Structure and thermochemistry of K$_2$Rb, KRb$_2$ and K$_2$Rb$_2$

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The formation and interaction of ultracold polar molecules is a topic of active research. Understanding possible reaction paths and molecular combinations requires accurate studies of the fragment and product energetics. We have calculated accurate gradient optimized ground state structures and zero point corrected atomization energies for the trimers and tetramers formed by the reaction of KRb with KRb and corresponding isolated atoms. The K$_2$Rb and KRb$_2$ trimers are found to have global minima at the $C_{2v}$ configuration with atomization energies of 6065 and 5931 cm$^{-1}$ while the tetramer is found to have two planar mirror structures, of $D_2h$ and $C_s$ symmetry, which have atomization energies of 11131 cm$^{-1}$ and 11133 cm$^{-1}$, respectively. We have calculated the minimum energy reaction path for the reaction KRb+KRb to K$_2$+Rb$_2$ and found it to be barrierless.

The formation and interaction of ultracold polar molecules is a topic of great current interest in physics. New techniques for the formation of rovibrational ground state polar molecules via STIRAP [1] (stimulated rapid adiabatic passage) or FOPA [2] (Feshbach-optimized photo-association) allow experiments to be performed with $v=0$ heteronuclear diatomic molecules, including KRb [3-6] and LiCs [7]. Proposals for quantum computation with polar molecules [8, 9] have generated a growing need for understanding of the dynamics of diatomic-diatom collisions. Such studies of diatomic dynamics require knowledge of the open and closed channels relevant in those reactions. The purpose of the present paper is to present accurate ab initio calculations of the structure and thermochemistry of several chemical species relevant to the study of KRb–KRb dimer interactions.

Theoretical work on electronic structure of few-body alkali systems has been limited to lighter homonuclear trimers, in particular doublet Li$_3$, doublet K$_3$ [12] and quartet Na$_3$ [13]. The recent work of Zuchowski and Hutson [14] has characterized the atomization energy of the alkali homo- and heteronuclear triatomic species formed from Li, Na, K, Rb, and Cs. These homonuclear trimers have $A'$ ground electronic states in $C_s$ symmetry that correlate to $B_2$ symmetry in $C_{2v}$. Previous mixed alkali tetramer studies have been limited to structure studies of Li$_n$X$_m$ (X=Na and K) [15, 16] and that of RbCs+RbCs [17]. To date no such calculations have been reported for the heteronuclear K$_n$Rb$_m$ tetramer molecules.

Electronic structure calculations were performed on K$_2$, Rb$_2$, KRb, K$_2$Rb, KRb$_2$, and K$_2$Rb$_2$ at the CCSD(T) [18] level of theory. As core-valence effects can be important in alkali metals, we correlate the inner valence electrons in potassium, keeping only 1s$^2$2s$^2$2p$^2$ in the core. Rubidium is different in that relativistic effects are significant, so we replace its inner shell electrons by the Stuttgart small-core relativistic (ECP28MDF) ECP [19]. Basis sets are taken from the Karlsruhe def2-TZVPP [20] and def2-QZVPP [21] orbital and fitting sets.

Optimized geometries for K$_2$, Rb$_2$, KRb, K$_2$Rb, KRb$_2$, and K$_2$Rb$_2$ were found at the CCSD(T)/def2-TZVPP level of theory. Calculation of the harmonic vibrational frequencies was done to verify that the calculated structures were minima on the potential energy surface, and the calculated frequencies were used to obtain vibrational zero point energy (ZPE) corrections. These structures were further optimized at the CCSD(T)/def2-QZVPP level of theory, leading to a 0.07 Å correction in the bond lengths and 60 cm$^{-1}$ in final atomization energies. The CCSD(T)/def2-QZVPP geometries are tabulated in Table I.

Evaluation of the contribution of scalar relativistic corrections to K$_2$ indicate a small 0.005 Å and < 8 cm$^{-1}$ contribution in all electron correlation calculations [24], while for Rb$_2$ it has been shown [25] that the small core Stuttgart pseudopotential gives an accurate representation of relativistic effects on the bond length and dissociation energy.

Single point energy calculations were then done using the CCSD(T)-F12b [26, 27] (explicitly correlated CCSD(T)) level of theory. The use of explicitly correlated methods accelerate the slow convergence of the one-particle basis set by including terms containing the inter-electron coordinates into the wavefunction [28], thus yielding very accurate results using triple and quadruple zeta basis sets. In addition, we estimate the complete basis set (CBS) limit using the two-point extrapolation formula of Helgaker et al [29]

$$E_{CBS} = \frac{n^3E_n - (n-1)^3E_{n-1}}{n^3 - (n-1)^3}. \quad (1)$$

In Table I the CCSD(T) and CCSD(T)-F12b dissociation energies for the def2-TZVPP and def2-QZVPP basis sets are tabulated as well as the zero point energy (ZPE) corrected atomization energies. After extrapolation, the diatomic CCSD(T)-F12b ZPE corrected dissociation energies agree very well with the experimental diatomic dissociation energies, as shown in Table I. The ab initio calculations were done using the Gaussian 09 [30] and MOLPRO [31, 33] packages.

We have found that both K$_2$Rb and KRb$_2$ have two energetically close local minima on the ground state surface, one of $C_{2v}$, symmetry and another less symmetric $C_s$...
minimum energy geometric configuration at long range. 

\[ \text{Rb} \]

sort proposed for \( \text{Li} \) and \( \text{K} \). Their stability is likely due to three-center bonds of the electronic structure of these two isomers is very similar, and generate minima on the potential energy surface. One is \( \text{K} \) and \( \text{Rb} \) atoms. These structures are bound by \( \text{Rb} \) to \( \text{K} \) distance is short and the \( \text{Rb} - \text{Rb} \) distance is long. 

successive basis sets and CBS extrapolated values (in cm\(^{-1}\)). Those recently published by˙Zuchowski and Hutson \[14\].

\[ \text{K}_2 \]
\[ 3.956 \]
\[ \text{Rb}_2 \]
\[ 4.233 \]
\[ \text{KRb} \]
\[ 4.160 \]

This is done by calculating \textit{ab initio} the dipole and quadrupole electrostatic moments of \( \text{K}_2 \), \( \text{Rb}_2 \) and \( \text{KRb} \) and then minimizing the long range electrostatic interaction energy \[34\] with respect to the angular configuration of the molecules. This minimization resulted in a T type geometry for both \( \text{K}_2 + \text{Rb}_2 \) and \( \text{KRb} + \text{KRb} \). We have recently shown that long-range expansions of this type accurately reproduce diatomic-diatom interaction energies \[35\]. From these initial geometries, the reaction path was followed by freezing the diatomic-diatom distance and optimizing the diatomic bond lengths and angular orientations at the frozen core CCSD(T)/def2-TZVPP level of theory. Single point energies were evaluated along this path using the CCSD(T)-F12b level of theory including the core-valence correlation energy and extrapolated to the CBS limit as discussed above. This procedure, in which a high level energy profile is evaluated along a reaction path calculated at a lower level of theory, is known to be a good approximation to the energy profile along the reaction path calculated at the high level of theory \[36\].

We find that the \( \text{KRb} + \text{KRb} \) dissociation limit connects to the \( D_{2h} \) minima while the \( \text{K}_2 + \text{Rb}_2 \) dissociation limit connects to the \( C_s \) minima, with no barrier found.
to either reaction. A similar conclusion was obtained for the RbCs+RbCs→Rb2+Cs2 reaction by Tscherbul et al\cite{17}. To finish characterizing the reaction path going from dissociation limit to the other, we locate the transition state and calculate the intrinsic reaction coordinate (IRC)\cite{37} reaction path connecting the Cs and D2h minima structures at the same level of theory as describe above. Optimizing the transition state geometry at the inner valence CCSD(T)/def2-TZVPP discussed previously and evaluating an accurate atomization energy using our CCSD(T)-f12b prescription we find that the transition state is 1167.3 cm\(^{-1}\) above the D2h dissociation energy. The calculated reaction path is plotted in Figure 1 using the approximate reaction coordinate

\[
\Delta R = (R_{Rb-Rb} + R_{Cs-Cs})/2 - (R_{Rb-Cs} + R_{Rb-Cs}')/2
\]

(2)

where \(R_{A-B}\) is the distance between atoms A and B.

The formation and trapping of rovibrational ground state KRb diatoms with a high phase space density\cite{5} offers the opportunity to study chemical reactions in the ultra-cold regime\cite{6}. As seen in Figure 2 the three-body reaction KRb+Rb→Rb2+K is energetically forbidden at ultra-cold temperatures, leaving the endothermic four-body reaction KRb+KRb→Rb2+K2 as the only pathway to forming Rb2 within the trap. Measurements of the population of Rb2 within the trap will then allow direct probing of the exchange reaction rate of KRb+KRb. Inherent in this exchange reaction is the possibility of studying the role of fermionic/bosonic spin statistics in ultra-cold chemical reactions\cite{38,44}. In this temperature regime, s-wave scattering of fermionic \(^{40}\)KRB is suppressed which should greatly diminish the reaction rate of \(^{40}\)KRb+\(^{40}\)KRb, thus leaving the trap stable to four-body losses. If instead the trap was formed with bosonic \(^{39}\)KRb or \(^{41}\)KRb molecules, no such collisional suppression is expected, where we then expect comparably large reaction rates to occur. It is also possible to explore recent theoretical predictions\cite{44} which show that if a bosonic dimer is composed of two fermions of very different masses the resulting exchange reaction should still be suppressed despite the overall bosonic nature. This could be accomplished by using fermionic \(^{40}\)K and a long lived \(^{84}\)Rb or \(^{86}\)Rb. The comparison between reaction rates in the above described interactions can then be used to directly study the effects of fermion/boson spin statistics to that of chemical reactions.

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