



# Theoretical investigation of the long-lived metastable $\text{AlO}^{2+}$ dication in gas phase



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## ABSTRACT

We report the results of a detailed theoretical study of the electronic ground and excited states of the gas-phase doubly charged ion  $\text{AlO}^{2+}$  using high-level ab initio computer calculations. Both standard and explicitly correlated methods were used to calculate their potential energy curves and spectroscopic parameters. These computations show that the ground state of  $\text{AlO}^{2+}$  is  $X^2\Pi$ . The internuclear equilibrium distance of  $\text{AlO}^{2+}(X^2\Pi)$  is computed 1.725 Å. We also deduced the adiabatic double ionization and charge stripping energies of  $\text{AlO}$  to be about 27.45 eV and 17.80 eV, respectively.

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## 1. Introduction

Aluminum oxide,  $\text{AlO}$ , and its ions are of interest to scientists in fields of plasmas, surface sputtering and solution, solid state, interstellar and atmospheric and environmental chemistry [1–5]. Obviously, deep characterization of neutral  $\text{AlO}$  and of its multi charged ions is necessary for a better understanding of its role and reactivity in these fields. For the neutral and singly charged  $\text{AlO}$  species, numerous studies, both theoretical and experimental, are available in the literature. They were treating these molecules in their electronic ground and excited states. They are detailed in our recent investigation of  $\text{AlO}$  and  $\text{AlO}^+$  [6]. For  $\text{AlO}^{2+}$  dication, reviews of the research on gas-phase diatomic dications have been provided by Mathur [7] and by Schröder and Schwarz [8] and more recently by Sabzyan et al. [9]. Briefly,  $\text{AlO}^{2+}$  was definitively identified as a metastable ion species in gas phase. It had been observed by Atom Probe Mass Spectrometry [10–17] and by Accelerator Mass Spectrometry [18–19]. More recently, Franzreb and Williams at Arizona State University used Secondary Ion Mass Spectrometry and detected in their mass spectra  $\text{AlO}^{2+}$  signal formed by sputtering of an aluminum metal sample by prolonged high-current energetic oxygen ion. This observation was briefly mentioned (experimental

data not shown) in the Supplementary Material of Ref. [20]. Some preliminary unpublished computations by Yáñez and co-workers [21] and by Kim [18] confirmed the metastability of this particular dication.

This work presents a detailed theoretical investigation of the electronic structure, spectroscopy and stability of  $\text{AlO}^{2+}$  in gas phase. We used both standard and explicitly correlated ab initio methodologies in conjunction with various basis sets to describe Al and O atoms. The explicitly correlated techniques are established to take into account large amount of electron correlation with reduced computation cost. First, we describe the benchmarks on the lowest electronic states of  $\text{AlO}^{2+}$ . Then, we provide a full set of the potential energy curves (PECs) of the electronic states of  $\text{AlO}^{2+}$  up to 6 eV above the ground state. Our calculations confirm the metastability of  $\text{AlO}^{2+}$  dication in gas phase where several potential wells along the internuclear separation are found. After nuclear motion treatment, a full set of accurate spectroscopic and thermodynamical data were deduced in order to be helpful for future practical characterization of this dication experimentally.

## 2. Methodologies

For electronic calculations, we used the MOLPRO (version 2012.1) [22] suite of programs. These computations are carried out in the  $C_{2v}$  point group where the  $B_1$  and  $B_2$  irreducible repre-

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representations are equivalently described. They are done using standard and explicitly correlated internally contracted multi-reference configuration interaction (MRCI) approach [23–25] and MRCI-F12 [26–28] subsequent to complete active space self-consistent field (CASSCF) [29,30] computations. Close to equilibrium, the wavefunctions of  $\text{AlO}^{2+}$  are mainly mono-configurational. Hence, additional standard (RCCSD(T) [31–33]) and explicitly correlated (RCCSD(T)-F12 [34–36]) Coupled Clusters computations with perturbative treatment of triple excitations, are performed.

Using the standard methods, the Al and O atoms were described using the aug-cc-pVXZ, aug-cc-pV(X+d)Z and the aug-cc-pVXZ-DK (X = T, Q, 5) basis sets [37–41]. The tight-d functions were added since they improve the description of this molecular system and hence its spectroscopic parameters. The aug-cc-pVXZ-DK basis sets were used to take into account relativistic corrections. Within the explicitly correlated treatments, we used the aug-cc-pVXZ in conjunction with the corresponding resolutions of the identity and density fitting functions as generated by MOLPRO [42–44] to treat the correlation energy of the valence electrons. Moreover, the ab initio energies for a specific method and a series of basis sets were extrapolated to the Complete Basis Set (CBS) limit for better accuracy. For that, we employed the mixed exponential/Gaussian formula of Peterson et al. [45]:

$$E_X = E_{\text{CBS}} + A \exp[-(X-1)] + B \exp[-(X-1)^2]$$

where X = 3, 4 and 5 and  $E_{\text{CBS}}$ , A and B were adjustable fitting parameters.

The configuration interaction computations started by complete active space self-consistent field (CASSCF) computations where the active space is constructed using the valence atomic orbitals of Al and O. All valence electrons were correlated. All electronic states having the same spin multiplicity were averaged together with equal weights. At the MRCI level, the active space was constructed after single and double excitations of all configurations of the CI expansion of the CASSCF wavefunctions. For instance, this results, for the doublet states of  $\text{AlO}^{2+}$ , in  $>2.5 \times 10^6$  ( $18.9 \times 10^6$ ) contracted (uncontracted) configuration state functions (CSFs) per  $C_{2v}$  symmetry to be treated. Afterwards, we evaluated the spin-orbit constants and integrals of the electronic states of  $\text{AlO}^{2+}$ . We followed the approach of Breit-Pauli [46] as implemented in MOLPRO. These computations are carried out at the CASSCF/MRCI/aug-cc-pVTZ level of theory, where the spin-orbit matrix elements have been calculated in Cartesian coordinates, using the CASSCF wavefunctions as the multi-electron basis for the two-step spin-orbit coupling calculations [47,48]. The spin-orbit results should be accurate to within 5%. Anyway, the spin-orbit effect in  $\text{AlO}^{2+}$  is relatively small (see below). This justifies the use of the  $\Lambda$ - $\Sigma$  formalism instead of the  $\Omega$  formalism for the treatment of this molecular species.

The PECs were incorporated later into variational and perturbative treatments of the nuclear motions using the Cooley approach [49]. The spectroscopic parameters are deduced using the derivatives at equilibrium and second order perturbation theory. The vibrational energies are obtained after variational resolution of the one-dimensional Schrödinger equation for the nuclear motion where all couplings were considered [50].

### 3. Characterization and spectroscopy of the electronic states of $\text{AlO}^{2+}$

For seven electrons isovalent diatomic molecules, the ordering of the lowest electronic states, and hence the nature of their electronic ground states, is not the same for all, where it can be a  ${}^2\Pi$  (e.g.  $\text{BeO}^+$  [51],  $\text{LiO}$  [52],  $\text{NaO}$  [53],  $\text{LiO}$  [54],  $\text{MgO}^+$  [55],  $\text{LiS}$  [52] and  $\text{NaS}$  [56]), a  ${}^2\Sigma^+$  (e.g.  $\text{KO}$  [57],  $\text{BN}^+$  [58] and  $\text{C}_2^+$  [59]) or a

${}^4\Sigma^-$  (e.g.  $\text{AlC}$  [60],  $\text{LiP}^-$  [52],  $\text{BC}$  [60]). Indeed, these three electronic states are lying close to each other. As widely discussed in the literature for the molecules given above, the origins of such electron state pattern change reside on the interplay between the dipole and quadrupole interactions, that stabilise the  ${}^2\Pi$  state, and the Pauli repulsion which is critical for the stabilisation of the  ${}^2\Sigma^+$  and  ${}^4\Sigma^-$  states. We started hence our investigations by performing a systematic study on the  ${}^2\Pi$ ,  ${}^4\Sigma^-$  and  ${}^2\Sigma^+$  states in order to establish the nature of the ground state of  $\text{AlO}^{2+}$ . The corresponding PECs and results are given in Fig. S1 of the Supplementary Material and Table 1, respectively. At all levels of theory, we found that the ground state is the  $X^2\Pi$  state, followed by the  $1^4\Sigma^-$  state and then by the  $1^2\Sigma^+$  state. The energy separation between these three electronic states depends on the electronic structure method and the basis set used (cf. Table 1). Nevertheless, the CBS values are almost coinciding, where the quartet and the doublet are located at  $\sim 0.25$  eV and  $\sim 0.55$  eV above  $\text{AlO}^{2+}(X^2\Pi)$ , respectively. The ground state of  $\text{AlO}^{2+}$  is obtained after removal of two electrons from the outermost  $2\pi$  and  $7\sigma$  molecular orbitals (MOs) of  $\text{AlO}$  (cf. Table 2 and Fig. 1). For  $1^4\Sigma^-$  and  $1^2\Sigma^+$ , they are formed after ejection of two electrons from the  $2\pi$  MO. Fig. 1 shows that these outermost MOs are non-bonding where the  $7\sigma$  MO is mainly located in Al and the  $2\pi$  MO is due to the lone pair of O. This results in the longer AlO distance in these electronic states compared to the neutral ( $R_e$  of  $\text{AlO}(X^2\Pi) = 1.6179$  Å [61]). Note that the wavefunctions of the  $X^2\Pi$  and  $1^4\Sigma^-$  states are described by a unique dominant determinant whereas the wavefunction of the  $1^2\Sigma^+$  is multiconfigurational in nature.

Fig. 2 depicts the evolution of the MRCI/aug-cc-pV5Z potential energy curves of the electronic states of  $\text{AlO}^{2+}$  along the internuclear distance (R). Here, we computed two  $\Sigma^+$ , one  $\Sigma^-$ , four  $\Pi$  and two  $\Delta$  doublet states; three  $\Sigma^-$  and two  $\Pi$  quartet states; one  $\Sigma^-$  and one  $\Pi$  sextet states. Table 2 lists their dominant electronic configurations quoted at  $R = 1.733$  Å together with the leading CI coefficients of the corresponding CASSCF wavefunction. These electronic states correlate adiabatically to the  $\text{Al}^+({}^1S) + \text{O}^+({}^4S)$ ,  $\text{Al}^+({}^1S) + \text{O}^+({}^2D)$ ,  $\text{Al}^+({}^3P) + \text{O}^+({}^4S)$ ,  $\text{Al}^+({}^1S) + \text{O}^+({}^2P)$  charge separation channels and to  $\text{Al}^{2+}({}^2S) + \text{O}({}^3P)$  and  $\text{Al}^{2+}({}^2S) + \text{O}({}^1D)$  charge retaining dissociation limits (cf. Fig. S2 of the Supplementary material). The energy position of the lowest asymptote,  $\text{Al}^+({}^1S) + \text{O}^+({}^4S)$ , is deduced from RCCSD(T)/aug-cc-pV5Z + BSSE (Basis Set Superposition Error) calculations on the separated fragments. The BSSE is evaluated as the total electronic energies difference of the diatom and the fragments where all energies are computed in the full basis set of the diatom. The higher limits were located using the experimental excitation energies and ionization energies of  $\text{Al}^+$ ,  $\text{Al}^{2+}$ , O and  $\text{O}^+$  as taken from [62]. We computed also those of the  $\text{Al}^+({}^1S) + \text{O}^+({}^2D)$ ,  $\text{Al}^{2+}({}^2S) + \text{O}({}^3P)$  and  $\text{Al}^{2+}({}^2S) + \text{O}({}^1D)$  channels. The results are listed in Table S1 of the Supplementary material. The comparison to the experimental energies shows  $\sim 0.2$  eV differences between the ab initio and the experimental determinations.

The shape of the ground potential is not conventional: For  $R < 15.5$  bohr, it has a Morse like potential. For  $R > 15.5$  bohr, it exhibits a  $1/R$  evolution till reaching the charge separation  $\text{Al}^+({}^1S) + \text{O}^+({}^2D)$  dissociation limit. This shape is due to an avoided crossing between the ground state and the upper  ${}^2\Pi$  state that occurs for  $R \sim 15.5$  bohr (Fig. 3). Indeed, the two lowest  ${}^2\Pi$  states correlate to the charge separation limit  $\text{Al}^+({}^1S) + \text{O}^+({}^2D)$  or to the covalent  $\text{Al}^{2+}({}^2S) + \text{O}({}^3P)$  charge retaining channel. The former provides the  $1/R$  shape because of coulombic repulsion between the two positive charges whereas the latter leads to the Morse like covalent potential. Such potential shape was already described for  $\text{MgO}^{2+}$  [63], for  $\text{GaF}^{2+}$  [64] and more recently for  $\text{VO}^{2+}$  [65].

At the MRCI/aug-cc-pV5Z level, we compute a potential well depth of  $\sim 2$  eV for the ground state of  $\text{AlO}^{2+}$ . This potential well

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