Formation Routes of Interstellar Metal Oxides: A Computational Chemistry Approach

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Abstract. We have investigated possible formation routes of interstellar oxides in gas phase via the reactions of the atoms of several metals (Mg, Ca, Al, Fe) with the OH radical and the reaction of atomic Ti with the HO_2 radical in a first explorative computational study based on DFT calculations. The aim is to understand if investing more effort in a higher-level theoretical characterization of these reactions can help to solve open issues on the formation of metal oxides in circumstellar envelopes (CSE) of O-rich AGB stars. The reactions of Ca and Fe with OH are blandly endothermic and can only occur at high temperature or if vibrationally excited OH radicals are involved. The reaction Mg + OH is too endothermic to be significant in the CSE chemistry, while the Al + OH reaction is exothermic and barrierless. Therefore, it is expected to be an efficient AlO formation route, also in other low temperature media.

The reaction Ti + HO_2 → TiO_2 + H is strongly exothermic and barrierless. It is, therefore, very efficient and able to establish a direct connection between TiO_2 and Ti atoms, provided that HO_2 has a non-negligible abundance, in the circumstellar envelopes of AGB stars. A competitive channel leads to the TiO + OH products.

From a computational perspective, the present computational approach, based on DFT, nicely reproduces the structures of the investigated species and provides a general view of the reaction mechanism. However, more accurate methods are needed to derive the energy of intermediates and transition states to be used in the calculations of the reaction rate coefficients.

Keywords: Computational chemistry · Density Functional Theory · Metal oxides · Interstellar Medium - ISM

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1 Introduction

The analysis of pre-solar dust grains in meteorites indicates that the refractory material from which the rocky objects of our solar system originated came from dying stars [1, 2]. In particular, the isotopic composition of those grains allows us to trace their origins back to either massive stars that exploded in core-collapse supernova events or to less massive stars that lose a considerable portion of their mass through stellar winds during the last stage of their evolution, that is, when they enter into the asymptotic giant branch (AGB) phase after having consumed most of the hydrogen and helium in their cores (see [1, 2] and references therein). The dust produced by late AGB stars plays a crucial role being the most important source of interstellar dust particles (accounting up to 70%). The role of interstellar dust is essential since it regulates the radiative transfer of photons and dominates the spectral energy distribution of galaxies and the heating of the gas in diffuse clouds and photodissociation regions. In addition, dust grains provide the surfaces for interstellar heterogeneous chemistry to occur and are the bricks from which planetesimals, and then new planets, are formed around young stars [2–4].

Infrared emission of circumstellar dust in oxygen-rich AGB stars indicates that their major components are amorphous Mg-Fe-silicates. However, is not trivial to reconstruct the processes that lead from gas-phase matter to solid matter. The gas-phase molecules identified in the dust-forming regions might help to unravel the chemical processes at play. In oxygen-rich AGB stars, metal oxides and hydroxides, such as SiO, AlO, AlOH, TiO, and TiO_2, have been detected as isolated molecules (see, for instance, [5–9]). In the inner edge where dust is observed the temperature still exceeds 1000 K, thus implying that the seeds of dust are formed before, closer to the central star with temperatures as high as 1200 K. Gail & Sedlmayr [10, 11] suggested that the direct nucleation of Mg, Fe and SiO from the gas phase cannot occur at temperatures above 1000 K (they estimated that SiO nucleation can only occur below 600 K). Considering their abundance and their bond energies, TiO and AlO emerge as good candidates to start nucleation at higher temperatures [10–12]. In particular, solid Ti/O species can be formed at temperature below 1500 K in rarefied gas at a pressure similar to the one of the circumstellar condensation zone [10–12]. However, it is not yet known for certain if TiO and TiO_2 are responsible for the formation of the seeds of nucleation [13]. TiO_2 emission extends well beyond the dust condensation radius and Ti atoms are observed even farther [5]. Therefore, either a large fraction of Ti is retained in the gas phase (thus questioning its role as one of the main drivers of the formation of nucleation seeds [5]) or Ti, TiO and TiO_2 are released back to the gas-phase by shocks.

Furthermore, even the chemistry that leads to the gas-phase oxides and hydroxides is uncertain and most of the above suggestions come from studies of equilibrium systems [13]. Considering circumstellar envelopes as equilibrium systems is questionable. A kinetics description is, instead, hampered by the missing information on the relevant processes. As an example, a few reactions leading to TiO are considered in the UMIST database [14] (data from one of the few experimental studies available [15]) and none in the KIDA database [16]. A recent model on TiO and TiO_2 formation proposed a series of reactions by analogy with SiO reactions and using the same kinetic parameters [17]. However, the bond energy of SiO (799.6 kJ/mol) and TiO (672.4 kJ/mol) are significantly

different and there is no reason to expect a similar chemistry and, especially, the same rate coefficients for their bimolecular reactions.

In this contribution, by using a computational chemistry approach (already employed in the past for other systems [18–21]) we analyzed the reactions of several metal atoms (Mg, Ca, Fe, Al) with the OH radical and the reaction of Ti atoms with the hydroperoxyl radical (HO_2) to verify if they are feasible formation routes of interstellar MgO, CaO, FeO, AlO and TiO_2. OH is an abundant radical in circumstellar envelopes where it was also seen in vibrationally excited states [22, 23]. HO_2, instead, has not been identified in circumstellar envelopes yet. So far, HO_2 has been detected only toward Ophiuchi A [24] where also H_2O_2 and O_2 have been identified [25, 26]. These species, and especially H_2O_2, were searched for as confirmation that water is produced on interstellar ice in star-forming regions, but several attempts have failed so far [27, 28]. In the conditions of AGB stars, where the pressure can be high enough to allow termolecular reactions, HO_2 could be formed by the association of H (always present) and O_2, a species predicted to be formed by all astrochemical models of O-rich circumstellar envelopes. HO_2 is an important radical in combustion and atmospheric chemistry being the leading oxidizing radical together with OH [29]. Its chemistry in the interstellar medium has not been explored much to date.

2 Theoretical Methods

The optimization of the stationary points of the potential energy surface (PES) of the investigated species has been performed applying a computational strategy already adopted in the past and recent studies [30–37]. In particular, in this first explorative study, the geometry optimizations and energy evaluations have been limited to a Density Functional Theory (DFT) approach using the ωB97X-D [38, 39] functional, and the 6−311 + G(d,p) basis set [40, 41]. In order to assign the saddle points to the relative reactants and products we performed intrinsic reaction coordinate (IRC) calculations [42, 43]. All the energies were corrected to 0 K by adding the zero point energy correction computed using the frequencies evaluated at DFT level. All the calculations were performed using Gaussian 09 [44], while the analysis of the vibrational frequencies was performed using Molekel [45, 46].

3 Results and Discussion

3.1 Formation of Metal Monoxides

We considered the reactions between metal atoms M and the OH radical leading to the metal oxide and hydrogen for M = Mg, Ca, Fe, Al.

In Table 1 we have reported the ΔH_0 values for the metal oxides formation reactions computed at DFT level using the ωB97X-D functional in conjunction with the 6−311 + G(d,p) basis set. These values are computed at 0 K and include the zero point energy corrections (ZPE). Let us consider the different oxide formation reactions in details. To be noted that, in most cases, the accepted value of the enthalpy of formation of metal oxides have been derived with indirect ways and there is a considerable uncertainty.

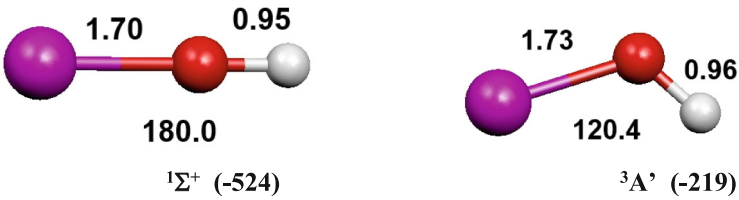

Fig. 1. Optimized geometries of the singlet and triplet AlOH minima. Relative energies (kJ/mol), with respect to the Al + OH reactants, are reported in parentheses. The exit channel, AlO + H, is −46 kJ/mol under the reactants. Bond lengths in Å, angles in degrees.

Table 1. ΔH_0 (kJ/mol, 0 K) and R(M-O) (Å) computed at ωB97X-D/6–311 + G(d,p) level for the reactions of formation of the metal oxides investigated. All the energies include zero-point energy correction. In parentheses the experimental values of the M-O distances obtained from NIST Chemistry Webbook [47, 48].

	$\Delta H^0{}_0$	R(M-O)
Mg + OH ($^2\Pi$) → MgO ($^1\Sigma^+$) + H	238	1.755 (1.749)
Ca + OH ($^2\Pi$) → CaO ($^1\Sigma^+$) + H	37	1.826 (1.822)
Fe + OH ($^2\Pi$) → FeO ($^5\Delta$) + H	29	1.605 (1.57)
Al + OH ($^2\Pi$) → AlO ($^2\Sigma^+$) + H	−46	1.636 (1.618)
Ti + HO_2 (^{2}A") → TiO_2 ($^1A_1$) + H	−534	1.627 (1.658)

MgO. The ground state of MgO is the singlet $^1\Sigma^+$, the Mg ground state is a singlet while the radical OH has a doublet ground state. The reaction therefore evolves on a doublet PES. According to our DFT calculations, this reaction is strongly endothermic by 238 kJ/mol. The estimated enthalpy of reaction is 90 kJ/mol when using the accepted enthalpies of formation [47]. Therefore, there is a strong discrepancy with the calculated value, suggesting that further investigations with a different theoretical methodology are required. The optimized geometry of MgO shows a Mg-O distance of 1.755 Å in very good agreement with the experimental value of 1.749 Å [48].

CaO. There has been a tentative detection of CaO toward the Galactic center molecular cloud G + 0.693−0.027 [49]. It was suggested that the radiative association of Ca^+ with O or O_2 could be responsible for its formation upon electron ion recombination. The reactions of Ca atoms with OH or O_2 have also been invoked [49]. The ground state of CaO is the singlet $^1\Sigma^+$, also Ca has a singlet ground state while the radical OH has a doublet ground state. The reaction therefore evolves on a doublet surface. This reaction is endothermic by 37 kJ/mol which can be compared with the estimate of 40 kJ/mol obtained from the values by Gurvich et al. [50] for $\Delta H°_{f,0}K$(CaO) and NIST [47] for the other species. The optimized geometry of CaO shows a Ca-O distance of 1.826 Å in very good agreement with the experimental value of 1.822 Å [48]. Given its endothermicity, this reaction cannot occur unless vibrationally excited OH (or other

sources of energy) are available. Interestingly, vibrationally excited OH radicals have been detected in several AGB systems [22, 23]. Therefore, it is conceivable that CaO is formed in those conditions, if Ca atoms are available.

FeO. The ground state of FeO is the quintet $^5\Delta$, also Fe has a quintet ground state while the radical OH has a doublet ground state. The reaction therefore evolves on a quartet surface. According to our calculations, this reaction is endothermic by 29 kJ/mol which can be compared with the estimate of 15 kJ/mol obtained from the NIST values of enthalpies of formation [47]. Therefore, this reaction can occur only in warm interstellar environments or with vibrationally excited OH. The optimized geometry of FeO shows a Fe-O distance of 1.605 Å in reasonable agreement with the experimental value of 1.57 Å [48].

AlO. The ground state of AlO is the doublet $^2\Sigma^+$, also Al has a doublet ground state as well as the radical OH. The reaction therefore can evolve on a singlet or triplet surface. The singlet PES has already been characterized by Gobrecht et al. [51] at the higher level of theory CBS-QB3. According to our calculations, this reaction is exothermic by 46 kJ/mol which can be compared with the estimate of 84 kJ/mol obtained from the experimental enthalpies of formation [47] and with the value of 72 kJ/mol derived by Gobrecht et al. [51]. Also in this case, it is clearly necessary to use a higher level of theory. The optimized geometry of AlO shows an Al-O distance of 1.636 Å in good agreement with the experimental value of 1.6179 Å [48] and the value of 1.630 Å by Gobrecht et al. [51]. The interaction of Al with OH leads to an intermediate AlOH both in the singlet and in the triplet PESs. The geometries of these species are reported in Fig. 1, together with their relative energies with respect to the reactants Al + OH. The singlet $^1\Sigma^+$ is linear and is more stable with respect to the reactants by 524 kJ/mol, in line with the value of 554 kJ/mol obtained by Gobrecht et al. [51]. The AlOH intermediate dissociates to AlO + H without any barrier. The triplet ^{3}A' shows an Al-O-H angle of 120.4° and is more stable than the reactants by 219 kJ/mol. The triplet intermediate also evolves towards the products in a barrierless process.

3.2 Formation of TiO_2

We considered the reactions between Ti atoms and the HO_2 radical to verify if TiO_2 can be formed directly from Ti atoms without the intermediacy of TiO formation. The spatial distributions TiO and TiO_2 were seen to be quite different in the case of VY Canis Majoris, while the emission of Ti is extended farther [52].

The ground state of TiO_2 is the singlet $^1A_1$, while Ti has a triplet ground state and the radical HO_2 has a doublet ground state. The reaction therefore evolves on a doublet surface. We considered only this potential energy surface, since we were interested on the formation of TiO_2 in its ground state. We will discuss the quartet surface elsewhere. The channel leading to TiO_2 + H is strongly exothermic with an enthalpy variation of 534 kJ/mol (to be compared with the estimate of −563 kJ/mol obtained from the experimental enthalpies of formation [47]). The competitive channel leading to TiO + OH is, instead, exothermic by 265 kJ/mol. The optimized distance of Ti-O in TiO_2 is 1.627 Å in reasonable agreement with the experimental value of 1.658 Å [47].

The interaction of Ti with the radical HO_2 gives rise, in a barrierless addition process, to a first minimum (MIN1) which is more stable than the reactants by 292 kJ/mol. The geometry of MIN1 is reported in Fig. 2. By overcoming a very small barrier of 6 kJ/mol (corresponding to the transition state, TS, shown in Fig. 2), MIN1 easily evolves to a second minimum (MIN2) which is much more stable (−833 kJ/mol with respect to the energy of the reactants). Because of the large internal energy content, MIN2 decomposed into the TiO_2 + H or into TiO + OH products without any exit barrier.

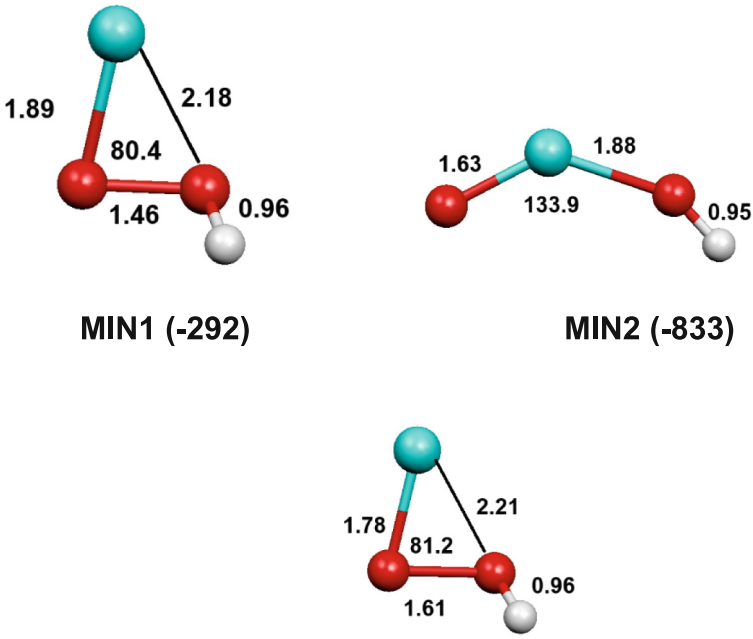

Fig. 2. Optimized geometries of the minima and the transition state obtained for the reaction of Ti with HO_2. Relative energies (kJ/mol), with respect to the reactants, are reported in parentheses. The exit channel, TiO_2 + H, is −534 kJ/mol below the energy of the reactants. Bond lengths in Å, angles in degrees.

4 Conclusions and Astrochemical Implications

In this first explorative computational study, we have investigated possible formation routes of interstellar oxides via the reactions of the atoms of several metals (Mg, Ca, Al, Fe) with the OH radical and the reaction of Ti atoms with HO_2 radicals. The main aim was to understand if it is worth investing more effort in a higher-level theoretical characterization of these reactions. The results are encouraging overall. From a computational perspective, it is clear that the computational approach we have used, based on DFT, is not accurate enough for the calculation of the energy variations and much

more accurate methods as, for instance, CCSD(T)/CBS are necessary, while the structure of the investigated species is in line with experimental determinations or previous calculations.

As far as the feasibility of the investigated reactions is concerned, it is quite obvious that CaO cannot be formed by the reaction between Ca and OH, unless OH is present in vibrationally excited state (the energy content of $v_{OH} = 1$ is 44.7 kJ/mol). This can actually be the case for AGB stars, while it is quite improbable in the case of the molecular cloud G + 0.693−0.027. Incidentally, also the other neutral-neutral reaction suggested by Rey-Montejo et al. [49], i.e. $Ca + O_2 \rightarrow CaO + O$, is endothermic by 110 kJ/mol [47] and, therefore, cannot occur in cold regions of the interstellar medium [53]. The $Mg + OH \rightarrow MgO + O$ is even more endothermic and, therefore, it is improbable that it plays any role. The reaction $Fe + OH \rightarrow FeO + H$ is instead a blandly endothermic reaction that can occur in high-temperature environments or in the presence of vibrationally excited OH. The role of excited OH was invoked by Decin et al. [5] in their model to account for the FeO formation in R Dor (they derive a column density N(FeO) of $1.1 \pm 0.9 \times 10^{15}$ cm^{-2} corresponding to a fractional abundance [FeO/H] $\sim 1.5 \times 10^{-8}$; upper limits for the abundance of CaO and MgO were also provided). Finally, our results on Al + OH are in line with a similar investigation at a higher level of theory that, however, did not consider the triplet PES [50].

Concerning the reaction $Ti + HO_2 \rightarrow TiO_2 + H$, we can conclude that it establishes a direct connection between TiO_2 and Ti atoms, provided that HO_2 (still undetected in the circumstellar envelopes of O-rich AGB stars, but plausibly present) has a non-negligible abundance. It can be an alternative pathway to TiO_2 formation without passing through TiO and its reaction with the OH radical or O_2. Kaminski et al. [4] clearly showed that in VY Canis Majoris not all titanium is depleted into dust particles and the emission of TiO and especially of TiO_2 extends outside the dust formation regions. Most models predict that Ti is converted to oxides in the inner outflow, but emission features of atomic Ti extend farther from the star than the gas with highest TiO abundance [52]. Ti is considered to be highly depleted in the diffuse interstellar medium. The observed optical emission of Ti is further evidence that the condensation of Ti species in VY Canis Majoris is not as efficient as previously estimated or that Ti atoms are originated by the dust destruction. However, in this last case, one would expect to see TiO and TiO_2, also released by dust destruction, at the same location which is not the case.

Clearly, a better understanding of the chemistry at play will help solving this and other open questions.

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