Highly polar molecules consisting of a copper or silver atom interacting with an alkali-metal or alkaline-earth-metal atom

Michał Śmiałkowski\textsuperscript{1,2} and Michal Tomza\textsuperscript{1,*}
\textsuperscript{1}Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw, Poland
\textsuperscript{2}Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland
(Dated: December 10, 2020)

We theoretically investigate the properties of highly polar diatomic molecules containing \textsuperscript{2}S-state transition-metal atoms. We calculate potential energy curves, permanent electric dipole moments, spectroscopic constants, and leading long-range dispersion-interaction coefficients for molecules consisting of either a Cu or Ag atom interacting with an alkali-metal (Li, Na, K, Rb, Cs, Fr) or alkaline-earth-metal (Be, Mg, Ca, Sr, Ba, Ra) atom. We use \textit{ab initio} electronic structure methods, such as the coupled cluster and configuration interaction ones, with large Gaussian basis sets and small-core relativistic energy-consistent pseudopotentials. We predict that the studied molecules in the ground electronic state are strongly bound with highly polarized covalent or ionic bonds resulting in very large permanent electric dipole moments. We find that highly excited vibrational levels have maximal electric dipole moments, e.g., exceeding 13 debye for CsAg and 6 debye for BaAg. Results for Cu\textsubscript{2}, Ag\textsubscript{2}, and CuAg are also reported. The studied molecules may find application in ultracold dipolar many-body physics, controlled chemistry, or precision measurement experiments.

\section{I. INTRODUCTION}

Remarkable progress has been achieved in ultracold matter studies in the last decades. The advancement of cooling and trapping techniques has allowed reaching sub-millikelvin temperatures for gaseous ensembles of dozens of different kinds of atoms and simple molecules, finding application in fundamental research and emerging quantum technologies \cite{1,2,3}. Experiments with ultracold polar molecules reveal intriguing perspectives based on both complex internal molecular structure and intermolecular interactions \cite{4,5}. The rich internal structure can be employed in high-precision spectroscopic measurements to test fundamental physics, including searches for the electric dipole moment of the electron \cite{6} and spatiotemporal variation of fundamental constants such as the electron-to-proton mass ratio \cite{7,8} and the fine structure constant \cite{9}, as well as tests of the quantum electrodynamics, parity violation, Lorentz symmetry, and general relativity \cite{10}. Long-range and controllable intermolecular interactions between ultracold polar molecules allow studying ultracold chemistry, including quantum-controlled chemical reactions \cite{11,12,13}, and quantum many-body physics, including quantum simulation of quantum many-body Hamiltonians of increasing complexity \cite{14,15,16,17}.

Ultracold molecules can be produced either directly by laser cooling \cite{18}, buffer-gas \cite{19} or sympathetic \cite{20} cooling, Stark \cite{21} or Zeeman \cite{22} deceleration, or velocity filtering \cite{23} from higher temperatures, or indirectly by associating from ultracold atoms employing photoassociation \cite{24} or magnetoassociation \cite{25}. Atomic species selected for pre-cooling and subsequent molecule formation have mostly been either alkali or alkaline-earth metals due to their electronic structure favorable for laser cooling. However, atoms of other elements have also been successfully laser-cooled. Bose-Einstein condensates of highly magnetic lanthanide Dy \cite{26} and Er \cite{27} atoms, and transition-metal Cr \cite{28} atoms were obtained at ultralow temperatures and employed in ground-breaking experiment \cite{29,30,31}. Magneto-optical cooling and trapping of other highly magnetic atoms such as Eu \cite{32,33,34,35} and Ho \cite{36} were also realized. On the other hand, alkali-metal-like transition-metal Cu and Ag atoms were produced and trapped at ultralow temperatures using buffer-gas cooling and magnetic trapping \cite{37} or magneto-optical cooling and trapping \cite{38}. All those atoms are available for the formation of new ultracold molecules with desirable properties. However, only the magnetoassociation into ultracold Er\textsubscript{2} dimers \cite{39} and photoassociation into spin-polarized Cr\textsubscript{2} dimers \cite{40} were experimentally demonstrated, while several heteronuclear paramagnetic and polar molecules formed of atoms with large magnetic dipole moments, such as CrRb \cite{41}, CrSr and CrYb \cite{42}, ErLi \cite{43}, EuK, EuRb, and EuCs \cite{44}, ErYb \cite{45}, and DyYb \cite{46} were theoretically proposed and studied.

Here, we propose the formation of ultracold highly polar diatomic molecules containing a transition-metal copper or silver atom interacting with an alkali-metal or alkaline-earth-metal atom. While such molecules have the ground-state electronic structure similar to alkali-metal or alkali-metal–alkaline-earth-metal dimers, they have a richer structure of excited electronic states owing to the possibility of d-electron excitations. A greater variety of excited electronic states may be beneficial for precision measurements \cite{10}. Already, atomic clocks based on metastable states of Cu, Ag, and Au atoms were proposed for timekeeping and searching for new physics \cite{47}, and the \( ^2S_{1/2} \rightarrow ^2D_{5/2} \) clock transition in Ag was observed by two-photon laser spectroscopy \cite{48}. RaCu and RaAg molecules were also proposed for mea-
suring the electric dipole moment of the electron and the scalar-pseudoscalar interaction [49]. Additionally, Cu and Ag atoms have high electronegativity as compared with alkali-metal and alkali-earth-metal atoms, promising strong bonding and large permanent electric dipole moments of the considered molecules. While the interactions of Cu and Ag atoms with noble gases have been the subject of several experimental [50–53] and theoretical [54–56] studies and the structure of the Cu₂, CuAg and Ag₂ dimers have been actively explored [57–68], the interactions of Cu and Ag atoms with alkali-metal and alkali-earth-metal metal atoms (and corresponding diatomic molecules) have been investigated in spectroscopic experiments occasionally [69–74] and in theoretical calculations rarely [49, 75–78].

In this paper, to fill this gap and to extend the range of species available for ultracold studies, we theoretically investigate the ground-state properties of highly polar diatomic molecules consisting of either a Cu or Ag atom interacting with an alkali-metal (Li, Na, K, Rb, Cs, Fr) or alkaline-earth-metal (Be, Mg, Ca, Sr, Ba, Ra) atom. We employ state-of-the-art ab initio electronic structure methods, such as the coupled cluster and configuration interaction ones, with large Gaussian basis sets and small-core relativistic energy-consistent pseudopotentials to account for the scalar relativistic effects. We calculate potential energy curves, permanent electric dipole moments, spectroscopic constants, and leading long-range dispersion-interaction coefficients. We predict that the studied molecules in the ground electronic state are strongly bound with highly polarized covalent or ionic bonds resulting in significant permanent electric dipole moments, significantly larger than in alkali-metal molecules. We find that maximal electric dipole moments, exceeding 13 debye for CsAg and 6 debye for BaAg, are for highly excited vibrational levels. Results for Cu₂, Ag₂, and CuAg are also reported. We show that most of the investigated molecules in the ground state are stable against atom-exchange chemical reactions. Finally, we indicate their possible application in ultracold dipolar many-body physics, controlled chemistry, or precision measurement experiments.

The structure of the paper is the following. In Section II, we describe the employed computational methods. In Section III, we present and discuss the obtained results. In section IV, we provide a summary and outlook.

II. COMPUTATIONAL DETAILS

The interaction of an open-shell copper or silver atom in the ground doublet 2S electronic state with an openshell alkali-metal atom, AM, also in the lowest 2S state, results in the ground molecular electronic state of the singlet X1Σ⁺ symmetry and the first excited electronic state of the triplet a3Σ⁺ symmetry of a AMCu or AMAg molecule. The interaction of a copper or silver atom in the 2S electronic state with a closed-shell alkaline-earth-metal atom, AEM, in the lowest singlet 1S state, results in the ground molecular electronic state of the doublet X2Σ⁺ symmetry of a AEMCu or AEMAg molecule.

To calculate potential energy curves in the Born-Oppenheimer approximation, we adopt the computational scheme successfully applied to the ground electronic states of other diatomic molecules containing alkali-metal or alkali-earth-metal atoms [41, 43, 79–81]. The considered doublet X2Σ⁺ and triplet a3Σ⁺ molecular electronic states are well described at all internuclear distances by single-reference methods. Therefore, we compute them with the spin-restricted open-shell coupled cluster method restricted to single, double, and non-iterative triple excitations (RCCSD(T)) [82, 83]. On the other hand, the singlet X1Σ⁺ molecular electronic states of the AMCu and AMAg molecules have single-reference nature at smaller internuclear distances and multireference nature at larger distances. Therefore, we compute these electronic states with the RCCSD(T) method in the vicinity of the interaction potential well at short and intermediate distances and smoothly merge them with results obtained with the multireference configuration interaction method restricted to single and double excitations (MRCISD) [84] at larger distances.

The interaction energy, $E_{\text{int}}(R)$, at the internuclear distance $R$, is computed with the supermolecular method with the basis set superposition error corrected by using the Boys-Bernardi counterpoise correction [85]

$$E_{\text{int}}(R) = E_{AB}(R) - E_A(R) - E_B(R),$$

where $E_{AB}(R)$ is the total energy of the molecule $AB$, and $E_A(R)$ and $E_B(R)$ are the total energies of the atoms $A$ and $B$ computed in the diatom basis set, all at the distance $R$.

The Li, Be, Na, and Mg atoms are described with the augmented correlation-consistent polarized core-valence quintuple-ζ quality basis sets (aug-cc-pCV5Z) [86]. The scalar relativistic effects in heavier atoms are included by employing the small-core relativistic energy-consistent pseudopotentials (ECP) to replace the inner-shell electrons [87]. The pseudopotentials from the Stuttgart library are used in all calculations. The K, Ca, Rb, Sr, Cs, Ba, Fr, and Ra atoms are described with the ECP10MDF, ECP10MDF, ECP28MDF, ECP28MDF, ECP46MDF, ECP46MDF, ECP78MDF, and ECP78MDF pseudopotentials [88, 89], respectively, together with the aug-cc-pCV5Z basis sets designed for those ECPs [90]. The atomic basis sets are additionally augmented in all calculations by the set of the [3s3p2d2f1g] bond functions to accelerate the convergence towards the complete basis set limit [91].

The interaction potential between two neutral atoms in the electronic ground state is asymptotically dominated by the dispersion interaction of the form [92]

$$E_{\text{int}}(R) = \frac{C_6}{R^6} + \ldots,$$
where the leading $C_6$ coefficient is given by

$$C_6 = \frac{3}{\pi} \int_0^{\infty} \alpha_A(i\omega)\alpha_B(i\omega) d\omega,$$

where $\alpha_A(B)(i\omega)$ is the dynamic electric dipole polarizability of the $A(B)$ atom at the imaginary frequency $i\omega$. The dynamic polarizabilities at the imaginary frequency of the alkali-metal and alkaline-earth-metal atoms are taken from Ref. [93], whereas the dynamic polarizabilities of the Cu and Ag atoms are constructed as a sum over states using experimental energies [94] and transition dipole moments from Refs. [54, 95].

The permanent electric dipole moments and static electric dipole and quadrupole polarizabilities are calculated with the finite field approach using the RCCSD(T) method. The $z$ axis is chosen along the internuclear axis, oriented from the Cu or Ag atom to the alkali-metal or alkaline-earth-metal atom.

All electronic structure calculations are performed with the Molpro package of ab initio programs [96, 97]. Vibrational eigenenergies and eigenstates are calculated using numerically exact diagonalization of the Hamiltonian for the nuclear motion within the discrete variable representation (DVR) on the non-equidistant grid [98]. Atomic masses of the most abundant isotopes are assumed.

III. RESULTS AND DISCUSSION

A. Atomic properties

An accurate description of atoms is essential for a proper evaluation of interatomic interactions. Therefore, to determine the ability of the employed ab initio approaches to produce accurate results, we examine the electronic properties of investigated atoms, which also decide the long-range interaction coefficients crucial for ultracold physics and chemistry.

Table I collects the static electric dipole and quadrupole polarizabilities, ionization potentials, and the lowest $S-P$ excitation energies of the alkali-metal, alkaline-earth-metal, Cu, and Ag atoms. Present theoretical values are compared with the most accurate available experimental or theoretical data. It confirms that the employed CCSD(T) method, basis sets, and energy-consistent pseudopotentials properly treat the relativistic effects and reproduce the correlation energy while being close to being converged in the size of the basis function set. Thus, the used methodology should also provide an accurate description of interatomic interactions and molecular properties investigated in the next subsections. Based on the above and our previous experience [81], we estimate the total uncertainty of the calculated ground-state $X^1\Sigma^+$ and $X^2\Sigma^+$ potential energy curves at the equilibrium distance to be of the order of 250-600 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. The relative uncertainty of the weakly bound $a^3\Sigma^+$ potential energy curves is ex-
pected to be a bit larger.

## B. Potential energy curves

The computed potential energy curves of the $X^1\Sigma^+$ symmetry for the $AM\text{Ag}$ and $AM\text{Cu}$ molecules, the $a^3\Sigma^+$ symmetry for the $AM\text{Ag}$ and $AM\text{Cu}$ molecules, and the $X^2\Sigma^+$ symmetry for the $AEM\text{Ag}$ and $AEM\text{Cu}$ molecules are presented in Fig. I. Calculations are performed for all alkali-metal ($AM=$Li, Na, K, Rb, Cs, Fr) and alkaline-earth-metal ($AEM=$Be, Mg, Ca, Sr, Ba, Ra) atoms. The corresponding long-range dispersion-interaction $C_6$ coefficients and spectroscopic characteristics such as the equilibrium interatomic distance $R_e$, well depth $D_e$, harmonic constant $\omega_e$, rotational constant $B_e$, and number of vibrational levels $N_v$ (for $j = 0$) are collected in Table II.

All potential energy curves presented in Fig. I show a smooth behavior with well-defined minima. Surprisingly, the potential energy curves for the $AM\text{Ag}$ and $AM\text{Cu}$ molecules exhibit very similar shapes with similar equilibrium interatomic distances and well depths, which do not depend significantly on involved alkali-metal atoms (contrary to properties of alkali-metal dimers [79, 111–113]). This suggests that the nature of their chemical bonds is mostly determined by the properties of the Ag and Cu atoms.

The $AM\text{Ag}$ and $AM\text{Cu}$ molecules in the ground $X^1\Sigma^+$ electronic state are the most strongly bound with the well depths between 12700 cm$^{-1}$ for FrAg and 15592 cm$^{-1}$ for LiAg among the $AM\text{Ag}$ molecules, and between 12685 cm$^{-1}$ for FrCu and 15959 cm$^{-1}$ for LiCu among the $AM\text{Cu}$ molecules. The LiAg and LiCu molecules clearly exhibit the strongest chemical bonds in both groups, with well depths over 20% larger than their analogs, which in turn do not differ by more than 5%. Their equilibrium distances systematically increase with increasing the atomic number of the alkali-metal atom and take values between 4.46 bohr for LiAg and 6.19 bohr for FrAg among the $AM\text{Ag}$ molecules and between 4.26 bohr for LiCu and 5.96 bohr for FrCu among the $AM\text{Cu}$ molecules. The number of vibrational levels is between 63 for LiCu or LiAg and 219 for FrAg among the molecules in the $X^1\Sigma^+$ state.

The $AM\text{Ag}$ and $AM\text{Cu}$ molecules in the first-excited $a^3\Sigma^+$ electronic state are weakly bound van der Waals complexes with the well depths between 168 cm$^{-1}$ for NaAg and 202 cm$^{-1}$ for LiAg and CuAg among the $AM\text{Ag}$ molecules, and between 147 cm$^{-1}$ for NaCu and 179 cm$^{-1}$ for LiCu among the $AM\text{Cu}$ molecules. Their equilibrium distances systematically increase with increasing the atomic number of the alkali-metal atom and take values between 7.65 bohr for LiAg and 9.45 bohr for FrAg among the $AM\text{Ag}$ molecules and between 7.63 bohr for LiCu and 9.58 bohr for FrCu among the $AM\text{Cu}$ molecules. The number of vibrational levels is between 11 for LiCu and 41 for FrAg among the molecules in the $a^3\Sigma^+$ state.

The $AM\text{Ag}$ and $AM\text{Cu}$ molecules in the ground $X^1\Sigma^+$ electronic state are significantly more strongly bound than analogous alkali-metal molecules [113], while the $AM\text{Ag}$ and $AM\text{Cu}$ molecules in the ground $a^3\Sigma^+$ electronic state are slightly less bound than analogous alkali-metal molecules [79]. All studied $AM\text{Ag}$ and $AM\text{Cu}$ molecules have shorter equilibrium distances than the corresponding homo- or heteronuclear alkali-metal dimers in respective electronic states.

The $AEM\text{Ag}$ and $AEM\text{Cu}$ molecules in the ground $X^2\Sigma^+$ electronic state are strongly bound with the well depths between 5995 cm$^{-1}$ for MgAg and 11822 cm$^{-1}$ for BaAg among the $AEM\text{Ag}$ molecules, and between 6527 cm$^{-1}$ for MgCu and 12437 cm$^{-1}$ for BaCu among the $AEM\text{Cu}$ molecules. The potential energy curves for the $AEM\text{Ag}$ and $AEM\text{Cu}$ molecules present a greater variety of well depths than the $AM\text{Ag}$ and $AM\text{Cu}$ ones. Their equilibrium distances, shorter than for other molecules, systematically increase with increasing the atomic number of the alkaline-earth-metal atom and take values between 4.11 bohr for BeAg and 5.96 bohr for RaAg among the $AEM\text{Ag}$ molecules and between 3.92 bohr for BeCu and 5.70 bohr for RaCu among the $AEM\text{Cu}$ molecules. The number of vibrational levels is between 34 for BeAg and 164 for BaAg among the molecules in the $X^2\Sigma^+$ state. The $AEM\text{Ag}$ and $AEM\text{Cu}$ molecules in the ground $X^2\Sigma^+$ electronic state are significantly more strongly bound with shorter equilibrium distances than analogous alkali-metal–alkaline-earth-metal molecules [114].

Among the investigated molecules, only a few have already been studied experimentally using photoionization spectroscopy [69–73]. For LiAg, the equilibrium distance of 4.55 bohr, the potential well depth of 15413(30) cm$^{-1}$, and the harmonic constant of 389.0 cm$^{-1}$ were measured [71, 73] in good agreement with the present values of 4.46 bohr, 15592 cm$^{-1}$, and 389.7 cm$^{-1}$, respectively. For LiCu, the equilibrium distance of 4.27 bohr, the potential well depth of 15961(12) cm$^{-1}$, and the harmonic constant of 465.9 cm$^{-1}$ were measured [73, 74] in good agreement with the present values of 4.26 bohr, 15959 cm$^{-1}$, and 399.1 cm$^{-1}$, respectively. For NaAg, the potential well depth of at least 12932 cm$^{-1}$ and the harmonic constant of 210 cm$^{-1}$ were measured [72] in good agreement with the present values of 13040 cm$^{-1}$ and 212.6 cm$^{-1}$, respectively. The overall agreement with the spectroscopic studies confirms that similar high accuracy of present calculations may be expected for other molecules. The present theoretical results agree much better with the experimental measurements than previous calculations [75–78], which underestimated well depths and overestimated equilibrium distances because they employed smaller basis sets and lower-level methods.

The large binding energies and short equilibrium distances of the investigated molecules in their ground electronic states indicate the highly polarized covalent or
even ionic nature of their chemical bonds \([71–73]\) and significant stabilizing contribution of the electrostatic and induction interactions. The large difference of the electronegativity of the Ag or Cu atoms and the alkali-metal or alkaline-earth-metal atoms is responsible for a significant bond polarization and considerable contribution of the AM\(^+\)Ag\(^-\), AEM\(^+\)Ag\(^-\), AM\(^+\)Cu\(^-\), and AEM\(^+\)Cu\(^-\) ionic configurations to their ground state bonds \([115]\). The electronegativity of the Ag and Cu atoms is twice larger than that of the alkali-metal and alkaline-earth-metal atoms. Phenomenological models based on the difference of the electronegativities imply the ionic character of about 20–30% for the investigated molecules, except ones involving the lightest alkaline-earth-metal
| Molecule | $R_e$ (bohr) | $D_e$ (cm$^{-1}$) | $\omega_e$ (cm$^{-1}$) | $B_e$ (cm$^{-1}$) | $d_e$ (D) | $d_e/d_{max}$ | $\alpha_e^\parallel$ (a.u.) | $\alpha_e^\perp$ (a.u.) | $N_v$ | $C_6$ (a.u.) |
|----------|-------------|------------------|----------------------|------------------|---------|-------------|----------------------|----------------------|------|------------|
| LiAg     | 7.649       | 202              | 34.7                 | 0.1563           | 0.077   | 0.0040      | 334.2                | 185.9                | 12   | 567        |
| NaAg     | 8.427       | 168              | 19.8                 | 0.0448           | 0.126   | 0.0059      | 401.9                | 269.2                | 18   | 611        |
| KAg      | 8.886       | 192              | 16.8                 | 0.0267           | 0.149   | 0.0066      | 458.6                | 302.9                | 25   | 937        |
| RbAg     | 9.121       | 192              | 13.9                 | 0.0153           | 0.148   | 0.0064      | 517.5                | 357.9                | 32   | 1031       |
| CsAg     | 9.362       | 202              | 11.6                 | 0.0116           | 0.130   | 0.0055      | 584.5                | 399.7                | 38   | 1234       |
| FrAg     | 9.451       | 193              | 10.5                 | 0.0093           | 0.130   | 0.0054      | 612.8                | 342.8                | 41   | 1116       |
| LiCu     | 7.634       | 179              | 32.8                 | 0.1637           | 0.017   | 0.0009      | 303.9                | 172.2                | 11   | 523        |
| NaCu     | 8.453       | 147              | 19.7                 | 0.0500           | 0.071   | 0.0033      | 385.3                | 255.7                | 16   | 564        |
| KCu      | 8.973       | 162              | 16.6                 | 0.0311           | 0.067   | 0.0029      | 429.3                | 297.5                | 21   | 864        |
| RbCu     | 9.228       | 161              | 13.3                 | 0.0196           | 0.063   | 0.0027      | 487.9                | 351.4                | 26   | 950        |
| CsCu     | 9.491       | 166              | 12.2                 | 0.0156           | 0.037   | 0.0015      | 550.4                | 389.0                | 30   | 1138       |
| FrCu     | 9.579       | 159              | 11.5                 | 0.0134           | 0.049   | 0.0020      | 469.4                | 339.1                | 31   | 1030       |
| Cu$_2$   | 5.082       | 548              | 70.7                 | 0.0741           | 0       | 0           | 176.8                | 83.1                 | 29   | 221        |
| AgCu     | 5.566       | 447              | 47.5                 | 0.0490           | 0.028   | 0.0050      | 174.2                | 82.3                 | 32   | 239        |
| Ag$_2$   | 5.937       | 459              | 38.0                 | 0.0319           | 0       | 0           | 173.9                | 80.5                 | 38   | 258        |
| BeAg     | 4.109       | 7722             | 438.9                | 0.4290           | -0.71   | 0.068       | 131.7                | 64.1                 | 37   | 231        |
| MgAg     | 4.829       | 5995             | 230.0                | 0.1318           | 1.09    | 0.089       | 177.3                | 92.8                 | 56   | 400        |
| CaAg     | 5.292       | 9300             | 179.0                | 0.0739           | 2.62    | 0.195       | 213.6                | 163.4                | 94   | 737        |
| SrAg     | 5.568       | 9586             | 132.1                | 0.0402           | 3.57    | 0.253       | 258.2                | 238.1                | 128  | 889        |
| BaAg     | 5.769       | 11822            | 114.4                | 0.0300           | 4.52    | 0.309       | 290.6                | 292.3                | 169  | 1136       |
| RaAg     | 5.959       | 9563             | 100.0                | 0.0234           | 5.08    | 0.336       | 293.9                | 297.3                | 164  | 1053       |
| BeCu     | 3.916       | 9108             | 505.9                | 0.4978           | -0.81   | 0.081       | 118.5                | 59.5                 | 38   | 214        |
| MgCu     | 4.606       | 6527             | 252.0                | 0.1634           | 0.94    | 0.080       | 157.4                | 84.3                 | 54   | 371        |
| CaCu     | 5.054       | 9796             | 197.2                | 0.0964           | 2.32    | 0.180       | 183.8                | 157.2                | 88   | 681        |
| SrCu     | 5.328       | 10006            | 153.0                | 0.0578           | 3.25    | 0.240       | 226.6                | 236.1                | 115  | 821        |
| BaCu     | 5.484       | 12437            | 137.1                | 0.0463           | 4.01    | 0.288       | 277.2                | 295.4                | 148  | 1049       |
| RaCu     | 5.700       | 9946             | 121.6                | 0.0376           | 4.65    | 0.321       | 275.9                | 299.4                | 138  | 972        |
Additional, our comparative multireference configurations 
for AgCu) electronic states. Corresponding potential energy curves are presented in Fig. 2 and spectroscopic characteristics are collected in Table II. The Cu2, Ag2, and AgCu dimers exhibit short, strong molecular bonding in the $X^1\Sigma^+$ state and weak van der Waals bonding in the $a^3\Sigma^+$ state, similarly to the AEMAg and AEMCu molecules. However, while the electrostatic and induction interactions dominantly stabilize the AEMAg and AEMCu molecules in the $X^1\Sigma^+$ state, the correlation of electrons from the $d$ orbitals of Cu and Ag atoms stabilizes the Cu2, Ag2 and AgCu molecules in the ground state [58].

The calculated well depths of 16329 cm$^{-1}$, 13902 cm$^{-1}$, and 15048 cm$^{-1}$, for Cu2, Ag2, and AgCu, agree well with experimental measurements of 16760(200) cm$^{-1}$ [61], 13403(250) cm$^{-1}$ [66], and 14149(800) cm$^{-1}$ [64], respectively. Similarly, the calculated harmonic constants of 253.9 cm$^{-1}$, 188.2 cm$^{-1}$, and 234.0 cm$^{-1}$, for Cu2, Ag2, and AgCu, agree well with experimental values of 266.4(6) cm$^{-1}$ [61], 192.4 cm$^{-1}$ [57], and 229.2(3) cm$^{-1}$ [64], respectively. Such a good agreement additionally validates the accuracy of the present results, which, also in the case of the dimers of noble-metal atoms, are much more accurate than previous calculations [59, 60, 67, 68].

C. Permanent electric dipole moments

Permanent electric dipole moments as functions of the interatomic distance for the AEMAg and AEMCu molecules in the $X^1\Sigma^+$ electronic states, the AEMAg and AEMCu molecules in the $a^3\Sigma^+$ electronic states, and the AEMAg and AEMCu molecules in the $X^2\Sigma^+$ electronic states are presented in Fig. 3. The corresponding values for equilibrium distances are collected in Table II.

The AEMAg and AEMCu molecules in the $X^1\Sigma^+$ electronic state have the largest permanent electric dipole moments ranging from 5.05 debye for LiCu to 9.75 debye for CsAg at the equilibrium distances and more for larger internuclear separations. To our best knowledge, these are one of the highest values predicted for neutral metal dimers, comparable to AMAu molecules [116]. These values are also significantly larger than values for corresponding alkali-metal molecules, with the maximum value of 5.5 debye for LiCs [111].

The AEMAg and AEMCu molecules in the $a^3\Sigma^+$ electronic state have the smallest permanent electric dipole moments ranging from 0.017 debye for CsAg to 0.13 debye for CsAg at the equilibrium distances and a bit more for larger internuclear separations. These values are smaller or comparable to values for corresponding alkali-metal molecules [79].

The AEMAg and AEMCu molecules in the $X^2\Sigma^+$ electronic state exhibit intermediate permanent electric dipole moments ranging from -0.81 debye for BeCu to 5.08 debye for RaAg at the equilibrium distances and more for larger internuclear separations. These values are similar or larger than values for corresponding alkali-
metal–alkaline-earth-metal molecules [114].

The observed very large permanent electric dipole moments of the investigated ground-state molecules are directly related to the highly polarized covalent or even ionic nature of their chemical bonds, discussed in the previous subsection. The observed trends agree with the differences in atomic electronegativity. Permanent electric dipole moments are larger for the molecules based on the alkali-metal atoms than those based on the alkaline-earth-metal atoms. They are also slightly larger for the molecules based on the Ag atom than those based on the Cu atom. Finally, for all the molecules, they systemat-
The long-range dipolar interaction,

\[ E_{dd}(R, \theta) = \frac{d^2(1 - \cos^2 \theta)}{R^3}, \quad (5) \]

between the polarized CsAg molecules with the largest dipole moment of \( d = 13.5 \text{ debye} \) will be as large as 28 kHz at \( R = 1 \mu\text{m} \) or 220 Hz at \( R = 5 \mu\text{m} \). If molecules are not polarized by an external electric field, then in their ground rotational states, their interaction is dominated by the effective isotropic term \(-C^\text{rot}_6/R^6\), resulting from the dipolar interaction in the second-order of perturbation theory and given by the long-range coefficient

\[ C^\text{rot}_6 = \frac{d^4}{6B_v}, \quad (6) \]

where \( B_v \) is the rotational constant for \( v \) vibrational state. For the CsAg molecules, this coefficient exceeds \( 10^9 \), which is two-to-three orders of magnitude larger than for alkali-metal dimers [117].

For the completeness of the analysis, we also calculate the perpendicular \( \alpha^\perp \) and parallel \( \alpha^\parallel \) components of the
static electric dipole polarizability tensor, which are important for the evaluation of intermolecular interactions and interactions with external electric or laser fields [112]. We report their values at the equilibrium distance, $\alpha_{\perp}$ and $\alpha_{\parallel}$, in Table II. Interestingly, both components for the $AMAg$ and $AMCu$ molecules in the $X^1\Sigma^+$ electronic state are smaller than the asymptotic sum of atomic values, $\alpha_{AM} + \alpha_{Ag(Cu)}$, because the strong decrease of the atomic polarizability of $AM^+$ is not compensated by the increase of the atomic polarizability of Ag$^-$ or Cu$^-$, as compared to $AM$ and Ag or Cu, again in agreement with the ionic nature of those molecules. This effect is not pronounced in the $AEMAg$ and $AEMCu$ molecules, as expected for more covalent $AB$ metal dimers, where $\alpha_{\perp} < \alpha_A + \alpha_B$ and $\alpha_{\parallel} > \alpha_A + \alpha_B$ [112]. The isotropic, $\bar{\alpha}=(2\alpha_{\perp}+\alpha_{\parallel})/3$, and anisotropic, $\Delta\alpha=\alpha_{\parallel}-\alpha_{\perp}$, components can also be obtained from $\alpha_{\perp}$ and $\alpha_{\parallel}$.

D. Chemical reactions

The calculated potential well depths, $D_v$, and related dissociation energies, $D_0 \approx D_v - \frac{1}{2}\omega_i$, may be used to assess the stability of the studied molecules against chemical reactions. In general, atom-exchange chemical reactions between ground-state heteronuclear molecules $AB$ [79, 81, 113]

$$AB + AB \rightarrow A_2 + B_2$$  \hspace{1cm} (7)

are energetically possible if the sum of the dissociation energies of $A_2$ and $B_2$ products is larger or equal to the sum of the dissociation energies of reactants $AB$

$$D_0(A_2) + D_0(B_2) \geq 2D_0(AB).$$  \hspace{1cm} (8)

Among the species investigated in this paper, the $AMAg$ and $AMCu$ molecules in the rovibrational ground state of the $X^1\Sigma^+$ electronic state are chemically stable against atom-exchange reactions for all alkali-metal atoms, e.g.,

$$2AMAg(X^1\Sigma^+) \not\rightarrow Ag_2(X^1\Sigma^+) + AM_2(X^1\Sigma^+).$$  \hspace{1cm} (9)

The $AMAg$ and $AMCu$ molecules in the weakly bound $a^3\Sigma^+$ electronic state, are reactive for all alkali-metal atoms, leading to $Ag_2$, $Cu_2$, and alkali-metal dimers in the $X^1\Sigma^+$ or $a^1\Sigma^+$ electronic state, e.g.,

$$2AMAg(a^3\Sigma^+) \rightarrow Ag_2(X^1\Sigma^+) + AM_2(X^1\Sigma^+),$$
$$2AMAg(a^3\Sigma^+) \rightarrow Ag_2(X^1\Sigma^+) + AM_2(a^3\Sigma^+),$$
$$2AMAg(a^3\Sigma^+) \rightarrow Ag_2(a^3\Sigma^+) + AM_2(X^1\Sigma^+),$$
$$2AMAg(a^3\Sigma^+) \rightarrow Ag_2(a^3\Sigma^+) + AM_2(a^3\Sigma^+).$$  \hspace{1cm} (10)

Additionally, for those molecules, the spin relaxation reactions are possible

$$2AMAg(a^3\Sigma^+) \rightarrow AMAg(X^1\Sigma^+) + AMAg(a^3\Sigma^+),$$
$$2AMAg(a^3\Sigma^+) \rightarrow 2AMAg(X^1\Sigma^+).$$  \hspace{1cm} (11)

The $AEMAg$ and $AEMCu$ molecules in the rovibrational ground state of the $X^2\Sigma^+$ electronic state are chemically stable against atom-exchange reactions for all alkaline-earth-metal atoms except MgAg and MgCu. For this two molecules, the following atom-exchange reaction is possible

$$2MgAg(X^2\Sigma^+) \rightarrow Ag_2(X^1\Sigma^+) + Mg_2(X^1\Sigma^+).$$  \hspace{1cm} (12)

Except for the atom-exchange formation, the trimers formation may be another path of chemical losses [79, 113]

$$AB + AB \rightarrow A_2B + B,$$  \hspace{1cm} (13)

which is energetically possible if the dissociation energy of a $A_2B$ trimer product is larger or equal to the sum of the dissociation energies of reactants $AB$

$$D_0(A_2B) \geq 2D_0(AB).$$  \hspace{1cm} (14)

However, three-body calculations for trimers containing Cu or Ag atoms are out of the scope of this paper.

The above-considered reactions, which are energetically forbidden in the lowest vibrational state ($v=0$), may be induced by the preparation or laser-field excitation of involved molecules to higher vibration levels.

IV. SUMMARY AND CONCLUSIONS

Ultracold gases of polar molecules, due to their rich and controllable internal molecular structure and intermolecular interactions, are excellent systems for experiments on precision measurements, quantum simulations of many-body physics, and controlled chemistry. Therefore, in this paper, we have proposed the formation and application of ultracold highly polar diatomic molecules containing a transition-metal copper or silver atom interacting with an alkali-metal or alkaline-earth-metal atom. To this end, we have employed state-of-the-art ab initio electronic structure methods to study their ground-state properties in a comparative way. We have calculated potential energy curves, permanent electric dipole moments, spectroscopic constants, and leading long-range dispersion-interaction coefficients [118].

We have predicted that the studied molecules in the ground electronic state are strongly bound with highly polarized covalent or ionic bonds resulting in significant permanent electric dipole moments, significantly larger than in alkali-metal molecules. We have found that maximal electric dipole moments, exceeding 13 debye for CsCu and 6 debye for BaAg, are for highly excited vibrational levels. To our best knowledge, these values are one of the highest predicted for neutral metal molecules. We have also shown that most of the investigated molecules in the ground state are stable against atom-exchange chemical reactions.

The above peculiar properties of the studied highly polar molecules open the way for their application in
ultracold physics and chemistry experiments. The extremely large permanent electric dipole moments combined with large reduced masses and small rotational constants for heavier molecules facilitate their orientation, alignment, and manipulation with external electric fields, on the one hand, and enhance intermolecular dipolar interactions, on the other hand. Thus, the studied molecules may be used in precision measurement of the electric dipole moment of the electron and the scalar-pseudoscalar interaction, as proposed for the RaCu and RaAg molecules [49]. They may also be employed in quantum simulations of strongly interacting dipolar quantum many-body systems, where significant intermolecular interactions may be expected already at lower densities or between distant sites of an optical lattice or between optical tweezers. Finally, they may be exploited in quantum-controlled chemical reactions manipulated with external electric fields and vibrational excitations.

The investigated molecules can be formed in the same manner as the alkali-metal and alkali-metal–alkaline-earth-metal molecules, i.e., by using the magnetoassociation within the vicinity of the Feshbach resonance [25] followed by the stimulated Raman adiabatic passage (STIRAP) [24]. A detailed analysis of their formation is out of the scope of this paper, but to facilitate their experimental realization and application, the excited molecular electronic states, photoassociation spectra, and specific laser-control schemes should be studied in the future.

ACKNOWLEDGMENTS

We would like to thank Tatiana Korona for useful discussions. Financial support from the National Science Centre Poland (Grants No. 2015/19/D/ST4/02173 and No. 2016/23/B/ST4/03231) and the Foundation for Polish Science within the First Team program co-financed by the European Union under the European Regional Development Fund is gratefully acknowledged. The computational part of this research has been partially supported by the PL-Grid Infrastructure.
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