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Comment on “The diatomic dication CuZn^{2+} in the gas phase” [J. Chem. Phys. 135, 034306 (2011)]

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Recently, Diez *et al.* reported the observation of the novel gas-phase diatomic dication CuZn^{2+} using mass spectrometry.¹ They also studied some low-lying electronic states of the neutral CuZn molecule and its mono- and dication using density functional theory (DFT), obtaining spectroscopic constants (R_e , D_e , ω_e) of all three species and adiabatic ionization energies for CuZn and CuZn^+ . The highlights of their combined theoretical and experimental work were: (i) They have provided experimental proof of existence of long-lived metastable CuZn^{2+} in the gas phase. (ii) Their DFT calculations found the ionization energy of CuZn^+ (with respect to the $^2\Sigma^+$ electronic ground state of CuZn^{2+}) to be very similar to the first ionization energy of Ar, which seemed to provide theoretical support for the suggested dication formation mechanism described by $\text{CuZn}^+ + \text{Ar}^+ \rightarrow \text{CuZn}^{2+} + \text{Ar}$.¹

However, there is a problem, because the calculated dissociation energy for the $^2\Sigma^+$ electronic ground state of CuZn^{2+} , that the authors of Ref. 1 had suggested to be involved in the above gas-phase collision process, was found to be essentially zero. This conclusion cannot be correct, since it is in conflict with the above experimental finding (i).¹ Therefore, more accurate calculations are clearly needed to clarify the dissociation energy and stability of CuZn^{2+} in the gas phase and the assignments of Ref. 1.

In this Comment we present new high-level *ab initio* results for CuZn^{n+} ($n = 0, 1, 2$) and compare them with the above-mentioned DFT results. In the present calculations, the coupled cluster (CC) approach with a perturbative estimate of triple excitation (RCCSD(T))^{2,3} was employed. The generally contracted correlation-consistent basis set of quintuple- ζ quality by Balabanov and Peterson,⁴ known as aug-cc-pV5Z-DK, was used for both atoms. The scalar relativistic effects for low-lying states of CuZn^{n+} ($n = 0, 1, 2$) were determined using the fifth order Douglas-Kroll-Hess (DK) method.^{5,6} All these calculations were carried out with the MOLPRO 2010.1 suite of programs.⁷ The spectroscopic parameters for all the electronic states were derived numerically from our potentials using the Numerov-Cooley procedure.⁸ The T1 diagnostic was used to determine whether

the electron correlation calculation from a single-reference wavefunction is appropriate.^{9,10} Values of T1 greater than 0.02 indicate that electron correlation effects should be calculated from a multi-reference wavefunction.

The first and second ionization energies for the Cu and Zn atoms were calculated at the RCCSD(T)+DK/aug-cc-pV5Z-DK level of theory. They amount to 7.71 eV and 20.27 eV for Cu and to 9.39 eV and 17.93 eV for Zn, respectively, in very good agreement with experimental data, see Ref. 1. For the Ar atom, we obtained a ionization energy of 15.77 eV, which is also very close to the experimental value of 15.76 eV, see also Ref. 1.

We note that for both molecular ions the T1 diagnostic is lower than 0.02 for all states considered except for the $^3\Sigma^+$ state of CuZn^+ , suggesting that the RCCSD level of theory should perform reasonably well. The $^3\Sigma^+$ state has a strong multi-reference character (T1 = 0.06) and therefore its CC spectroscopic constants are not included in the Table I.

Table I contains a comparison of the RCCSD results for different electronic states of CuZn^{n+} ($n = 0, 1, 2$) with those based on the previous DFT calculations.¹ It is shown from this table that the energy ordering of the two lowest electronic states of neutral CuZn calculated using the RCCSD(T) method is the same as that obtained with the DFT procedure. However, the $^2\Delta$ state is higher in energy than the three quartet states $^4\Pi$, $^4\Sigma^+$, and $^4\Delta$. For the monocation, the RCCSD(T) method predicts the $^3\Delta$ and $^3\Pi$ states to be very close in energy ($\Delta E_{\text{CC}} = 0.003$ eV). Their relative ordering is reversed with respect to previous DFT calculations. In the case of CuZn^{2+} , the RCCSD method predicts the $^2\Sigma^+$ to be repulsive. A similar result was obtained using DFT in Ref. 1, but the inclusion of spin-orbit corrections to the DFT scheme seemed to predict a very shallow minimum. At the RCCSD(T) level of theory, the $^2\Delta$ metastable state is very slightly lower in energy ($\Delta E_{\text{CC}} = 0.007$ eV) than the $^2\Pi$ metastable state, see Fig. 1, which is the opposite result to the DFT finding.

The present results clarify, in contrast to the previous conclusion of Ref. 1, that the $^2\Sigma^+$ electronic ground state of CuZn^{2+} is repulsive and, thus, cannot participate into dication formation. The other two doublet, metastable excited states of CuZn^{2+} , that is, $^2\Delta$ and $^2\Pi$, are very close in energy according to present RCCSD(T) results and are

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TABLE I. Spectroscopic constants of the low-lying electronic states of CuZn^{n+} ($n = 0, 1, 2$) obtained at the RCCSD(T)+DK/aug-cc-pV5Z-DK level of theory. Equilibrium bond distances (R_e in Å), harmonic frequencies (ω_e in cm^{-1}), anharmonicity corrections ($\omega_e x_e$ in cm^{-1}), rotational constants (B_e in cm^{-1}), vibrational-rotational coupling constants ($\alpha_e \times 10^3$ in cm^{-1}), dissociation energies (D_0 in eV), energy separations (T_0 in eV), and adiabatic ionization energies (IE in eV). Results from Ref. 1 are labeled PBE/TZ2P NR and PBE/TZ2P SO-NC.

Species	State	Method	R_e	ω_e	$\omega_e x_e$	B_e	$\alpha_e \times 10^3$	D_0	T_0	IE
CuZn	$X^2\Sigma^+$	Present work	2.367	184	1.95	0.095	0.98	0.53	0.0	
		PBE/TZ2P NR	2.39	186				0.72		
		PBE/TZ2P SO-NC	2.36	195				0.76		
	$^2\Pi$	Present work	2.207	272	1.14	0.109	0.59	2.40	2.00	
		PBE/TZ2P NR	2.18	300				2.65		
	$^4\Pi$	Present work	2.351	231	0.88	0.096	0.49	1.25	4.30	
	$^4\Sigma^+$	Present work	2.377	225	0.69	0.094	0.48	1.23	4.32	
	$^4\Delta$	Present work	2.383	225	0.71	0.094	0.45	1.33	4.46	
	$^2\Delta$	Present work	2.277	233	1.24	0.102	0.67	1.64	5.81	
PBE/TZ2P NR		2.16	300				1.65			
CuZn ⁺	$X^1\Sigma^+$	Present work	2.301	223	1.09	0.100	0.68	1.83	0.0	6.53
		PBE/TZ2P NR	2.29	236				2.17		6.83
		PBE/TZ2P SO-NC	2.28	237				2.25		7.01
	$^3\Sigma^+$	PBE/TZ2P NR	2.73	99				1.17		
	$^3\Delta$	Present work	2.545	174	0.91	0.082	0.48	1.63	3.04	
		PBE/TZ2P NR	2.59	157				1.45		
	$^3\Pi$	Present work	2.573	172	0.87	0.080	0.45	1.64	3.046	
PBE/TZ2P NR		2.61	156				1.72			
CuZn ²⁺	$^2\Sigma^+$	Present work	Repulsive							
	$^2\Sigma^+$	PBE/TZ2P NR	Repulsive							
	$^2\Sigma^+$	PBE/TZ2P SO-NC	2.72	70				...		15.75
	$^2\Delta$	Present work	2.438	212	1.10	0.089	0.52	0.65 ^a		16.66
		PBE/TZTP NR	2.54	204				0.53 ^a		17.80
	$^2\Pi$	Present work	2.465	210	1.10	0.087	0.49	0.64 ^a	0.01	16.67
PBE/TZ2P NR		2.56	203				0.52 ^a		17.53	

^aDissociation energy with respect to the top of the barrier.

separated by 0.27 eV according to the DFT results of Ref. 1. Thus, considering those doublet states in the calculation of the ionization energy of CuZn^+ , a shift to higher values is observed. The RCCSD(T) approach predicts ionization energies of 16.66 eV and 16.67 eV for $^2\Delta$ and $^2\Pi$, respectively. DFT, on the other hand, predicts ionization energies of 17.53 eV and 17.80 eV for $^2\Delta$ and $^2\Pi$, respectively. We then note differences of about 0.9 eV and 1.77 eV between the calculated values of the first ionization energy of CuZn^+ (with respect to the excited states of CuZn^{2+}) and the first ionization energy of Ar, at the RCCSD(T) and DFT levels of theory, respectively. The former, more accurate RCCSD(T) value is

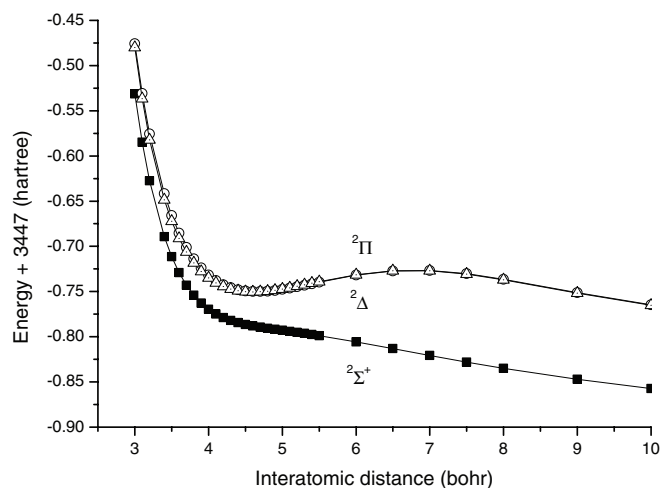


FIG. 1. RCCSD(T)+DK/aug-cc-pV5Z-DK potential energy curves of three low-lying states of CuZn^{2+} .

not necessarily in conflict with the dication formation mechanism suggested in Ref. 1. It is very likely that the sputtering of a brass surface with a 8-keV Ar^+ ion beam¹ not only produces emission of CuZn^+ in its ro-vibrational ground state but also generates a wide distribution of internally excited (hot) sputtered molecules.¹¹ In this way, the proposed formation mechanism of CuZn^{2+} seems to be supported by the existence of two excited metastable states of CuZn^{2+} according to the RCCSD(T) method.

In summary, it was wrong in Ref. 1 to suggest that the ground state of CuZn^{2+} had been detected in the experiment. To the contrary, based on our new RCCSD(T) calculations, we now conclude instead that the ground state is unstable and that two excited metastable states of CuZn^{2+} had been observed in the experiment, but their ionization energies had been previously overestimated by the DFT calculations.

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