

Supplementary material

I. Estimate of the ETMD electron kinetic energies for the $\text{He}_2^+-\text{Ak}_1\text{Ak}_2(^1\Sigma^+)$ systems

Table 1 shows the estimated kinetic energy values E_e of the ETMD electron for the $\text{He}_2^+-\text{Ak}_1\text{Ak}_2(^1\Sigma^+)$ systems studied in this work. The values of E_e were calculated using the following electron kinetic energy balance:

$$E_e = E(\text{He}_2^+) - E_i(\text{Ak}_1) - E_i(\text{Ak}_2) - E_K([\text{Ak}_1\text{Ak}_2]^{2+}) + E_b(\text{Ak}_1\text{Ak}_2) + E_b(\text{He}_2^+-\text{Ak}_1\text{Ak}_2) - E_b(\text{He}_2-[\text{Ak}_1\text{Ak}_2]^{2+})$$

where $E(\text{He}_2^+)$ is the energy difference between the ionized and ground states of He_2 at the He_2^+ equilibrium distance of 1.1 Å [1, 2, 3], E_i is the ionization energy of the dopants $\text{Ak}_{1,2}$, and $E_K([\text{Ak}_1\text{Ak}_2]^{2+})$ denotes the kinetic energy release (KER) of the two Coulomb-exploding alkali ions. $E_b(\text{He}_2^+-\text{Ak}_1\text{Ak}_2)$ is the binding energy of He_2^+ to the alkali dimer in the entrance channel, and approximately equal to zero at geometries where the decay is efficient [4]. $E_b(\text{He}_2-[\text{Ak}_1\text{Ak}_2]^{2+})$ is the binding energy of He_2 to the dicationic alkali dimer in the exit channel. It is negative and its absolute value is < 1 eV.

Table 1: Estimated ETMD electron energies for different $\text{He}_2^+-\text{Ak}_1\text{Ak}_2(^1\Sigma^+)$ systems

	Na ₂	K ₂	Rb ₂	NaK	NaRb	KRb
$E(\text{He}_2^+)$ [eV]	19.77	19.77	19.77	19.77	19.77	19.77
$E_i(\text{Ak}_1)$ [eV] + $E_i(\text{Ak}_2)$ [eV]	10.28	8.68	8.35	9.48	9.32	8.52
$E_K([\text{Ak}_1\text{Ak}_2]^{2+})$ [eV]	4.69	3.67	3.44	4.20	3.88	3.55
$E_b(\text{Ak}_1\text{Ak}_2)$ [eV]	- 0.74 [5]	- 0.55 [6]	- 0.50 [7]	- 0.65 [8]	- 0.55 [9]	- 0.50 [10]
$E_b(\text{He}_2^+-\text{Ak}_1\text{Ak}_2)$ [eV]	~ 0	~ 0	~ 0	~ 0	~ 0	~ 0
$E_b(\text{He}_2-[\text{Ak}_1\text{Ak}_2]^{2+})$ [eV]	- 0.06	- 0.02	- 0.54	- 0.04	- 0.30	- 0.30
E_e [eV]	~ 4.12	~ 6.89	~ 8.02	~ 5.48	~ 6.32	~ 7.50

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II. ETMD electron spectra for He-Na₂ and He-KRb: *ab initio* calculations

The ETMD electron spectra in He-Na₂ and He-KRb were obtained by the procedure used for the He-Li₂ spectra reported in Ref. [1]. To that end we first constructed the potential energy surfaces (PES) $E_d(\mathbf{R})$ of the decaying $\text{He}^+-\text{Ak}_1\text{Ak}_2$ and $E_f(\mathbf{R})$ of the final $\text{He}-[\text{Ak}_1\text{Ak}_2]^{2+}$ states. On the decaying state's PES, we first selected the points corresponding to the energy $E=E_d(\mathbf{R}_{eq})$, where \mathbf{R}_{eq} designates the neutral cluster's equilibrium geometry. From these points we selected a subset $\{\mathbf{R}_{ip}\}$, which corresponds to shorter distances between He^+ and the alkali dimer's center-of-mass (CoM). The electron spectrum is given by the difference $E_d(\mathbf{R}) - E_f(\mathbf{R})$ computed at $\{\mathbf{R}_{ip}\}$. To simplify the calculations, we used the fact that alkali dimers are strongly bound in the $^1\Sigma^+$ state and weakly bound in the $^3\Sigma^+$ state. This allowed us to reduce the number of coordinates from three to two without strongly compromising the accuracy. The Ak_1-Ak_2 distance was kept constant for the $^1\Sigma^+$ state of the dimer, and the angle between the dimer's axis and the line connecting He^+ to the dimer's CoM was kept constant in the $^3\Sigma^+$ state. In the following, we will refer to the PES and the respective states of the trimer by the state of the alkali dimer whenever appropriate.

We computed the $^1\Sigma^+$ and $^3\Sigma^+$ PES of the decaying He^+-Na_2 states by freezing 20 core electrons on Na atoms and employing for the three active electrons the full Configuration Interaction (FCI) method as implemented in the GAMESS-US package [2, 3]. The reference state was the electronic ground state of HeNa_2 , which was obtained in the restricted Hartree-Fock (RHF) approximation. The aug-cc-pVTZ-DK basis set [4] was used on both the He and Na atoms. The final states were obtained in the FCI calculation with two active electrons and using the same reference state and basis sets.

The PES of the decaying $^1\Sigma^+$ state of He^+-KRb was obtained by first computing the surface of the respective ionization energy using ADC(2)x method for the Green's function [5]. The reference electronic ground state of He-KRb was obtained using the second-order Douglas-Kroll-Hess Hamiltonian as implemented in the MOLCAS package [6] and ANO-RCC-VQZP basis set on all atoms. The $1s$, $2s$, $2p$ orbitals of K, and the $1s$, $2s$, $2p$, $3s$, $3p$, $3d$ orbitals of Rb (19 lowest orbitals) were frozen in the ADC calculation. The ADC ionization energy was added to the ground state PES, which we obtained by the CCSD(T) method as implemented in the GAMESS-US package. The PES of the decaying $^3\Sigma^+$ state of He^+-KRb was obtained by the FCI method as implemented in the GAMESS-US package by using the RHF He-KRb reference state. To describe the effect of the core electrons of K and Rb we used respectively the ECP18SDF and ECP36SDF relativistic pseudopotentials [7, 8]. The PES of the final $\text{He-K}^+-\text{Rb}^+$ state was obtained by the CCSD(T) method as implemented in the GAMESS-US package using the RHF $\text{He-K}^+-\text{Rb}^+$ reference state.

The binding energies in the dicationic final $\text{He}-(\text{Ak}_1\text{Ak}_2)^{2+}$ states shown in Table 1 were estimated as the binding energy of the He and $(\text{Ak}_1\text{Ak}_2)^{2+}$ fragments, with the Ak-Ak distance held constant and equal to the equilibrium distance in the neutral $^1\Sigma^+$ ground state. The energy calculations were done by using the CCSD(T) method as implemented in the GAMESS-US package. SPK-TZP Sapporo family of non-relativistic basis sets was used in the calculations together with the SBKJC effective core potentials for the metal atoms.

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