 for Na, 0.27 and 0.09 for K, 0.21 and 0.07 for both Rb and Cs and f functions with exponents 0.13 for Li, 0.1 for Na, 0.09 for K, 0.07 for both Rb and Cs.