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Cold interactions and chemical reactions of linear polyatomic anions with alkali-metal and alkaline-earth-metal atoms

We consider collisional studies of linear polyatomic ions immersed in ultracold atomic gases and investigate the intermolecular interactions and chemical reactions of several molecular anions (OH⁻, CN⁻, NCO⁻, C₂H⁻, C₄H⁻) with alkali-metal (Li, Na, K, Rb, Cs) and alkaline-earth-metal (Mg, Ca, Sr, Ba) atoms. State-of-the-art *ab initio* techniques are applied to compute the potential energy surfaces (PESs) for these systems. The coupled cluster method restricted to single, double, and noniterative triple excitations, CCSD(T), is employed and the scalar relativistic effects in heavier metal atoms are modeled within the small-core energy-consistent pseudopotentials. The leading long-range isotropic and anisotropic induction and dispersion interaction coefficients are obtained within the perturbation theory. The PESs are characterized in detail and their universal similarities typical for systems dominated by the induction interaction are discussed. The two-dimensional PESs are provided for selected systems and

can be employed in scattering calculations. The possible channels of chemical reactions and their control are analyzed based on the energetics of the reactants. The present study of the electronic

structure is the first step towards the evaluation of prospects for sympathetic cooling and controlled

chemistry of linear polyatomic ions with ultracold atoms.

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1 Introduction

Experiments at low and ultralow temperatures allow physics and chemistry to be investigated at the fundamental quantum limit.¹ The realization of ultracold atomic gases has significantly increased our understanding of quantum many-body systems.² The production of ultracold gases of polar diatomic molecules has resulted in groundbreaking experiments on controlled chemical reactions in the quantum regime.³ The hybrid systems of laser-cooled trapped ions combined with ultracold atoms in a single experimental setup have also recently become a new platform for investigating quantum matter.⁴ Polyatomic molecules and molecular ions have additional rotational and vibrational degrees of freedom that could potentially be used for various applications,⁵ therefore the first experiments on the cooling of trapped polyatomic molecules have been launched.⁶⁻¹⁰

The hybrid systems of laser-cooled trapped ions immersed in ultracold atomic gases⁴ combine the best features of two wellestablished fields of research: ultracold atoms² and trapped ions.¹¹ Their potential applications range from cold controlled ion–atom collisions and chemical reactions^{12–15} to quantum simulations of solid-state physics^{16,17} and quantum computations.¹⁸ Cold molecular ions can be formed from cold mixtures of atomic ions and atoms^{19–21} or they can be cooled down from room temperature using laser, buffer-gas, or sympathetic cooling.^{22–24} The potential applications of molecular ions include precision measurements,^{25,26} cold controlled chemistry,^{27,28} and novel quantum simulations.²⁹

Recently, the first experiments combining simple diatomic molecular ions with ultracold atoms have been launched. The dynamics of N_2^+ molecular cations immersed in ultracold Rb atoms³⁰ and BaCl⁺ cations immersed in ultracold Ca atoms^{22,24} was investigated. The collisions of OH⁻ molecular anions with ultracold Rb atoms were studied both experimentally^{31,32} and theoretically.³²⁻³⁶ The cooling of simple molecular ions such as MgH⁺, NH₂⁻, and OH⁻ immersed in cold buffer gases of helium or molecular hydrogen was also experimentally^{23,37-41} and theoretically⁴²⁻⁴⁴ investigated. Unfortunately, there is very little knowledge of cold and ultracold interactions, collisions, and reactions between polyatomic molecular ions and alkalimetal or alkaline-earth-metal atoms at the moment; hence the prospects for sympathetic cooling of polyatomic molecular ions down to low and ultralow temperatures are not known.

In the present work, we investigate the intermolecular interactions of several molecular anions $(OH^-, CN^-, NCO^-, C_2H^-, C_4H^-)$ with alkali-metal (Li, Na, K, Rb, Cs) and alkaline-earth-metal

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(Mg, Ca, Sr, Ba) atoms. We calculate and characterize the potential energy surfaces, long-range induction and dispersion interaction coefficients, and possible channels of chemical reactions and their control by using state-of-the-art ab initio techniques. Selected diatomic molecular anions are important in many areas of chemistry, whereas the considered polyatomic molecular anions are of great interest to astrochemistry.45 Surprisingly, a number of cations, but just a few anions, have been conclusively detected in the interstellar space. At the moment, six anions confirmed in the interstellar medium are CN⁻, C₄H⁻, C₆H⁻, C₈H⁻, C₃N⁻, and C₅N⁻.^{46,47} The NCO⁻ anion was also detected but is believed to be trapped in astronomical ices.48 The conditions in ultracold ion-atom experiments with alkali-metal and alkaline-earth-metal atoms are more extreme and unlike those that occur in the interstellar space. Nevertheless, precision spectroscopy of cold polyatomic molecular anions and investigations of their stability, properties of valence and dipole-bound excited states, as well as detailed studies of cold chemical reactions and their mechanisms can potentially shed new light on the chemistry of anions in the universe.⁴⁶

The selected molecular anions have a relativity simple, closed-shell electronic structure, large dipole moments, and high binding energies,⁴⁹ which makes them convenient candidates both for theoretical and experimental studies. These and other similar molecular ions were also already spectroscopically investigated in ion traps;⁵⁰ therefore the experimental realization of the considered hybrid systems should be feasible. The results for diatomic molecular anions can serve as a benchmark and reference for studies of polyatomic anions.

The plan of this paper is as follows. Section 2 describes the theoretical methods used in the *ab initio* electronic structure calculations. Section 3 presents and discusses the properties of considered molecular ions and atoms, the potential energy surfaces, and the leading long-range induction and dispersion interaction coefficients. The prospects for chemical reactions and their control are also analyzed. Section 4 summarizes our paper and presents future possible applications.

2 Computational details

The electronic ground state of the OH⁻, CN⁻, NCO⁻, C₂H⁻, and C₄H⁻ molecular anions is of the singlet ${}^{1}\Sigma^{+}$ symmetry; thus these ions are closed-shell and can be accurately described with *ab initio* electronic structure methods of quantum chemistry. The interaction between a closed-shell ${}^{1}\Sigma^{+}$ -state molecular anion and an open-shell ${}^{2}S$ -state alkali-metal atom (a closed-shell ${}^{1}S$ -state alkaline-earth-metal atom) results in one electronic state of the ${}^{2}A'$ (${}^{1}A'$) symmetry. In this paper, working within the Born–Oppenheimer approximation, we describe linear molecular anion and an atom. Therefore, the potential energy surfaces (PESs) are functions of two coordinates $V(R,\theta)$, where *R* is the distance between an atom and the center of mass of a molecular anion, and θ is the angle between the axis of a molecular anion

(oriented from a heavier atom to a lighter one) and the axis connecting an atom with the center of mass of a molecular anion (oriented from a molecular anion to an atom).

In order to obtain potential energy surfaces, we adopt the computational scheme successfully applied to the ground-state interactions between polar alkali-metal dimers,⁵¹ an ytterbium cation with a lithium atom,²⁰ a chromium atom with alkaline-earth-metal atoms,⁵² and a europium atom with alkali-metal and alkaline-earth-metal atoms.⁵³ Thus, to calculate PESs for anions interacting with alkaline-earth-metal atoms (alkali-metal atoms) we employ the closed-shell (spin-restricted open-shell) coupled cluster method restricted to single, double, and non-iterative triple excitations, starting from the restricted closed-shell (open-shell) Hartree–Fock orbitals, CCSD(T).^{54,55} The interaction energies are obtained with the supermolecule method and the basis set superposition error is corrected by using the counterpoise correction⁵⁶

$$Y_{\text{ion+atom}} = E_{\text{ion+atom}} - E_{\text{ion}} - E_{\text{atom}}, \qquad (1)$$

where $E_{\text{ion+atom}}$ denotes the total energy of a molecular ion interacting with an atom, and E_{ion} and E_{atom} are the total energies of a molecular ion and an atom computed in a dimer basis set.

The Li, Na, and Mg atoms are described with the augmented correlation-consistent polarized core-valence quadruple- ζ quality basis sets (aug-cc-pCVQZ),⁵⁷ whereas the H, C, N, and O atoms are described with the aug-cc-pVQZ^{58,59} basis sets in calculations of intermolecular interaction and with the aug-cc-pCV5Z basis sets58,59 in calculations of molecular properties. The scalar relativistic effects in the K, Rb, Cs, Ca, Sr and Ba atoms are included by employing the small-core relativistic energyconsistent pseudopotentials (ECP) to replace the inner-shells electrons.⁶⁰ The use of the pseudopotentials allows one to use larger basis sets to describe the valence electrons and models the inner-shell electron density as accurately as the high quality atomic calculation used to fit the pseudopotentials. The pseudopotentials from the Stuttgart library are employed in all calculations. The K, Ca, Rb, Sr, Cs, and Ba atoms are described with the ECP10MDF, ECP10MDF, ECP28MDF, ECP28MDF, ECP46MDF, and ECP46MDF pseudopotentials^{61,62} and the [11s11p5d3f], [12s12p7d4f2g], [14s14p7d6f1g], [14s11p6d5f4g], [12s11p6d4f2g], and [13s12p6d5f4g] basis sets, respectively, obtained by decontracting and augmenting the basis sets suggested in ref. 61 and 62. The used basis sets were optimized in ref. 52, 53, 63 and 64. The basis sets are additionally augmented in all calculations by the set of the [3s3p2d1f1g] bond functions.⁶⁵

The potential energy surfaces from the molecular body-fixed calculations $V(R,\theta)$ can be expanded into the basis of the Legendre polynomials $P_{\lambda}(\cdot)^{66}$

$$V(R,\theta) = \sum_{\lambda=0}^{\lambda_{\max}-1} V_{\lambda}(R) P_{\lambda}(\cos\theta).$$
(2)

Such a decomposition is especially convenient for coupled channel scattering calculations.⁶⁷ Here, we calculate the potential energy surfaces $V(R,\theta)$ on a two-dimensional grid consisting of around

25 points in the ion-atom distance *R* with values between around 2.5 Bohr and 30 Bohr and 12 points in the angle θ with values between 0 and 180 degrees chosen to be the quadratures for the Legendre polynomial of the order $\lambda_{\text{max}} = 12$. The Legendre components $V_{\lambda}(R)$ are obtained by integrating out *ab initio* points.

The intermolecular interaction energy between a linear closed-shell polar molecular ion and a S-state atom, both in the electronic ground state, at large intermolecular distances R, in the molecular frame, is of the form:⁶⁸

$$V(R,\theta) \approx -\frac{C_4^{\text{ind}}}{R^4} - \frac{C_{5,1}^{\text{ind}}}{R^5} \cos \theta - \frac{C_{6,0}^{\text{ind}}}{R^6} - \frac{C_{6,0}^{\text{disp}}}{R^6} - \frac{C_{6,0}^{\text{disp}}}{R^6} - \frac{C_{6,0}^{\text{disp}}}{R^6} + \frac{C_{6,2}^{\text{disp}}}{R^6} \right) P_2(\cos \theta) + \dots,$$
(3)

and the Legendre components of eqn (2) are:

$$V_{0}(R) \approx -\frac{C_{4}^{\text{ind}}}{R^{4}} - \frac{C_{6,0}^{\text{ind}}}{R^{6}} - \frac{C_{6,0}^{\text{disp}}}{R^{6}} + \dots$$

$$V_{1}(R) \approx -\frac{C_{5,1}^{\text{ind}}}{R^{5}} + \dots$$

$$V_{2}(R) \approx -\frac{C_{6,2}^{\text{ind}}}{R^{6}} - \frac{C_{6,2}^{\text{disp}}}{R^{6}} + \dots$$
(4)

Proper treatment of the interaction potential at large internuclear distances is especially important for ultracold collisions. Different V_{λ} terms govern inelastic rotational transitions, changing molecular rotation by $\Delta j = \pm \lambda$.

The leading long-range induction coefficients are

$$C_{4}^{\text{ind}} = \frac{1}{2}q^{2}\alpha_{\text{atom}},$$

$$C_{5,1}^{\text{ind}} = 2d_{\text{ion}}q\alpha_{\text{atom}},$$

$$C_{6,0}^{\text{ind}} = \frac{1}{2}q^{2}\beta_{\text{atom}} + d_{\text{ion}}^{2}\alpha_{\text{atom}},$$

$$C_{6,2}^{\text{ind}} = 2\Theta_{\text{ion}}q\alpha_{\text{atom}} + d_{\text{ion}}^{2}\alpha_{\text{atom}},$$
(5)

where *q* is the charge of the molecular ion, α_{atom} is the static electric dipole polarizability of the atom, d_{ion} is the permanent electric dipole moment of the molecular ion, Θ_{ion} is the permanent electric quadruple moment of the molecular ion, and β_{atom} is the static electric quadrupole polarizability of the atom. The leading long-range dispersion coefficients are:

$$C_{6,0}^{\text{disp}} = \frac{3}{\pi} \int_0^\infty \bar{\alpha}_{\text{ion}}(i\omega) \alpha_{\text{atom}}(i\omega) d\omega,$$

$$C_{6,2}^{\text{disp}} = \frac{1}{\pi} \int_0^\infty \Delta \alpha_{\text{ion}}(i\omega) \alpha_{\text{atom}}(i\omega) d\omega,$$
(6)

where $\alpha_{atom(ion)}(i\omega)$ is the dynamic polarizability of the atom(ion) at an imaginary frequency and the average polarizability and polarizability anisotropy are given by $\bar{\alpha} = (\alpha_{\parallel} + 2\alpha_{\perp})/3$ and $\Delta \alpha = \alpha_{\parallel} - \alpha_{\perp}$, respectively, with α_{\parallel} and α_{\perp} being the components of the polarizability tensor parallel and perpendicular to the internuclear axis of the molecular ion.

Eqn (3)–(6) result from the long-range multipole expansion of the intermolecular interaction energy within the perturbation theory, therefore different terms are given by electric properties of monomers.⁶⁸ The $-C_4^{\text{ind}}/R^4$ term describes the interaction between the charge of the molecular ion and the induced electric dipole moment of the atom. The $-C_{5,1}^{ind}/R^5 \cos \theta$ term describes the interaction between the permanent electric dipole moment of the molecular ion and the induced electric dipole moment of the atom. The first term in $-C_{6.0}^{\text{ind}}/R^6$ describes the interaction between the charge of the molecular ion and the induced electric quadruple moment of the atom, whereas the second one describes the interaction between the permanent electric dipole moment of the molecular ion and the higher-order induced electric dipole moment of the atom. The first term in $-C_{6,2}^{ind}/R^6$ describes the interaction between the permanent electric quadruple moment of the molecular ion and the induced electric dipole moment of the atom, and the second one is the same as in $-C_{60}^{ind}/R^6$. The dispersion terms result from the interaction between instantaneous dipoleinduced dipole moments of the molecular ion and atom arising due to quantum fluctuations.

The dynamic electric dipole polarizabilities at imaginary frequency $\alpha(i\omega)$ of alkali-metal and alkaline-earth-metal atoms are taken from ref. 69, whereas the dynamic polarizabilities of molecular anions are obtained by using the explicitly connected representation of the expectation value and polarization propagator within the coupled cluster method⁷⁰ and the best approximation proposed in ref. 71.

The static electric dipole and quadrupole polarizabilities of atoms and the permanent electric dipole and quadrupole moments of molecular anions are calculated with the CCSD(T) and finite field methods.

All electronic structure calculations are performed with the Molpro package of *ab initio* programs.⁷²

3 Numerical results and discussion

3.1 Properties of molecular anions and atoms

An accurate description of monomers and reproduction of their properties are essential for a proper evaluation of intermolecular interactions and chemical reactions. Therefore, in this subsection, we examine the electronic properties of the investigated molecular anions and atoms, which also define the long-range interaction coefficients crucial for cold physics and chemistry.

The *ab initio* description of anions is usually more challenging as compared to calculations involving cations. Specifically, such calculations require basis sets with diffuse functions to account for the expanded character of anionic valence and dipole-bound ground and excited electronic states.⁷³ Therefore, we use the augmented polarized basis sets of at least quadruple- ζ quality, which combined with relatively large binding energies of selected closed-shell molecular anions should provide accurate results.

Fig. 1 shows the equilibrium geometries of molecular anions calculated with the aug-cc-pCV5Z basis set. They agree very well with the experimental internuclear equilibrium distances of

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Fig. 1 The equilibrium geometries of molecular anions calculated with the CCSD(T) method and aug-cc-pCV5Z basis sets. Bond distances are in Bohr. The numerical uncertainty is ± 0.002 Bohr.

1.822 Bohr and 2.224 Bohr for OH^{-83} and $CN^{-,84}$ respectively, while the N–C and C–O experimental equilibrium distances in NCO⁻ are 2.211 Bohr and 2.381 Bohr.⁸⁴ The C–C and C–H experimental equilibrium distances in C_2H^{-} are 2.40 Bohr and 2.02 Bohr,⁸⁵ whereas no experimental data exists for C_4H^{-} .

Table 1 presents the permanent electric dipole moments, permanent electric quadrupole moments, parallel and perpendicular components of the static electric dipole polarizability, and vertical electron detachment energies of the investigated molecular anions calculated at the equilibrium geometries with two basis sets: aug-cc-pVQZ and aug-cc-pCV5Z. The former basis set is used in calculations of intermolecular interactions, whereas the latter one is the largest basis set, which can be used to obtain the molecular properties of the considered anions. The values obtained with these two basis sets agree with each other within 1-3%. This confirms that already the smaller basis set can provide an accurate description of the considered systems. The experimental molecular electron affinities determined by photoelectron spectroscopy are 14741.01(3) cm⁻¹, 31150(30) cm⁻¹, 29110(30) cm⁻¹, 23950(50) cm⁻¹, and 28700(120) cm⁻¹ for OH, CN, NCO, C₂H, and C₄H, respectively.⁷³ They agree with the calculated vertical electron detachment energies of the corresponding molecular anions within 63-1300 cm⁻¹ that correspond to an error of 0.4-4.4%. The calculated permanent electric dipole moments also agree with previous theoretical results within a few percent.^{86,87} The above agreement suggests

Table 1 Characteristics of molecular anions at the equilibrium geometry: permanent electric dipole moment d_{e} , permanent electric quadrupole moment Θ_{e} , parallel α_{e}^{\parallel} and perpendicular α_{e}^{\perp} components of the static electric dipole polarizability, and vertical electron detachment energy ED. The results for two basis sets are presented: A – aug-cc-pVQZ and B – aug-cc-pCV5Z

Ion	Set	$d_{\rm e}$ (D)	$\Theta_{\rm e}$ (a.u.)	$\alpha_{e}^{^{\parallel}} \ (a.u.)$	$\alpha_{e}^{\perp}~(a.u.)$	$ED(cm^{-1})$
OH-	А	1.08	3.03	22.0	30.1	14 505
	В	1.07	3.09	23.2	32.6	14678
CN^{-}	А	-0.652	-5.50	37.3	27.6	31 329
	В	-0.655	-5.48	37.2	27.7	31 543
NCO^{-}	А	-1.54	-12.8	44.8	24.7	30 452
	В	-1.52	-12.8	45.0	24.8	30718
C_2H^-	Α	3.22	-2.20	55.8	40.8	24478
	В	3.22	-2.18	55.5	41.0	24 587
C_4H^-	А	6.19	-18.5	117.0	46.7	29 892
	в	6.20	-18.4	116.6	46.9	30 0 26

that the employed method can correctly describe the considered anions.

Table 2 collects the static electric dipole and quadrupole polarizabilities, ionization potentials, electron affinities, and the lowest S-P excitation energies of alkali-metal and alkalineearth-metal atoms. The present theoretical values are compared with the most accurate available experimental or theoretical data. The calculated static electric dipole and quadrupole polarizabilities coincide with previous data within 0.1-5.7 a.u. and 9-314 a.u. that correspond to an error of 0.1-2.2% and 0.6-3.7%, respectively. The ionization potentials and the lowest S-P excitation energies agree with the experimental data within 23–255 cm^{-1} and 7–190 cm^{-1} that is 0.05–0.6% and 0.05-1%, respectively. The electron affinities of alkali-metal atoms coincide with the experimental data within 13–85 cm^{-1} (0.3-2%). The Mg⁻ anion is unstable and other alkaline-earthmetal anions are weakly bound,77 therefore calculations of electron affinities for alkaline-earth-metal atoms are less accurate. Nevertheless, the overal agreement between the calculated atomic properties and the most accurate available experimental or theoretical data is very good.

The overall high accuracy of the calculated properties of molecular anions and atoms confirms that the employed CCSD(T) method, basis sets, and energy-consistent pseudopotentials properly treat relativistic effects and reproduce correlation energy, while being close to converged in the size of the basis function set. Thus, the used methodology should also provide an accurate description of the intermolecular interactions and energetics of chemical reactions investigated in the next subsections. Based on the above and our previous experience, we estimate the total uncertainty of the calculated potential energy surfaces at the global minimum to be of the order of 200–500 cm⁻¹ that corresponds to 2–5% of the interaction energy. The uncertainty of the long-range interaction coefficients is of the same order of magnitude.

Table 2 Characteristics of alkali-metal and alkaline-earth-metal atoms: static electric dipole polarizability α , static electric quadrupole polarizability β , ionization potential IP, electron affinity EA, and the lowest S–P excitation energy ($^{2}S-^{2}P$ for alkali-metal atoms and $^{1}S-^{3}P$ for alkaline-earth-metal atoms). Present theoretical values are compared with the most accurate available experimental or theoretical data

Atom	α (a.u.)	β (a.u.)	$IP(cm^{-1})$	$EA(cm^{-1})$	S–P (cm^{-1})
Li	164.3	1414	43 464	4970	14 911
	164.2^{74}	1423^{75}	43487^{76}	4885^{77}	14904^{76}
Na	166.4	1920	41 217	4406	16799
	162.7^{78}	1895^{79}	41449^{76}	4419^{77}	16968^{76}
Κ	290.8	4970	34 949	4015	13 022
	290.0^{80}	4947 ⁷⁹	35010^{76}	4045^{77}	13024^{76}
Rb	319.5	6578	33 566	3887	12 686
	320.1^{80}	6491^{79}	33691^{76}	3919 ⁷⁷	12737^{76}
Cs	395.5	10343	31 331	3728	11594
	401.2^{80}	10470^{81}	31406^{76}	3804^{77}	11548^{76}
Mg	71.8	821	61 466	-1824	21 701
U	71.3^{82}	812^{82}	61671^{76}	$< 0^{77}$	21891^{76}
Ca	156.9	2946	49 243	-491	15 190
	157.1^{82}	3081^{82}	49306^{76}	198^{77}	15263^{76}
Sr	199.2	4551	45 814	-4.3	14639
	197.2^{82}	4630^{82}	45932^{76}	420^{77}	14705^{76}
Ва	276.8	8586	41780	580	13 106
	273.5^{82}	8900^{82}	42035^{76}	1166 ⁷⁷	13099^{76}

3.2 Potential energy surfaces

Fig. 2 and 3 present one-dimensional cuts through the groundstate potential energy surfaces at the linear arrangement of the CN^- , NCO^- , C_2H^- , and C_4H^- molecular anions interacting with the Li, Na, K, Rb and Cs alkali-metal and Mg, Ca, Sr and Ba alkaline-earth-metal atoms, respectively. For the NCO⁻, C_2H^- , and C_4H^- molecular anions, the presented minima are global. The equilibrium intermolecular distances R_e and well depths D_e corresponding to the presented arrangement and for the second linear geometry are collected in Table 3. The leading long-range induction and dispersion interaction coefficients are also reported in Table 3.

An inspection of the potential energy curves for different anions presented in Fig. 2 and 3 reveals remarkable similarities. All potential energy curves show a smooth behavior with welldefined minima. The pattern of shapes and relative positions of curves with different atoms at the linear geometry is very similar for all investigated anions. The similarity at large internuclear distances is not surprising since the leading long-range induction interactions are determined by the polarizability of atoms and the charge of anions. The similarity at small internuclear distances shows that all investigated anions behave similarly with regard to the short-range electrostatic and exchange interactions with alkali-metal and alkaline-earth-metal atoms. This observation suggests that, on one hand, the potential energy surfaces obtained for some anion-atom systems can be used to describe other anion-atom systems by proper scaling of energy and length, and on the other hand, the effective potential energy surfaces can be generated by combining the long-range multipole expansion of the intermolecular interaction energy with some short-range repulsion term intended to reproduce typical binding energies.

For all the investigated anion-atom systems, the equilibrium intermolecular distance increases with the mass of an atom (*e.g.* from 3.18 Bohr for $OH^- + Li$ to 4.40 Bohr for $OH^- + Ba$, and from 7.54 Bohr $C_4H^- + Li$ to 8.92 Bohr for $C_4H^- + Ba$). Instead, the well depth decreases with the mass of an atom for alkali-metal atoms and increases with the mass of an atom for alkaline-earth-metal atoms. The different trends for alkali-metal atoms as compared with alkaline-earth-metal atoms are typical for non-covalent interactions and were also observed for interactions of these atoms with chromium,^{52,88} europium,⁵³ and closed-shell^{89,90} atoms. It can be explained by the fact that the formal order of the chemical bond is equal to half for the complexes of closed-shell species with alkali-metal atoms and zero for the ones with alkaline-earth-metal atoms. For this reason the former ones are chemically bound whereas the latter



Fig. 2 One-dimensional cuts through the ground-state potential energy surfaces of molecular anions interacting with alkali-metal atoms at the linear arrangement.



Fig. 3 One-dimensional cuts through the ground-state potential energy surfaces of molecular anions interacting with alkaline-earth-metal atoms at the linear arrangement.

ones are stabilized by the induction and dispersion interactions only.

Among anion–alkali-metal-atom systems, the largest binding energy is for complexes with the lithium atom (the well depth is between 14 885 cm² for C₄H⁻ + Li and 23 917 cm² for OH⁻ + Li), while the binding energies for the complexes with other alkali-metal atoms are 30% smaller. Among anion– alkaline-earth-metal-atom systems, the largest binding energy is for the complexes with the barium atom (the well depth is between 15 049 cm² for C₄H⁻ + Ba and 27 552 cm² for OH⁻ + Ba) and the smallest binding energy is for the complexes with the magnesium atom (the well depth is between 9585 cm² for C₄H⁻ + Mg and 20 283 cm² for OH⁻ + Mg).

Fig. 4 presents the ground-state potential energy surfaces for the CN⁻, NCO⁻, C₂H⁻, and C₄H⁻ molecular anions interacting with the Rb atom. For the CN⁻ anion the global minimum is at the non-linear geometry ($R_e = 5.44$ Bohr, $\theta_e = 108^\circ$, $D_e = 9723$ cm⁻¹), whereas for other anions, the global minima are at the linear geometry in the configuration where the Rb atom approaches the molecular anion from its more charged side. The calculated potential energy surfaces have two minima for CN⁻ and one minimum for other anions and are strongly anisotropic with the anisotropy increasing with the size of the molecular anion. For the CN⁻ and OCN⁻ anions, the second anisotropic Legendre term is larger than the first one, $V_2(R) > V_1(R)$, which means that the potential energy surfaces are relatively symmetric with respect to exchange in the C and N or O and N atoms in the CN⁻ or OCN⁻ anions, respectively. For the C₂H⁻ anion, the first anisotropic Legendre term $V_1(R)$ is almost as large as the isotropic one $V_0(R)$, whereas for the C₄H⁻ anion the PES is heavily anisotropic with several anisotropic terms larger than the isotropic one. The large dipole moment, related to the localization of the charge on the ending carbon atom, and increasing size of the considered molecular anions are responsible for the observed large anisotropy. The topology of potential energy surfaces for the considered anions interacting with other alkali-metal and alkaline-earth-metal atoms is similar.

The potential energy surfaces were previously investigated for $OH^- + Rb^{33}$ and $CN^- + Rb/Sr^{29}$ anion-atom systems. The authors of the former reference used an approach similar to the present one and obtained very similar results, whereas the authors of the latter reference used larger basis sets but their results also agree within 0.5% of the present ones.

Unfortunately, at the moment, even the most accurate PESs do not allow one to predict accurately the scattering lengths for collisions between many-electron atoms and molecules. Nevertheless, the general characteristics of cold elastic and inelastic collisions, and thus the prospects for sympathetic cooling, can

Table 3 Characteristics of the potential energy surfaces for molecular anions interacting with alkali-metal and alkaline-earth-metal atoms, all in the electronic ground state: equilibrium intermolecular distance R_e and well depth D_e for the two linear geometries (C_{2v} symmetry) corresponding to global minimum, local minimum, or saddle point, and induction $C_{n,k}^{ind}$ and dispersion $C_{n,k}^{disp}$ coefficients describing the long-range part of the interaction. Long-range coefficients are in atomic units

System	$R_{\rm e}$ (Bohr)	$D_{\rm e} \left({\rm cm}^{-1} \right)$	R_{e}' (Bohr)	$D_{e}' (cm^{-1})$	C_4^{ind}	$C_{5,1}^{\mathrm{ind}}$	$C_{6,0}^{\mathrm{ind}}$	$C_{6,2}^{\mathrm{ind}}$	$C_{6,0}^{\mathrm{disp}}$	$C_{6,2}^{\mathrm{disp}}$
$OH^- + Li$	3.18	23 917	4.85	6672	82.1	-139	736	-987	387	-22.8
$OH^- + Na$	3.91	16700	5.44	5246	83.2	-141	990	-1000	426	-23.5
$OH^- + K$	4.44	16 693	5.86	6314	145.4	-246	2308	-1747	648	-38.1
$OH^- + Rb$	4.62	16 498	6.04	6377	159.8	-270	3346	-1919	721	-41.3
$OH^- + Cs$	4.82	17 138	6.24	6904	197.7	-334	5242	-2376	868	-49.6
$OH^- + Mg$	3.58	20 283	5.54	3792	35.9	-60.6	423	-431	312	-11.1
$OH^- + Ca$	3.98	25514	5.63	6833	78.5	-133	1501	-942	548	-24.0
$OH^{-} + Sr$	4.21	25458	5.79	7581	99.6	-168	2311	-1197	658	-29.7
$OH^{-} + Ba$	4.40	27 552	5.91	9246	138.4	-234	4342	-1663	832	-39.6
$CN^{-} + Li$	4.54	14 994	5.01	14224	82.1	84.6	718	1813	436	43.7
$CN^{-} + Na$	5.26	10 325	5.71	9960	83.2	85.7	971	1836	484	48.2
$CN^{-} + K$	5.90	10045	6.40	9540	145.4	150	2275	3208	732	72.7
$CN^{-} + Rb$	6.14	9625	6.66	9096	159.8	165	3310	3525	817	80.9
$CN^{-} + Cs$	6.42	9732	6.95	9150	197.7	204	5198	4363	985	97.2
$CN^{-} + Mg$	4.98	9793	5.49	8653	35.9	37.0	415	792	372	36.1
$CN^{-} + Ca$	5.41	13 920	5.93	12 571	78.5	80.8	1483	1731	641	62.8
$CN^{-} + Sr$	5.68	13 942	6.20	12 650	99.6	103	2289	2198	767	75.1
$CN^{-} + Ba$	5.91	15 281	6.43	14 038	138.4	143	4311	3054	965	94.6
$NCO^{-} + 1$	F 02	15.000	F 44	12.400	00.1	107	700	4050	170	104
NCO + LI	5.83	15 666	5.44	13 486	82.1	197	/66	4252	476	104
NCO + Na	6.55	10/02	6.18	8945	83.2	200	1020	4307	532	116
NCO + K	7.17	10 422	6.78	8965	145.4	349	2361	/526	804	1/4
NCO + RD	7.41	10 003	7.02	8622	159.8	384	3404	8269	901	194
NCO + CS	7.68	10 138	7.28	8/80	197.7	4/5	5314	10236	1087	233
NCO + Mg	6.25	10/33	5.90	8/2/	35.9	86.2	436	1858	418	88.0
NCO + Ca	6.6/	14 986	6.29	12 966	/8.5	188	1530	4061	/13	152
NCO + Sr	6.94	149/0	6.55	13 004	99.6	239	2347	5156	854	181
NCO + Ba	7.16	16352	6.79	14 231	138.4	332	4392	/164	10/3	228
$C_2H^- + Li$	5.05	17 041	6.69	2445	82.1	-417	971	982	621	68.3
$C_2H^- + Na$	5.74	12 158	7.38	1930	83.2	-422	1228	995	687	75.3
$C_2H^- + K$	6.42	11524	7.73	2740	145.4	-738	2724	1738	1039	114
$C_2H^- + Rb$	6.66	11047	7.95	2795	159.8	-810	3803	1910	1157	126
$C_2H^- + Cs$	6.94	11 143	8.19	3089	197.7	-1003	5808	2364	1392	152
$C_2H^- + Mg$	5.46	11 870	8.36	854	35.9	-182	526	429	516	56.0
$C_2H^- + Ca$	5.92	15 923	7.90	1892	78.5	-398	1725	938	896	97.5
$C_2H^- + Sr$	6.19	15 916	7.93	2357	99.6	-505	2596	1191	1074	117
$C_2H^- + Ba$	6.41	17 513	7.92	3314	138.4	-702	4738	1654	1353	147
$C_4H^- + Li$	7.54	14 885	11.24	473	82.1	-801	1684	7030	989	320
$C_4H^- + Na$	8.24	10332	11.46	465	83.2	-811	1949	7119	1096	351
$C_4H^- + K$	8.93	9825	11.09	791	145.4	-1418	3985	12442	1656	529
$C_4H^- + Rb$	9.19	9367	11.18	873	159.8	-1558	5188	13 670	1847	586
$C_4H^- + Cs$	9.47	9441	11.27	1066	197.7	-1929	7523	16922	2222	702
$C_4H^- + Mg$	7.98	9585	11.89	296	35.9	-350	837	3072	832	254
$C_4H^- + Ca$	8.43	13 536	12.16	481	78.5	-765	2406	6713	1439	447
$C_4H^- + Sr$	8.70	13 564	12.16	577	99.6	-971	3460	8523	1723	535
$C_4H^- + Ba$	8.92	15 049	11.96	769	138.4	-1350	5938	11 843	2169	676

be determined from scattering calculations by tuning the scattering lengths around values typical for ion–atom interactions and testing them against the uncertainty of PESs.^{20,91} Furthermore, in the future the presented PESs can be corrected using the scattering data from experiments, thereby allowing for fully quantitative predictions.

3.3 **Prospects for chemical reactions**

The prospects for sympathetic cooling and applications of molecular ions immersed into ultracold atomic gases can be jeopardized by possible chemical reactions, on one hand, however cold and controlled chemical reactions in these systems can be an interesting subject of study on its own, on the other hand.

In cold mixtures of molecular anions and atoms, several types of possible chemical reactions induced by intermolecular interactions or external fields during collisions can be envisioned.

(i) The spontaneous radiative charge transfer

$$A^{-} + M \rightarrow A + M^{-} + h\nu, \qquad (7)$$

where the electron is spontaneously transferred from a molecular anion A^- to an atom M emitting a photon of an energy $h\nu$.



Fig. 4 The ground-state potential energy surfaces for: (a) $CN^- + Rb$, (b) $NCO^- + Rb$, (c) $C_2H^- + Rb$, and (d) $C_4H^- + Rb$. Insets show the corresponding Legendre components.

This process is possible if the electron affinity (EA) of a neutral atom is larger than the electron detachment energy (ED) of a molecular anion. The electron detachment energy of a molecular anion is usually very close to the electron affinity of a corresponding neutral molecule. The energy of a produced photon is equal to the difference of the EA and ED energies.

The spontaneous non-radiative charge transfer is also possible for the same energetic conditions if the electronic states associated with $A^- + M$ and $A + M^-$ thresholds form an avoided crossing or conical intersection at short internuclear distances.

(ii) The spontaneous radiative association

$$A^{-} + M \rightarrow (MA)^{-} + h\nu, \qquad (8)$$

where a molecular anion A^- and an atom M spontaneously form an ionic complex (MA)⁻ emitting a photon with an energy $h\nu$. Such a process driven by the transition between two electronic states is possible when the reaction (i) is energetically allowed or when the interaction energy in a complex (MA)⁻ is greater or equal to the missing difference of the EA and ED energies. The spontaneous radiative association driven by the transition between rovibrational states of one electronic state is also possible (but very unlikely) for all polar complexes (MA)⁻. (iii) The photo-induced charge transfer

$$A^{-} + M + h\nu \rightarrow A^{-} + M^{*}(A^{*-} + M) \rightarrow A + M^{-},$$
 (9)

where the spontaneous radiative charge transfer is energetically not allowed and the missing energy is introduced by exiting a molecular anion A^- or an atom M with a laser field $h\nu$. A photon of smaller energy $h\nu' < h\nu$ can be produced in such a process, too. Once the charge transfer is photo-induced, the spontaneous radiative association (ii) is also possible.

(iv) The electron detachment association (associative electron detachment)

$$A^{-} + M \rightarrow MA + e^{-}, \qquad (10)$$

where a molecular anion A^- and an atom M form a neutral complex MA and at the same time the electron is detached from the system. Such a process is possible when the interaction energy in a neutral complex MA is greater or equal to the electron detachment energy of a molecular anion.

(v) The collision-induced isomerization

$$ABC^{-} + M \rightarrow ACB^{-} + M, \qquad (11)$$

where one metastable isomer of a molecular anion ABC⁻ is transformed into another isomer ACB⁻ as a result of a collision with an atom M. In such a scenario, the anion-atom interactions provide the energy needed to overcome the isomerization energy barrier, thus an atom serves as a catalyzer.

(vi) The proper chemical reaction with the rearrangement of atoms between reactants

$$AB^{-} + M \rightarrow A^{-} + MB(A + MB^{-}), \qquad (12)$$

where an atom B is transfered from a molecular anion AB⁻ to an atom M forming a neutral molecule MB or a molecular anion MB⁻. Such a process is possible when the dissociation energy of MB or MB⁻ is larger than the dissociation energy of AB⁻.

Processes (iv), (v), and (vi), if energetically forbidden, can also be photo-induced by exiting a molecular anion or an atom with a laser field.

For all investigated anion-atom systems, the spontaneous radiative and non-radiative charge transfer, reaction (i), is energetically not allowed because the electron detachment energy of the OH⁻, CN⁻, NCO⁻, C₂H⁻, and C₄H⁻ molecular anions (*cf.* Table 1) is much larger than the electron affinity of the Li, Na, K, Rb, Cs, Mg, Ca, Sr, and Ba atoms (*cf.* Table 2). The charge transfer reaction can be most easily photo-induced, reaction (iii), for collisions between the OH⁻ molecular anion and alkali-metal atoms. For these systems the lowest S–P excitation of alkali-metal atoms provides a sufficient amount of energy. For other anion-atom systems, higher excitation of atoms or anions is needed.

The above observed stability of molecular anions against spontaneous radiative charge transfer in collisions with alkalimetal and alkaline-earth-metal atoms is typical and should also be expected for other anions. In contrast, most molecular cations are expected to experience radiative-charge-transfer losses in collisions with alkalimetal and alkaline-earth-metal atoms because of the relatively low ionization energy of these atoms.²¹

The spontaneous radiative association, reaction (ii), is energetically allowed only for collisions between the OH⁻ molecular anion and alkali-metal atoms. This process was already investigated for OH⁻ + Rb both experimentally³¹ and theoretically.³⁵ For other investigated anion–atom systems the interaction energy (*cf.* Table 3) is not large enough to overcome the electron detachment energy of molecular anions (*cf.* Table 1). However, the lowest S–P excitation of alkali-metal and alkaline-earth-metal atoms provides a sufficient amount of energy to photo-induce reaction (ii) with the C₂H⁻ anion and for several other anion–atom systems.

The electron detachment association, reaction (iv), may be energetically allowed only for collisions between the OH⁻ molecular anion and alkali-metal atoms, because the electron detachment energy of other molecular anions is too large. This reaction can potentially be also photo-induced, however more detailed studies are needed for specific anion–atom systems.

The collision-induced isomerization, reaction (v), is feasible only for the NCO⁻ cyanate anion which can exist in a metastable isomeric form as the CNO⁻ fulminate anion.⁹² The activation energy (reaction barrier) for the CNO⁻ \rightarrow NCO⁻ isomerization is predicted to be around 16 000 cm^{-1 93,94} which is of the same order of magnitude as the interaction energy between the NCO⁻ anion and alkali-metal and alkaline-earthmetal atoms (*cf.* Table 3). Thus, the anion–atom interaction energy can potentially be sufficient to overcome the isomerization energy barrier, however more detailed studies are needed.

The proper chemical reactions with breaking and formation of bonds are not expected for collisions between the OH⁻, CN⁻, and NCO⁻ molecular anions and considered atoms, because these anions are strongly bound as compared to species consisting of alkali-metal or alkaline-earth-metal atoms with C, N, and H atoms. For example, the complete analysis of chemical reaction channels for the Rb + OH⁻ system is presented in ref. 35. For the C₂H⁻ and C₄H⁻ molecular anions, breaking the C-H bound, $C_nH^- \rightarrow C_n + H^-$ or $C_nH^- \rightarrow C_n^- + H$, should be the easiest. Unfortunately, the dissociation energies for these reactions are almost 60 000 cm^{-1} and 40 000 cm^{-1} (64 000 cm^{-1} and 70 000 cm⁻¹) for C_2H^- (C_4H^-), respectively, whereas the dissociation energies of neutral or anionic hydrides of alkali-metal and alkaline-earth-metal atoms do not exceed 30000 cm^{-1,95,96} Thus, the proper chemical reactions are also energetically not allowed for collisions between the C₂H⁻ and C₄H⁻ molecular anions and alkali-metal and alkaline-earth-metal atoms.

4 Summary and conclusions

After many spectacular successes in the field of ultracold atoms, the scientific community has drawn its attention to the research on ultracold molecules. Recently, ultracold gases of diatomic molecules have been produced and explored. The next emerging goal is the preparation of polyatomic molecules at ultralow temperatures and the first experiments have been launched. Molecular ions are easier to prepare, trap, and detect as compared to neutral molecules. They are also important in many areas of chemistry ranging from organic and inorganic chemistry to astrochemistry. Therefore polyatomic molecular ions are promising systems to start investigating cold polyatomic dynamics and chemical reactions at the quantum level.

Here, we have investigated the electronic structure and intermolecular interactions of several molecular anions (OH⁻, CN⁻, NCO⁻, C₂H⁻, C₄H⁻) with alkali-metal (Li, Na, K, Rb, Cs) and alkaline-earth-metal (Mg, Ca, Sr, Ba) atoms. We have calculated and characterized the potential energy surfaces, long-range induction and dispersion interaction coefficients, and possible channels of chemical reactions and their control by using state-of-the-art *ab initio* techniques: the coupled cluster method restricted to single, double, and noniterative triple excitations, CCSD(T), combined with large Gaussian basis sets and small-core energy-consistent pseudopotentials.

We have shown that most of the considered anion-atom systems are stable against chemical reactions and charge transfer processes, which however can be induced by exciting atoms or anions with the laser field. Thus, the present work opens up routes for collisional studies of linear polyatomic ions immersed in ultracold atomic gases and their applications in controlled chemistry, precision measurements, and quantum simulations.

The first experiments combining diatomic molecular ions with ultracold atoms have used a Paul trap to trap ions.^{22,30,31} This trapping technique is indispensably associated with the micromotion of ions induced by the rf field. In such a scenario, sympathetic cooling can be prevented and ion–atom collisions can lead to heating, *e.g.* if atoms are heavier than ions.⁹⁷ One can potentially avoid this kind of heating by using an optical dipole trap to trap ions, as it was demonstrated for atomic ions⁹⁸ and suggested for diatomic anions.⁹⁹ The possible detection schemes for molecular anions include laser-induced fluorescence or molecular-ion trap-depletion spectroscopy.¹⁰⁰ However, more detailed studies of both trapping and detection techniques are needed for the anions considered here and molecular ions in general.

The present study of the electronic structure is the first step towards the evaluation of prospects for sympathetic cooling and controlled chemistry of linear polyatomic anions with ultracold alkali-metal or alkaline-earth-metal atoms. This work also establishes the computational scheme for future *ab initio* investigations of intermolecular interactions in other polyatomic anion-atom systems relevant for ultracold physics or chemistry and can serve as the benchmark for investigations of more challenging polyatomic cation-atom systems. In the future, the obtained potential energy surfaces and long-range interaction coefficients will be employed in time-independent scattering calculations for both elastic and inelastic collisions at low and ultralow temperatures and their control with magnetic and laser fields.

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