Theor Chem Acc (2011) 129:401–407
DOI 10.1007/s00214-010-0863-y

REGULAR ARTICLE

On the stability and lifetime of GaO^{2+} in the gas phase

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Received: 5 October 2010 / Accepted: 19 November 2010 / Published online: 12 December 2010

Abstract The electronic structure, stability, and lifetime of GaO^{2+} have been investigated using high-level ab initio calculations. The potential energy curves have been calculated at the CCSD(T)/aug-cc-pV5Z and at the MS-CASPT2/ANO-RCC levels of theory. Lifetimes were evaluated using the Exterior Complex Scaling (ECS) method and B-spline basis functions. Our calculations show that GaO^{2+} is a metastable species in the gas phase, since the diatomic dication, in its ground state, lies 97.1 kcal/mol above the Ga^+ (^1S) + O^+ (^4S) dissociation limit. However, the energy barrier that has to be overcome to reach this limit is 3 kcal/mol high so that five vibrational resonances can be accommodated between the bottom of the well and the top of the barrier. The evaluated lifetimes vary from hundreds of femtoseconds to approximately 1 s, so at least two of them have long enough lifetimes (1 s and 91 μs) to be detected using mass spectrometry techniques, in agreement with the experimental evidence. In the experiment (Fiser et al. in Eur J Mass Spectrom 15:315–324, 2009), GaO^{2+} was observed for an ion flight time of about $\sim$12 μs through a magnetic-sector mass spectrometer and unambiguously identified by its isotopic abundance. Our results also show that isotopic effects on the resonances' energies and on their lifetimes, when ^{70}Ga is replaced by ^{69}Ga or ^{71}Ga, are very small ($\sim$0.1 and $\sim$1%, respectively), reflecting the large mass of the system.

Keywords Doubly charged species · Lifetimes · Ab initio calculations · Coulomb explosion · GaO · Gas phase

1 Introduction

Elusive chemical species constitute a particularly attractive ensemble within the vast universe of chemical compounds, as they usually represent a challenge as far as their synthesis and/or their detection and characterization are concerned. Not surprising, the existence of many of these species was proposed based on theoretical calculations. One paradigmatic example is oxywater (H_2OO), whose existence was suggested in 1955 on the basis of isotope-labeled experiments [1]. Many years later Pople and coworkers pointed out, based on MP4 calculations, that oxywater was a shallow minimum on the potential energy surface [2]. New high-level ab inito calculations concluded, some years later, that the activation barrier connecting hydrogen peroxide and oxywater was as high as 3.3 kcal mol^{-1} and that oxywater should be amenable to synthesis [3]. Little later, Schröder et al. proved the existence of this molecule by means of neutralization-reionization mass spectrometric experiments [4]. Many other systems were also proposed by means of theoretical calculations prior to their synthesis or their detection, and in this respect, the work carried out by Pyykkö was particularly relevant. He predicted, for instance, the existence of $AuXe^+$ and $XeAuXe^+$ in 1995 [5], and both species were observed experimentally by mass spectrometry techniques 3 years later [6]. Previously, he had predicted also the stability of exotic species like FCF^{2+},

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This paper is dedicated to Prof. Pekka Pyykkö on the occasion of his 70 birthday and published as part of the Pyykkö Festschrift Issue.

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FNF^{3+} or OOO^{2+}, or SBeNe, $SBNe^{+}$, $SCNe^{2+}$, and $SNNe^{3+}$ [5, 7].

Among elusive systems, doubly or multiply charged species are particularly interesting, because they are usually metastable with respect to their Coulomb explosion. As a matter of fact, the stability of some polyatomic doubly charged species was not free of controversy. This has been, for instance, the case of $M(L)^{2+}$ complexes, where M is a transition metal dication and L a polyatomic base. The existence of $[NH_3Cu]^{2+}$ and $[H_2OCu]^{2+}$ was predicted on theoretical grounds [8], but refuted based on experiments carried out on $[Cu(H_2O)_n]^{2+}$ and $[Cu(NH_3)_n]^{2+}$ clusters [9], although little later both complexes were experimentally detected by means of mass spectrometry techniques [10], and their lifetimes evaluated [11]. Similarly, the complexes between He^{2+} and HCN and HNC have been found to be metastable with respect to the loss of H^{+}, but with huge lifetimes for resonances below $\upsilon = 3$ [12]. The situation is simpler when dealing with diatomic dications $[AB]^{2+}$, because only one Coulomb explosion is possible. Besides an $[AB]^{2+}$ species can be thermodynamically stable if the lowest dissociation asymptote corresponds to $A^{2+} + B$ (or $A + B^{2+}$), that is if the ionization energy (IE) of A^{+} is smaller than the IE of B, or vice versa, if the IE of B^{+} is smaller than that of A [13]. However, most of the $[AB]^{2+}$ dications do not fulfill the aforementioned conditions and they dissociate into the two monocations [13]. This renders the synthesis and detection of these species a real challenge. It is true that some of these thermodynamically unstable dications can be kinetically metastable if the barrier between $[AB]^{2+}$ and the singly charged products of the Coulomb explosion, $A^{+} + B^{+}$, is large enough as to ensure the existence of some vibrational resonances below the top of the barrier [11–13]. However, this does not warrant that they can be detected, because this would be only possible if their lifetimes are longer or similar to the response time of the experimental technique.

Recently, Franzreb and coworkers have produced a number of doubly charged diatomic systems by means of ion beam sputtering techniques [14, 15]. Among the reported species, many are oxygen-containing dications (GaO^{2+}, BeO^{2+}, AsO^{2+}, SbO^{2+}, AgO^{2+}, and CrO^{2+}), which were produced by prolonged high-current $^{16}O^{-}$ ion surface bombardment [16], but very few (for example, BeO^{2+}[16]) were studied from the theoretical viewpoint. The aim of this paper is to investigate through the use of high-level ab initio techniques the electronic structure, stability, and lifetime of GaO^{2+}. This is a particularly interesting case, because it has been detected and unambiguously identified [16] using the aforementioned ion beam sputtering techniques, but not when other techniques such as Atom Probe Field-Ion Microscopy were used [17].

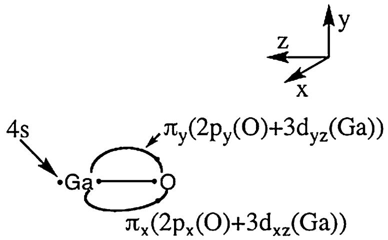
2 Computational details

2.1 Potential energy curves of GaO^{2+}

The potential energy curves for the dissociation of the GaO^{2+} dication were obtained at full coupled cluster level of theory with single and double excitations perturbatively corrected for triple excitations CCSD(T) [18, 19] in conjunction with the correlation consistent basis sets of Dunning: aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z [20, 21].

The reliability of the monoconfigurational CC protocol for the calculation of the coulomb explosion $Ga^{+} + O^{+}$ curve was evaluated using the complete active space self-consistent field (CASSCF) approach [22] followed by a multistate second-order perturbation treatment (MS-CASPT2) [23] to account for dynamical correlation. This level of theory was also employed for the calculation of the dissociation profile corresponding to the first excited state of the same multiplicity of the ground state.

Multiconfigurational calculations were performed using the relativistic and core correlated atomic natural orbital basis set ANO-RCC contracted to Ga [6s5p3d2f1g]/O [4s3p2d1f] [24]. The active space of the CASSCF wavefunction consists of 17 electrons and 13 orbitals (17, 13). This active space was initially designed to include the valence space of Ga (4s, 3d, and 4p orbitals) and O (2s and 2p orbitals). However, at distances $R_{Ga–O} \leq 2.4$ Å, a more stable wavefunction is obtained from the exchange of the $3d_{x^2-y^2}$(Ga), $3d_{xz}$(Ga), $3d_{yz}$(Ga), $2p_x$(O), and $2p_y$(O) orbitals of the active space for the following orbitals oriented in the direction of the Ga–O bond: 1s(O), 3s(Ga), $3p_z$(Ga), 3s(O), and $3p_z$(O) (The orientation of the atomic orbitals is defined in Scheme 1). In an attempt to find a unique active space valid for the whole range of internuclear distances, the new active space (17,15), containing the 13 orbitals of the (17,13) active space in addition to the 3s and $3p_z$ orbitals from the oxygen, was considered for the calculation of GaO^{2+} dissociation curves. However, the increase in two orders of magnitude in the number of configuration state functions added to problems with the convergence of the wavefunction prevented us from using such a large



Scheme 1

active space. Taking into account the too large (ca. 2) or too low (ca. 0) occupation numbers of the exchanged orbitals, we considered as a third and final possibility the use of the (17,13) active space optimal for small Ga–O bond distances, for the complete description of the Ga–O dissociation process. All single-point energy calculations were performed state average over the two first roots equally weighted and using no symmetry constraints.

All MS-CASPT2/CASSCF calculations were done with MOLCAS 7.4 suite of programs [25]. Single configuration CC calculations were carried out with Gaussian 03 program [26].

2.2 GaO^{2+}'s lifetimes estimation

The existence of an energy barrier in the potential energy curve leads to vibrational states appearing as resonances embedded in the vibrational continuum. Characterization of these metastable states with small barrier heights, as those shown for the ground state of GaO^{2+} with respect to its coulomb explosion, requires a prediction of their widths (Γ), i.e. their lifetimes ($\tau = 1/\Gamma$). For instance, tunneling lifetimes may be too short to be detected with mass spectrometry techniques. For small barrier heights, these states present high anharmonicity. In order to accurately evaluate the energy positions and lifetimes, we solve the one-dimensional time-independent Schrödinger equation:

$$\left[\frac{-\nabla_R^2}{2\mu} + V(R)\right]\phi_v(R) = E_v\phi_v(R) \tag{1}$$

where μ is the reduced mass of the dissociated molecule, $V(R)$ is the potential energy curve, and R the internuclear distance. Equation 1 corresponds to the rotational state $J = 0$. We use an Exterior Complex Scaling (ECS) transformation [27, 28] of the nuclear Hamiltonian written in a basis set of B-spline basis functions defined in a finite box, leading to a discretization of the vibrational continuum in the complex contour. Details on this implementation can be found in ref. [29]. For resonant states, a converged B-spline-ECS representation gives stable values of $E_{\text{res}} = E_v - i\Gamma/2$, where E_v is the energy of the state of vibrational quantum number v and $\Gamma/2$ corresponds to half the resonance width. The calculated values hereby presented have been obtained on the Coulomb explosion potential energy curves calculated at CCSD(T)/aug-cc-pV5Z, in a converged basis of 1500 B-splines functions of order 10, defined in a box of size 40.0 Bohr, and using a complex scaling as $R \to R\,e^{i\Theta}$ for $R > 25.0$ Bohr, where $\Theta = 30°$.

Moreover, for an estimation of the lifetime of the long-lived states (narrow widths), associated to the lowest vibrational quantum numbers, we have used the semiclassical WKB (Wentzel–Kramers–Brillouin) method, in which the lifetime can be obtained by using:

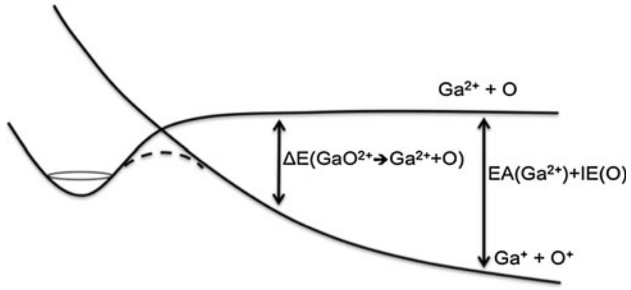
$$\tau = \frac{1}{\Gamma} = \frac{\int_{R_v^l}^{R_v^r} \mathrm{d}R\sqrt{2\mu/[E_v - V(R)]}}{\exp\left(-2\int_{R_v^l}^{R_v^m} \mathrm{d}R\sqrt{2\mu[V(R) - E_v]}\right)} \tag{2}$$

where R_v^l and R_v^r are, respectively, the internuclear distances for the left and right classical turning points of the nuclear potential energy curve $V(R)$ for each metastable vibrational state of energy E_v. R_v^m is the internuclear distance at which $V(R)$ and E_v cross beyond the maximum of the energy barrier. Integrals are evaluated using a gauss quadrature by fitting the numerical potential with B-spline functions.

3 Results and discussion

As mentioned in the Introduction, the thermodynamic stability of a certain diatomic doubly charged species AB^{2+} can be easily predicted from the ionization energies of the neutral atoms, that of their corresponding monocations and the dissociation energy of AB^{2+} into neutral (A) and dicationic (B^{2+}) fragments. For the particular case of GaO^{2+}, at CCSD(T,full)/aug-cc-pV5Z level of theory, the greater electron affinity of Ga^{2+} ($EA_{Ga^{2+}} = 462.6$ kcal mol^{-1}) compared to the ionization energy of the oxygen atom ($IE_O = 313$ kcal mol^{-1}) together with the fact that the sum of these two quantities ($EA_{Ga^{2+}} + IE_O = 149.6$ kcal mol^{-1}) exceeds the dissociation energy of GaO^{2+} into $Ga^{2+} + O$ ($\Delta E = 52.5$ kcal mol^{-1}) reveal that GaO^{2+} is thermodynamically unstable (see Scheme 2). The existence of this species, however, is determined by the height and width of the energetic barrier that separates the minimum GaO^{2+} from the fragments $Ga^+ + O^+$.

Figure 1 collects the CC ground state potential energy curves for GaO^{2+} obtained with several Dunning's basis sets differing in their size. The origin of these curves can be regarded as the overlap of two dissociation profiles of GaO^{2+} leading to two different dissociation channels: the first one, which follows the equation



Scheme 2

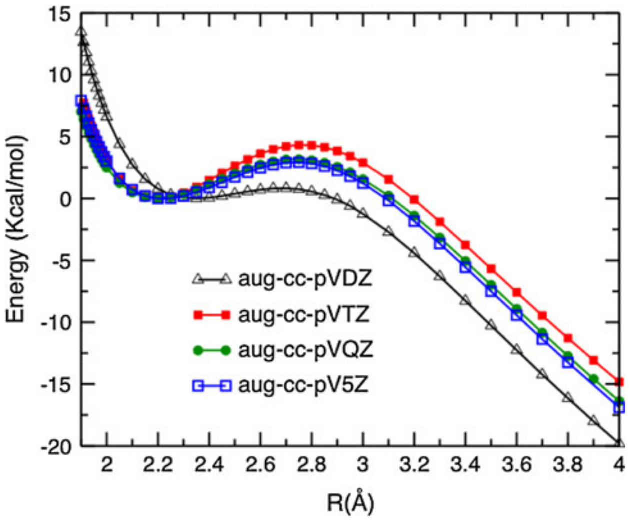


Fig. 1 Comparison of the CCSD(T,full) potential energy curves calculated with different Dunning's aug-cc-pVXZ basis sets (*black* (X = D), *red* (X = T), *green* (X = Q), *blue* (X = 5))

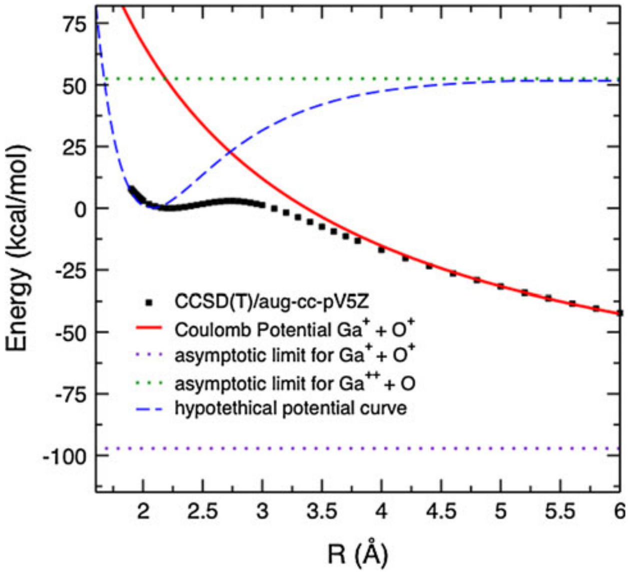


Fig. 2 CCSD(T,full)/aug-cc-pV5Z GaO^{2+} dissociation curve (*black squares*). Coulomb repulsion potential for $Ga^+ + O^+$ (*red full thick line*), see Eq. 3. *Violet* and *green dotted lines* are the asymptotic limits for the dissociative channels $Ga^+ + O^+$ (−97.1 kcal/mol) and $Ga^{2+} + O$ (52.5 kcal/mol), respectively, also calculated at CCSD(T,full)/aug-cc-pV5Z level of theory. *Blue dashed line* is an estimation of the dissociation profile of the dication (i.e. hypothetical potential curve) into $Ga^{2+} + O$

$$\Delta E = \frac{e^2}{R} - \Delta E(\mathrm{Ga}^+ + \mathrm{O}^+)_{\mathrm{dist}=\infty} \qquad (3)$$

(red curve in Fig. 2) corresponds to the Coulomb explosion curve of GaO^{2+} into the monocations Ga^+ (^1S) + O^+ (^4S), and the second (Fig. 2 blue dashed curve) connected to the dissociation of GaO^{2+} into Ga^{2+} (^2S) and neutral oxygen (^3P). These two channels are located at CCSD(T,full)/aug-cc-pV5Z level of theory at 97.1 kcal mol^{-1} below and 52.5 kcal mol^{-1} above the ground state minimum, respectively. The superposition of these two curves leads for this species to an energy barrier whose height and width was found to depend on the flexibility of the basis set used (see Fig. 1).

In general, the increase in the quality of the basis set is reflected in the gradual narrowing and decrease in the width and height of the barrier, i.e. on going from the triple ς to the quintuple ς quality basis set the barrier decreases ca. 1.5 kcal mol^{-1} in energy and by a tenth of an Angstrom in width. The same trend, however, was not observed for the aug-cc-pVDZ basis set, which predicts the lowest and narrowest barrier (0.82 kcal mol^{-1}) among all the basis sets considered. However, the good agreement between the quadruple ς and the quintuple ς estimates, clearly indicate that our results could be considered as converged. However, it should be taken into account that the aug-cc-pVnZ basis sets for Ga do not contain polarization functions for the inner shells which may be important when high accuracy is desired. This can be particularly important in dications, where core-valence-effects may play a more significant role than in neutral systems. In order to have an estimation of these effects, the potential energy curve shown in Fig. 1, was reevaluated by using the cc-pwCVnZ basis sets, recently developed by DeYonker et al. [30] for main group atoms gallium to krypton. The barrier obtained at the cc-pwCV5Z level differs from the one obtained by using aug-cc-pV5Z in about 1 kcal/mol, which is within the precision of the theoretical models used, indicating that core–core and core–valence correlation effects seem not to be significant. It is worth noting however that for cases like the one investigated here, where the activation barrier is rather low, the inclusion of these effects may have a non-negligible effect on the estimated life times.

The ground state of GaO^{2+} is of $^4\Sigma$ symmetry, with the three unpaired electrons lying in the $\sigma^*_{\mathrm{Ga–O}}$ orbital and the two π orbitals perpendicular to the direction of the sigma bond (see Scheme 1).

The suitability of a monoconfigurational zero order wavefunction for the description of the ground state of GaO^{2+} was evaluated through the comparison of the CCSD(T,full)/aug-cc-pV5Z and the MS-CASPT2/ANO-RCC potential energy curves (see Fig. 3). Both the mono- and multi-configurational approaches predict very similar potential energy curves, where the small differences in the height and width of the potential energy barrier could be in principle attributed to the use of different basis sets or to the limitations of the active space chosen for the CASSCF calculations. These findings are consistent with the coefficients of the CI expansion optimized for the wavefunction of the ground state, for which the dominant configuration state function presents a weight higher than 97% in the

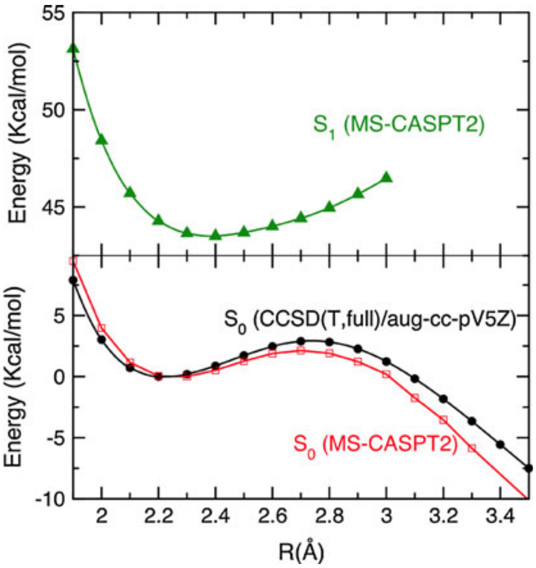


Fig. 3 Comparison of the CCSD(T,full)/aug-cc-pV5Z (*black*) and MS-CASPT2//CASSCF/ANO-RCC (*red*) ground state potential energy curves. The *green curve* corresponds to the first excited state of quartet multiplicity

whole range of interatomic distances considered. The good agreement between the aforementioned CCSD(T,full) calculations and the MS-CASPT2 ones, carried out with ANO-RCC basis sets, which account for scalar relativistic effects, may be taken as an indication that relativistic effects are not significant in estimating the barrier high.

Figure 3 also reports the potential energy curve along the $R_{\mathrm{Ga–O}}$ internuclear distance for the first excited state of the same multiplicity. The $^4\Pi$ state, which is doubly degenerated, arises from the promotion of an electron from the σ_{GaO} bonding orbital into one of the two possible π orbitals, half occupied in the ground state. This state, located in average 40–50 kcal mol^{-1} above the S_0 minimum, lies always parallel to the ground state curve and therefore is not expected to influence the lifetimes of GaO^{2+}.

The well in the potential energy curve for the ground state of GaO^{2+} contains five vibrational states. Calculated energy positions (referenced to the minimum of the well in the potential energy curve) and lifetimes are shown in Table 1. Lifetimes have been obtained using both the B-spline-ECS implementation and the semiclassical method WKB. The lifetime for the long-lived vibrational state $v = 0$ (~ 1 s) is only estimated within the WKB approximation, because of its narrow width.

These metastable states (values in kcal/mol) are plotted on the potential energy curve in Fig. 4, indicating their lifetimes. Although these states eventually undergo a Coulomb explosion (since the longest lifetime for $v = 0$ is around 1 s), they live long enough to be detected in mass spectrometry. Both isotopes, $^{69}\mathrm{Ga}^{16}\mathrm{O}^{2+}$ and $^{71}\mathrm{Ga}^{16}\mathrm{O}^{2+}$, have been observed and unambiguously identified by their isotopic abundance using secondary ion mass spectrometry [16]. However, such a small energy barrier, i.e. relatively short lifetimes, may make it difficult to obtain the dication in those metastable vibrational states, and only if the lowest vibrational resonances are populated, a sufficiently long-lived species would be obtained. This could explain the lack of evidence of the existence of GaO^{2+} when generated by using other techniques, as the Atom Probe Field-Ion Microscopy [17]. It is worth noting that other doubly charged complexes with similar reduced masses [11] present bound vibrational states in their ground electronic state, because of their higher and wider energy barriers. Moreover, Fig. 5 shows the potential energy curves for the ground states of the neutral, the monocation, and dication (GaO, GaO^+ and GaO^{2+}). Taking into account the poor overlap among the Frank–Condon regions of the neutral and/or monocationic species with that corresponding to the lowest vibrational states of the dication, lying in the

Table 1 Energy positions in atomic units (E_v) for each metastable vibrational state (v is the vibrational quantum number) and their calculated lifetimes in seconds, respectively, using the B-spline ECS implementation ($\tau_{\mathrm{B\text{-}ECS}}$) and the WKB approximation (τ_{WKB})

v	E_v (a.u.)	$t_{\mathrm{B\text{-}ECS}}$ (s)	t_{WKB} (s)
0	$5.72416068 \times 10^{-4}$	–	0.80
1	$1.72742438 \times 10^{-3}$	9.14×10^{-5}	9.40×10^{-5}
2	$2.81372646 \times 10^{-3}$	3.76×10^{-8}	3.83×10^{-8}
3	$3.80655045 \times 10^{-3}$	4.63×10^{-11}	4.65×10^{-11}
4	$4.62790013 \times 10^{-3}$	3.46×10^{-13}	2.99×10^{-13}

Energies are given with respect to the minimum of the well in the potential energy curve

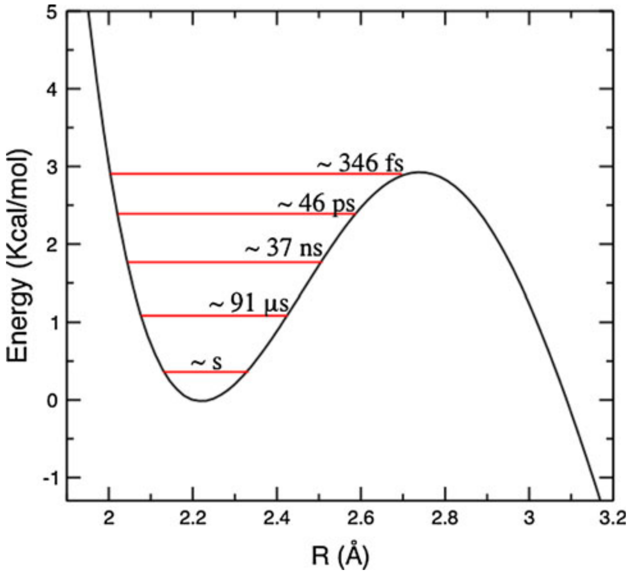


Fig. 4 Metastable vibrational states (with their corresponding lifetimes) contained in the potential energy curve corresponding to the Coulomb explosion of GaO^{2+}

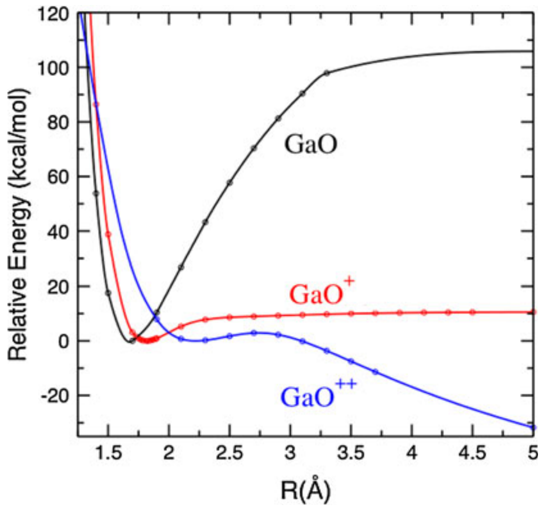


Fig. 5 Potential energy curves for the ground states of neutral GaO, GaO^{+} monocation, and GaO^{2+} dication, respectively. Relative energies referred to the value of their minima

interval of internuclear distances from 2.0 to 2.5 Å, the effective population of long-live metastable states of GaO^{2+} is not expected from vertical transitions from the GaO or GaO^{+}. Therefore, the dication could be, in principle, generated by means of photoabsorption from vibrationally excited GaO and GaO^{+} or even from the low vibrational levels of those if using electromagnetic radiation with wide energy bandwidths, as short pulses. With respect to the observation of GaO^{2+} in the experiment of ref. [16], it is speculated [17] that GaO^{2+} might have been formed a few µm in front of the sputtered surface via dissociative ionization in gas-phase collisions between sputter-ejected triatomic ${GaO_2}^{+}$ (or GaO_2) molecules and energetic incoming O^{-} primary ions.

Furthermore, considering both gallium isotopes $^{69}Ga^{16}O^{2+}$ and $^{71}Ga^{16}O^{2+}$, we find that energy positions differ ~0.1% and lifetimes ~1% with respect to the values shown in Table 1 (obtained using 69.723, the standard atomic weight for gallium). Such small isotopic effect on the position of the resonances and in their lifetimes is expected given the large mass of the system.

4 Conclusions

High-level ab initio calculations show that GaO^{2+} is a metastable species in the gas phase, since the diatomic dication lies 97.1 kcal/mol above the Ga^{+} (^1S) + O^{+} (^4S) dissociation limit. However, the energy barrier that has to be overcome to reach this limit is 3 kcal/mol high, so that five vibrational resonances can be accommodated between the local minimum and the top of the barrier. The evaluated lifetimes vary from 1 s to 346 fs, so at least two of them have a lifetime (1 s and 91 µs) to be detected using mass spectrometry techniques, in agreement with the experimental evidence (GaO^{2+} has been observed for an ion flight time of about ~12 µs) [16]. The small energy barrier may explain why conversely GaO^{2+} dications are not detected when Atom Probe Field-Ion Microscopy techniques are used.

Our results also show that isotopic effects on the resonances' energies and on their lifetimes, when ^{70}Ga is replaced by ^{69}Ga or ^{71}Ga, are very small (~0.1 and ~1%, respectively), reflecting the large mass of the system.

Acknowledgments We thank Klaus Franzreb for sending us his experimental results (ref.16) and his suggestion to calculate GaO^{2+}. This work has been partially supported by the DGI Project No. CTQ2009-13129-C01, by the Project MADRISOLAR2, Ref.: S2009PPQ/1533 of the Comunidad Autónoma de Madrid, by Consolider on Molecular Nanoscience CSC2007-00010, and by the COST Action CM0702. IC and AP gratefully acknowledge a Juan de la Cierva post-doctoral contract from the Ministerio de Ciencia e Innovación of Spain. A generous allocation of computing time at the CCC of the UAM is also acknowledged.

References

1. Bain O, Giguere PA (1955) Can J Chem 33:527–545
2. Pople JA, Raghavachari K, Frisch MJ, Binkley JS, Schleyer PV (1983) J Am Chem Soc 105:6389–6398
3. Huang HH, Xie YM, Schaefer HF (1996) J Phys Chem 100:6076–6080
4. Schroder D, Schalley CA, Goldberg N, Hrusak J, Schwarz H (1996) Chem Eur J 2:1235–1242
5. Pyykkö P (1995) J Am Chem Soc 117:2067–2070
6. Schroder D, Schwarz H, Hrusak J, Pyykkö P (1998) Inorg Chem 37:624–632
7. Pyykkö P (1989) Chem Phys Lett 162:349–354
8. El-Nahas AM (2000) Chem Phys Lett 329:176–178
9. Stace AJ, Walker NR, Wright RR, Firth S (2000) Chem Phys Lett 329:173–175
10. Schroder D, Schwarz H, Wu JL, Wesdemiotis C (2001) Chem Phys Lett 343:258–264
11. Palacios A, Corral I, Mó O, Martín F, Yáñez M (2005) J Chem Phys 123:014315 (014311-014315)
12. Palacios A, Martín F, Mó O, Yáñez M, Maksic ZB (2004) Phys Rev Lett 92:133001
13. Schroder D, Schwarz H (1999) J Phys Chem A 103:7385–7394
14. Franzreb K, Hrusak J, Alikhani ME, Lorincik J, Sobers RC, Williams P (2004) J Chem Phys 121:12293–12302
15. Franzreb K, Sobers RC, Lorincik J, Williams P (2004) J Chem Phys 120:7983–7986
16. Fiser J, Franzreb K, Lorincik J, Williams P (2009) Eur J Mass Spectrom 15:315–324
17. Ohno Y, Kuroda T, Nakamura S (1978) Surf Sci 75:689–702
18. Cársky P, Paldus J, Pittner J (2010) Recent progress in coupled cluster methods. Theory and applications. Springer, Dordrecht
19. Helgaker T, Jorgensen P, Olsen P (2000) Molecular electronic-structure theory. Wiley, Chichester
20. Dunning TH Jr (1989) J Chem Phys 90:1007
21. Wilson AK, Woon DE, Peterson KA, Dunning TH Jr (1999) J Chem Phys 110:7667
22. Roos BO (1987) In: Lawley KP (ed) Advances in Chemical Physics: Ab initio methods in quantum chem, Part II. Wiley, New York

23. Finley J, Malmqvist P-A, Roos BO, Serrano-Andrés L (1998) Chem Phys Lett 288:299
24. Roos BO, Lindh R, Malmqvist P-A, Veryazov V, Widmark P-O (2005) J Phys Chem A 108:2851
25. Karlström G (2003) Comput Mater Sci 28:222
26. Frisch MJ (2004) GAUSSIAN 03, revision C.02. Gaussian, Inc., Wallingford
27. McCurdy CW, Rescigno TN (1997) Phys Rev A 56:R4369
28. McCurdy CW, Rescigno TN, Byrum D (1997) Phys Rev A 56:1958
29. McCurdy CW, Martín F (2004) J Phys B 37:917
30. DeYonker NJ, Peterson KA, Wilson AK (2007) J Phys Chem A 111:11383–11393