

Theoretical Study of the Chemiluminescence of the Al + H₂O Reaction

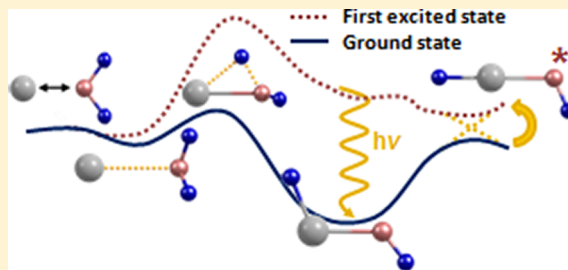
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S Supporting Information

ABSTRACT: We performed surface hopping simulations of Al + H₂O collisions by a direct semiempirical method, reproducing the conditions of previous beam-gas experiments.^{1,2} We observed the formation of the HALOH species, that dissociates to ALOH + H after a lifetime of about 0.6 ps. This species undergoes nonadiabatic transitions to its first excited state and is responsible for chemiluminescence in the visible range, while the Al–H₂O complex emits in the infrared. The computed emission band in the visible is red-shifted with respect to the experimental one,^{1,2} because of slight inaccuracies of the potential energy surfaces. However, collisions with more water molecules and exciplex formation with excited Al(²S, ⁴P) atoms may also contribute to the short wavelength emission, as we show by accurate ab initio calculations.



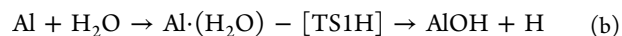
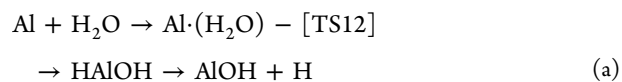
1. INTRODUCTION

The reaction of Al with water in the gas phase has been the subject of a number of experimental^{1–7} and theoretical studies.^{8,9} McClean et al. have studied the kinetics of the title reaction by a laser-induced fluorescence technique, which monitors the decay of Al atoms.⁴ Jones and Brewster have employed high-energy conditions and found that the reaction ultimately generates Al₂O₃ particles.³ Hauge et al.⁵ as well as Douglas et al.⁷ have performed co-condensation experiments in which HALOH and ALOH, and perhaps hydrated forms, appear to be formed.⁶

Perhaps one of the most interesting aspects of previous work is the observation that the title reaction is accompanied by a chemiluminescent glow both under single or multiple collision conditions.^{1,2} Apart from the general chemical significance of that finding, it had, at the time those works were conducted, the interest of being an explanation to the Al seeding experiments conducted in the upper atmosphere. The authors use a molecular beam apparatus in which a high-temperature thermal beam of Al collides with a tenuous atmosphere of an oxidant, for instance, water, and the emission is recorded. Contrary to other likely oxidants, water appears to produce a chemiluminescent continuum, which is nearly identical to that of the upper atmosphere glows; and that happens both under very low (10^{–5} Torr) or higher pressures (>10^{–3} Torr), which are considered to produce “single” and “multiple” collision conditions.¹ The authors reason that the likely emitter has to be a polyatomic species, otherwise there would be no continuum (but rather, for instance, the characteristic features of excited state AlO or of atomic species). Considering previous theoretical and experimental information, the authors conclude that the emitter should be complex formed by Al and several

water molecules or a HALOH species.¹ However, to our knowledge, there is no new experimental nor any theoretical information about the reaction’s chemiluminescence.

The major product of the gas-phase reaction in its ground state appears to be ALOH + H, which should come mostly from the fragmentation of HALOH. We have found two competitive mechanisms:⁸



As shown by previous electronic structure studies of the Al(H₂O) system,^{10–15} Al·(H₂O) is a Al–OH₂ complex,^{16,17} which may undergo fragmentation (through TS1H) or hydrogen shift to HALOH (TS12); those processes have also been found in other atom–water systems.^{18,19} We have found that the process (a) is much more important (faster) even at very high *T* (1000 K).⁸ It is interesting to note that the ALOH molecule has recently been detected in interstellar space,²⁰ so, in a way, those mechanisms could be of astrophysical importance.

It must also be noted that additional water molecules can have a catalytic effect for they would enable Grotthuss-like molecular mechanisms in the evolution of multihydrated complexes, i.e. processes of the type Al·(H₂O)_{*n*} – [TS12]_{*n–1*} → HALOH·(*n* – 1)H₂O.^{21,22} Those mechanisms may lower the

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energy barrier below the level of (ground state) $\text{Al} + (\text{H}_2\text{O})_n$, which according to previous results, is something which happens for $n = 2$ already. Perhaps it must also be noted that the $\text{HALOH} \cdot (n - 1)\text{H}_2\text{O}$ and $\text{ALOH} \cdot (n - 1)\text{H}_2\text{O}$ systems ultimately produce higher hydroxides by processes leading to H_2 elimination, which involve neutral intermediates.²¹

As said, the purpose of the present work is to perform the first theoretical study of the chemiluminescence of the gas phase $\text{Al} + \text{H}_2\text{O}$ reaction, by a simulation that mimics as much as possible the experimental conditions.

2. THEORETICAL APPROACH

2.1. General Aspects. The theoretical treatment of the reaction rate for the collision of an uncollimated effusive beam characterized by a temperature T_B and with a stationary gas with temperature T_G reduces to the standard expression for gas mixtures, provided that the relative speed and the averaged cross section is defined by an average temperature T_a defined as²³

$$T_a = (m_B T_B + m_G T_G) / (m_B + m_G) \quad (1)$$

where m_B and m_G stand for the masses of the beam and stationary gas particles, respectively. One is assuming the stationary gas and also the beam are Maxwellian, and also that the gas is isotropic so the result should be independent of the direction of the beam. Moreover, since the beam temperature is much higher than the one of the gas, most nonreactive collisions will slow down the beam atoms. Since we are dealing with activated processes, the possible contribution of those slowed-down atoms should be negligible. Therefore, one can restrict the treatment to the first collision of each beam atom, before the thermal equilibration process proceeds. In the end one gets that the bimolecular rate constant can be expressed as

$$k(T_a) = \left(\frac{8kT_a}{\pi\mu} \right)^{1/2} \sigma_T(T_a) \quad (2)$$

Here $\sigma_T(T_a)$ is the T -dependent reaction cross section, which relates to the energy-dependent one by:

$$\sigma_T(T_a) = (kT_a)^{-2} \int_0^\infty \sigma(E_r) e^{-E_r/(kT_a)} E_r dE_r \quad (3)$$

where E_r represents the collision energy. The latter cross section relates to the opacity function $P(E_r, b)$ by:

$$\sigma(E_r) = 2\pi \int_0^{b_{\max}} P(E_r, b) b db \quad (4)$$

where b is the impact parameter. $P(E_r, b)$ represents the reaction probability corresponding to particular values of collision energy and impact parameters.

In a trajectory computation it can be quantified as:²⁴

$$P(E_r, b) = N_r(E_r, b) / N_t \quad (5)$$

Here $N_r(E_r, b)$ and N_t represent the number of reactive trajectories for a particular pair and the total number of trajectories, respectively.

That definition can be extended to processes other than reaction, for instance, photoemission. We could compute the emission probability as:

$$P_{pe}(E_r, b) = N_t^{-1} \left[\sum_{m=1}^{N_t} \left(\sum_j^{i(t)-1} \int A_{i(t),j}(t) dt \right)_{(m)} \right] \quad (6)$$

Here $A_{i(t),j}(t)$ represents the Einstein emission coefficient for a $i(t) \rightarrow j$ transition and $i(t)$ is the current electronic state, at time t , for trajectory m . $P_{pe}(E_r, b)$ computed this way is meaningful as long as the emission rate as given by the Einstein coefficient is small in relation with the time scale of the collision event. A differential (frequency specific) probability can be defined as follows:

$$P_{pe}(E_r, b, [\nu_a, \nu_b]) = N_t^{-1} \left[\sum_{m=1}^{N_t} \left(\sum_j^{i(t)-1} \int A_{i(t),j}(t; [\nu_a, \nu_b]) dt \right)_{(m)} \right] \quad (7)$$

Here $A_{i(t),j}(t; [\nu_a, \nu_b])$ is simply $A_{i(t),j}(t)$ but set to zero if the frequency as defined by $(E^{i(t)} - E^j)/h$ is not within the interval $[\nu_a, \nu_b]$ (i.e., $A_{i(t),j}(t)$ multiplied by a rectangular step function). Using 7 or 6 instead of 5 in expressions 3 and 4 the corresponding E or T dependent cross sections can be computed. The integrals over the impact parameter 4, the collision energies 3 or t 6 and 7 have been computed numerically.

2.2. Nonadiabatic Trajectory Simulations. We have considered the interaction of $\text{Al}(^2\text{P})$ with H_2O in its three levels ($^2\text{B}_1$, $^2\text{B}_2$, and $^2\text{A}_1$ for C_{2v} conformations); in other words, we have considered emission from the lowest two excited states into the ground state.

We have performed “on the fly” trajectories with surface hopping (TSH) using the semiempirical floating occupation molecular orbital configuration interaction (FOMO-CI) method.^{25,26} The AM1 Hamiltonian²⁷ has been reparametrized to reproduce accurate ab initio data¹⁷ (see the Supporting Information for more details). We also applied state-specific and geometry-dependent corrections of the semiempirical PES's, with a procedure that maintains the consistence of electronic energies and wave functions (no displacement of PES crossing loci).²⁸ The optimized semiempirical parameters and the state-specific correction functions can be found in the Supporting Information (tables SM_T1 and SM_T2). The method is noted as AM1(*)-FOMO-CI.

The (simplified) potential energy surfaces (PES) of the ground and first excited state are depicted schematically in Figure 1. Overall, the AM1(*)-FOMO-CI method with ad hoc parametrization and PES correction is a reasonable compromise between accuracy and computational speed. It must be noted that, compared to high-level ab initio results (which include scalar relativistic effects),¹⁷ it gives rather good relative energies for M1 and TS12. It underestimates though the depth of the ground state ($^2\text{A}'$) M2 well by about 0.20 eV (1600 cm^{-1}). The energy of the M2 minimum for the first excited state relative to the reactants, is in very good agreement with the ab initio reference, but this means that photon emission originating from this geometry (M2*) tends to be displaced to longer wavelengths because the energy gap with the ground state is too small. The main difference between the ground and excited state equilibrium geometries is the H–Al–O angle: 112.7° in $\text{X}^2\text{A}'$ and 180.0° in $\text{I}^2\text{A}'$ (both values still very close to the ab initio ones, 114.8° and 179.4° see ref 17, figure SM_F1 and table SM_T3 of the Supporting Information). The vertical transition energy of M2 (2.62 eV = 21100 cm^{-1}) also agrees very well with the ab initio one (20657 cm^{-1}); in other words, the $\text{I}^2\text{A}''$ energy at this geometry is too high by as much as the $\text{X}^2\text{A}'$ one. We note that this transition energy almost coincides with the main peak in the emission spectrum.

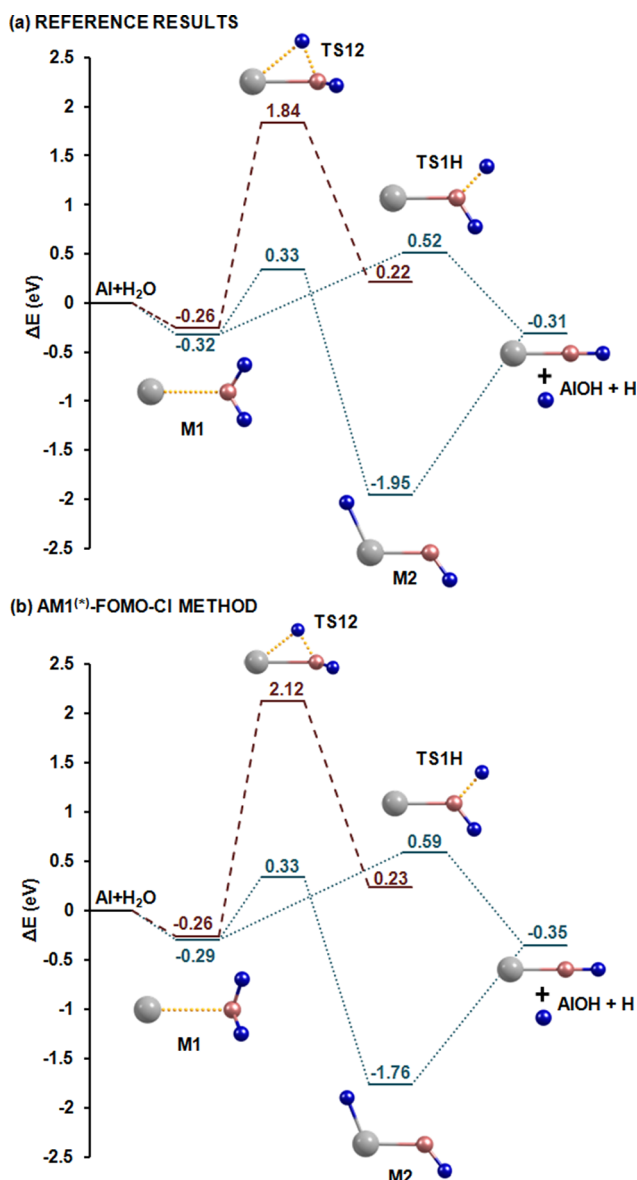


Figure 1. Simplified potential energy surface (PES) of the ground (blue) and first excited state (dark red) (relative energies with respect to $\text{Al} + \text{H}_2\text{O}$, ZPEs are not included). Reference results include high-level (HL) ab initio values for the ground state (see ref 17), while for the first excited state we have employed CASSCF/6-311++G**//CASSCF/6-311++G**^{33–35} energies as follows: relative energies have been computed as $\Delta E_{X^*}^{\text{HL-corr}} = \Delta E_X^{\text{HL}} + \Delta E_{X^*}^{\text{CASSCF}}$ with $\Delta E_{X^*}^{\text{CASSCF}} = E_{X^*}^{\text{CASSCF}} - E_X^{\text{CASSCF}}$, where X refers to the structure of interest. Note that the excited state energies are computed on their respective optimized geometries. The MOLPRO 2006 package has been used.³⁶ (See more details of the structures in the figure SM_F1 and table SM_T3 of the Supporting Information).

The transition moments vary very much with the geometry; taking the important $1^2A' \rightarrow X^2A'$ transition at the equilibrium geometry of M2 as a measure, we have that the $\text{AM1}^{(*)}$ -FOMO-CI value is 0.7194 au as compared to a relatively high-level ab initio value of 0.8401 au¹⁷ (MRCI/aVTZ//QCISD(T)/6-311++G(2df,p) -multireference configuration interaction- using a state-averaged CASSCF -complete active space SCF- wave function as reference^{29–36}). In general, $\text{AM1}^{(*)}$ -FOMO-CI gives somewhat lower values for the transition moments than MRCI calculations, which would imply that our

computed emission cross sections are somewhat underestimated.

Concerning the initial conditions for the internal energy of water, we have employed a canonical distribution of the rotational energy for $T = 300$ K; besides, it has been taken in its vibrational ground state, represented by the normal coordinate approximation and a classical sampling of coordinates and momenta for the three vibrational degrees of freedom has been applied. On the other hand, we have employed $T_a = 860.5$ K which corresponds to a beam temperature of 1700 K.

We have run a total of 169200 trajectories in the following way. We have considered a set of 48 collision energies ($0 < E_r \leq 2.3$ eV) for a number of impact parameters for each energy such that $0 \leq b \leq 2.8$ Å (see table SM_T4 of the Supporting Information). For each energy and impact parameter the trajectories are started at $R = 10$ Å where R is the distance between the center of mass of water and Al; 1/3 of those trajectories are started at each electronic term (which, as said, can be labeled as 2A_1 , 2B_1 and 2B_2 for C_{2v} conformations).

The time-dependent Schrödinger equation for the propagation of the electronic wave function is solved at each trajectory time step by a local diabaticization method, thus providing the state probabilities $P_k(t)$.²⁵ The variation in time of the $P_k(t)$ probabilities brings about nonadiabatic transitions in the form of surface hopping events, according to Tully's fewest switches algorithm³⁷ with quantum decoherence corrections.³⁸ The nonadiabatic dynamics as well as the FOMO-CI method are implemented in a development version of the MOPAC2002 package³⁹ that has been used throughout this work.

3. RESULTS AND DISCUSSION

3.1. The Reaction and Photoemission Cross Sections.

Figure 2 displays the computed reaction and total photoemission cross sections as a function of the collision energy up to 1.2 eV, eventually weighted with the relative energy distribution function as

$$\sigma(E_r, T_a) = (kT_a)^{-2} E_r \sigma(E_r) e^{-E_r/kT_a} \quad (8)$$

where $\sigma(E_r, T_a)$ or $\sigma(E_r)$ correspond to either the reaction ($\sigma_r(E_r, T_a)$, $\sigma_r(E_r)$) or the photoemission ($\sigma_p(E_r, T_a)$, $\sigma_p(E_r)$) processes. Note that 8 corresponds to the integrand of eq 3. Since both cross sections, $\sigma_r(E_r)$ and $\sigma_p(E_r)$ are very small at low collision energies ($E_r < 0.6$ eV), the noise to signal ratio of the computed raw data is rather high, in spite of the large number of trajectories. Therefore, we have applied a smoothing procedure by convolution with a Gaussian function of E_r , both in the numerical integration and in the plots of Figure 2, by replacing $\sigma(E_r)$ with

$$\sigma'(E_r) = \frac{1}{N} \sum_{i=1}^m \sigma(E_i) N_i^{1/2} \exp\left(-\frac{(E_r - E_i)^2}{\Delta E^2}\right) \quad (9)$$

Here $N = \sum_{i=1}^m N_i^{1/2} \exp(-(E_r - E_i)^2/(\Delta E^2))$ and N_i is the number of trajectories in the batch i , from which the data $\sigma(E_i)$ were obtained. ΔE is an arbitrary width parameter, in this case 0.05 eV.

It is readily seen that the contributions to the temperature dependent cross sections become almost zero for $E_r > 1$ eV, and that is so because of the Boltzmann factor. The computed reaction and total photoemission cross sections are 6.3×10^{-3} Å² and 2.7×10^{-8} Å², respectively. The onset of the reaction cross section is at about 0.23 eV, which is, approximately, the energy of the saddle point TS12 relative to the ground state

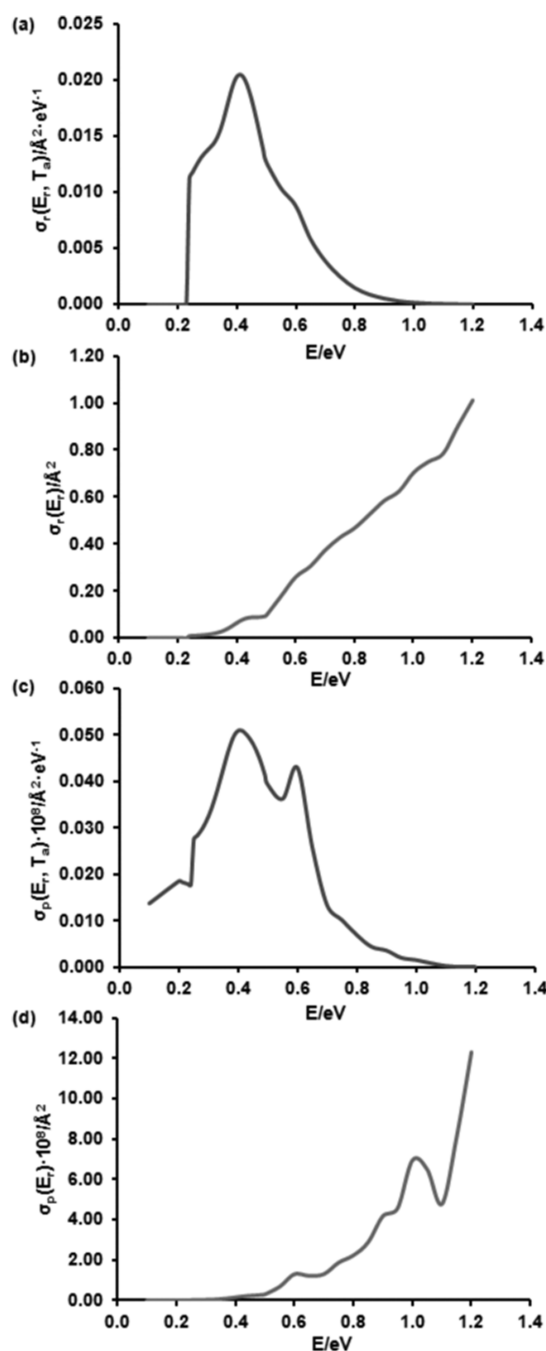


Figure 2. Cross sections as a function of the collision energy. (a) Reaction cross section multiplied by the appropriate Boltzmann factor (see eq 8). (b) Reaction cross section without Boltzmann factor. (c) Photoemission cross section multiplied by the Boltzmann factor. (d) Photoemission cross section without Boltzmann factor.

reactants if one includes ZPEs (zero point energies). We have a significant contribution to the emission cross section for lower energies, which comes from M1 and the “entrance channel” (the Al – OH₂ interaction). The rest of the emission comes mostly from M2, that is why it disappears whenever the reaction cross section fades away ($E_r > 1$ eV). It must be noted that tunneling is not taken into account in the present TSH simulations (it is quite difficult in multidimensional computations); however, it should not have a very important impact, especially in the high frequency part of the emission (vide infra), because the tunneling transmission factor is normally

close to unity for the effective temperature considered in the present work ($T_a = 860.5$ K)¹⁷

Figure 3 displays the photoemission cross section as a function of the frequency of the emitted radiation. It is readily

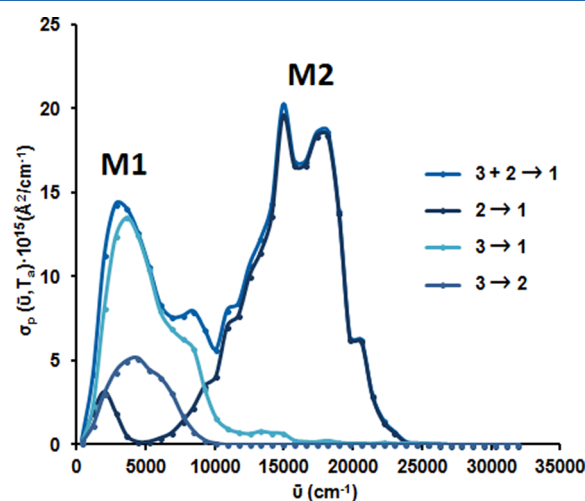


Figure 3. Photoemission cross sections ($\text{\AA}^2/\text{cm}^{-1}$) as a function of the wavenumber (cm^{-1}). Here, 3 and 2 mean the second and first excited states and 1 stands for the ground state.

seen that we have two bands, one in the infrared, which, as we have verified, corresponds to M1 and the Al–OH₂ collision, and the other starting at approximately 10000 cm^{-1} with maximum intensity in the visible, which corresponds to the emission from, quite specifically, the first excited state of M2. It must be noted that, at the molecular geometry of TS12, the first excited state lies above the ground state by approximately 1.8 eV. As a consequence, in order to approach the M2 geometry the system must be on the electronic ground state, which is what is actually observed in the trajectories. After that, the trajectories which contribute to the emission probability undergo surface hopping into the first excited state. The system eventually decays into the ground state, frequently after more than one hop back into the excited state. There are typically two or three raids into the excited state, before the system goes into the ground state (see Figure 4) and dissociates to AlOH + H. It turns out the hops occur between the ground and the first excited state where they are quite close in energy, namely at $\angle\text{HAIO}$ angles close to 180°. The emission corresponding to the higher frequencies arises from geometries with a much smaller angle. Note also that there is a conical intersection between the first and the second excited state, which accounts for some population of the latter resulting in very weak emissions to the first excited state (contributing to low frequencies) and to the ground state (higher frequencies). As a matter of fact, emission from the second excited state to the first excited and the ground state has a sizable impact mostly for M1 and the entrance channel. It is too high in energy to contribute to the emission at the M2 geometry.

It must be noted that the emission recorded in the experiments cannot be caused by (excited state) AlOH or even AlO, for AlOH* and AlO($B^2\Sigma^+$) cannot be formed from Al(X^2P) + H₂O and AlO($A^2\Pi$) would give a band very much shifted to the low-frequency region (see Figure 5). It must be noted that we have not observed AlO formation in the present simulations.

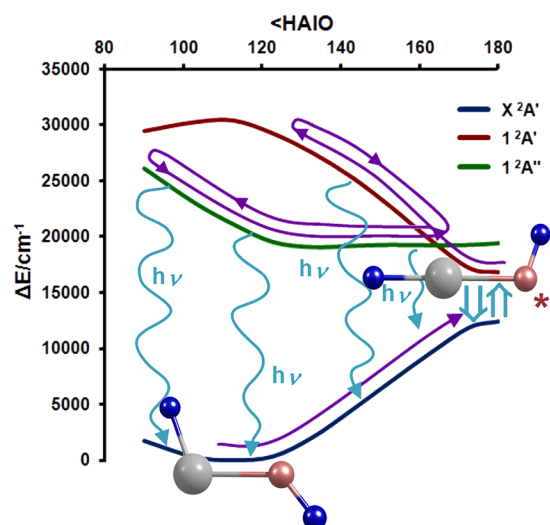


Figure 4. Schematic representation of a typical trajectory contributing to the M2* photoemission probability. The energy profiles are obtained at the AM1(*)-FMO-CI level using the frame of the ground state optimized geometry. Hops occur at conformations with $\angle\text{HAIO}$ angles close to 180° . Recall that the total energy is conserved, while the diagram points to potential energy variations.

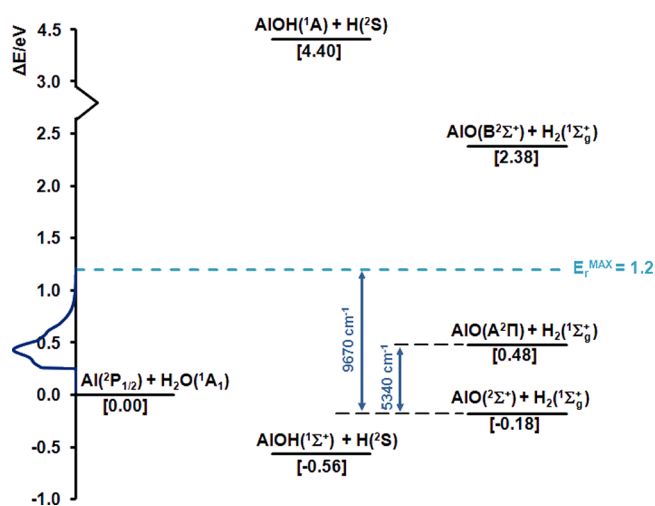


Figure 5. Relative energies (in eV) for the ground state and first excited state of AlO and AlOH species. For the ground state the values are those of a high-level procedure (see ref 17) (ZPE's are included). For the first excited state, the experimental vertical excitation energy tabulated in NIST were added to the ground state value. A schematic curve representing the reaction cross section is given in the y axis. Relative energies (in brackets) are computed with respect to $\text{Al} + \text{H}_2\text{O}$.

It is also interesting to note that there seem to be two peaks in the visible band of the computed spectrum: one is located at approximately $15\,000\text{ cm}^{-1}$ and the other at approximately $17\,500\text{ cm}^{-1}$. We have found that the low-frequency one arises from accumulation of the emission probability at geometries of the first excited state which are not far to its equilibrium geometry, which happens to be quite close to that of the cis-trans transition structure of the ground state, while the high-frequency one has contributions from emissions taking place at geometries more similar to the M2 (ground state) minimum, where the first excited state is $^2\text{A}''$ (for planar geometries).

In Figure 6, we have displayed the cross section as a function of both the collision energy and the emission frequency. The

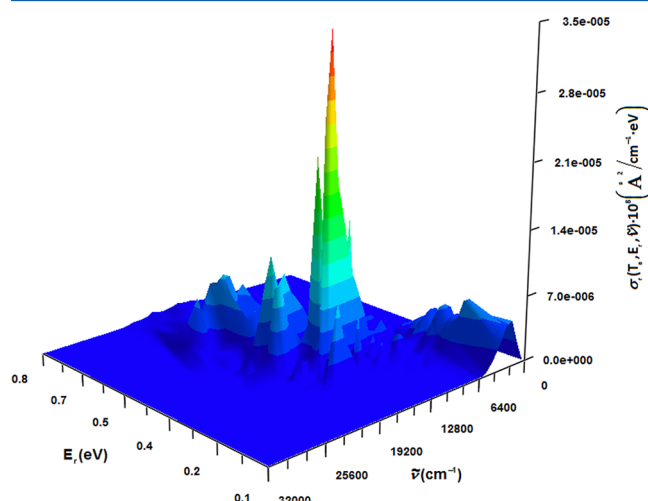


Figure 6. Wavenumber-dependent photoemission cross section. The values include the Boltzmann factor of eq 3.

origin of the peaks of Figure 6 can be traced to the trajectory energy E_r . Again, the very low-frequency (IR) emission comes from nonreactive trajectories. Low-energy reactive trajectories contribute to both the high ($17\,500\text{ cm}^{-1}$) and the low ($15\,000\text{ cm}^{-1}$) frequency peaks, while the high-energy range contributes to the high-frequency peak and extends the emission to approximately $23\,000\text{ cm}^{-1}$. It must be noted the peaks of the photoemission cross sections are very dependent on T_a since most of the emission is caused by high-energy trajectories. We have checked that an increase in T_a beyond 860.5 K very much augments the height of the $15\,000$ – $17\,500\text{ cm}^{-1}$ peaks, especially as compared to the low-frequency band; however it does not substantially extend the reach of the band to higher wavenumbers.

3.2. Comparison to the Experiment. The experimental emission is a wide band starting approximately from 3500 Å ($28\,570\text{ cm}^{-1}$ or 3.5 eV), with a weak tail at long wavelengths that was recorded up to 8200 Å ($12\,200\text{ cm}^{-1}$ or 1.5 eV).^{1,2} The short wavelength band is the most unsatisfactory feature of the computed emission spectrum (Figure 3), for the experimental spectrum^{1,2} extends well into about $29\,000\text{ cm}^{-1}$, the maximum appearing at about $22\,000\text{ cm}^{-1}$. Part of the difference comes from the fact that, at the ground state geometry of M2, both the $\text{X}^2\text{A}'$ and $1^2\text{A}''$ state energies are overestimated (less deep with respect to $\text{Al} + \text{H}_2\text{O}$) by roughly 0.20 eV ($\text{X}^2\text{A}'$ by 1550 cm^{-1} and $1^2\text{A}''$ by 1900 cm^{-1}). As a consequence, after hopping to the excited state at large H–Al–O angles, the system finds a steep slope (steeper than the ab initio calculations do suggest) along the H–Al–O bending coordinate, i.e. the geometry deformation leading to larger $\text{X}^2\text{A}'$ – $1^2\text{A}''$ energy gaps. This fact may explain why the high frequency emission region is reached less frequently in our simulations. The limitations of the TSH treatment with respect to quantum wavepacket dynamics (no tunneling, energy conservation imposed to each trajectory after a surface hopping) may also contribute to decrease the probability of climbing to high potential energies in the excited state.

The above considerations are not the only possible explanation for the 4500 cm^{-1} red shift of the computed

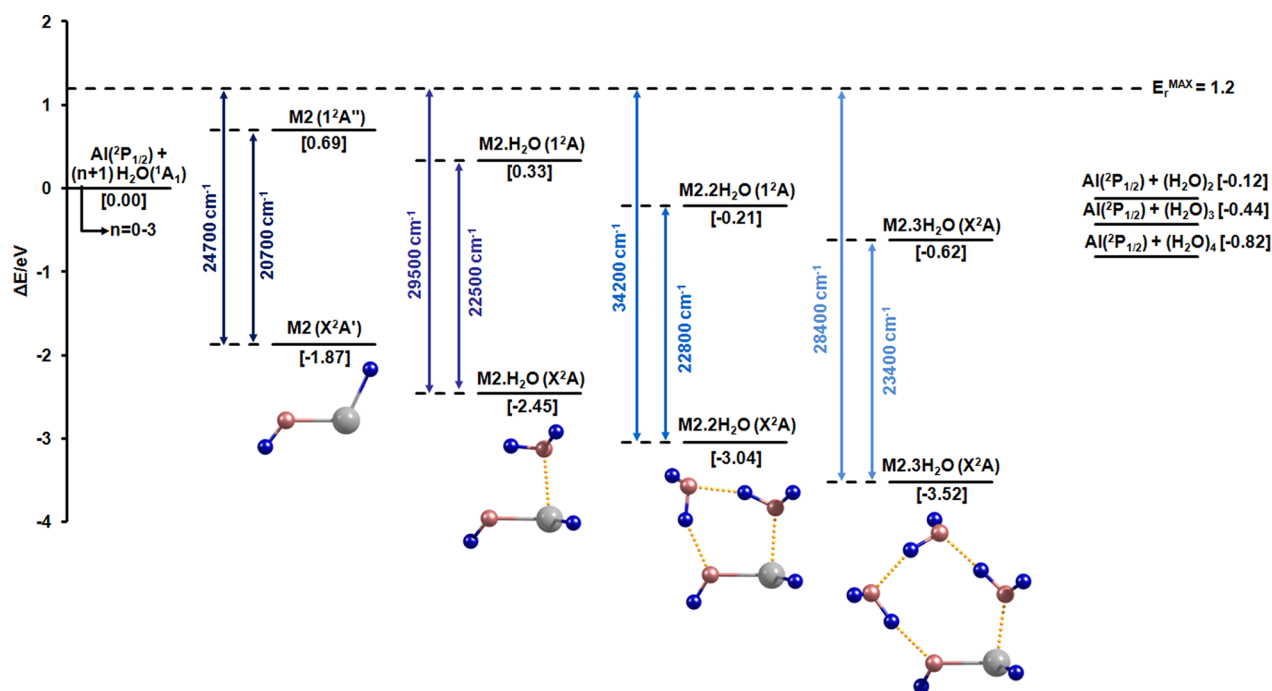


Figure 7. Representation of a possible origin of the short-wavelength emission band. The maximum collision energy has been given a common value taken from the Al + H₂O collisions. The relative energies of ground state M2-*n*(H₂O) have been computed by the high-level procedure of ref 22, while the values of the corresponding first excited state have been computed by adding $T_{e,M2,nH_2O}^{MRCI,corr} = T_{e,M2}^{MRCI} + \Delta T_{e,M2,nH_2O}^{TD-DFT}$ with $\Delta T_{e,M2,nH_2O}^{TD-DFT} = T_{e,M2,nH_2O}^{TD-DFT} - T_{e,M2}^{TD-DFT}$, where $T_{e,M2}^{MRCI}$ is computed at the MRCI/aug-cc-pVTZ//QCISD/6-311++G(2df,p)^{29–32} level and $T_{e,M2,nH_2O}^{TD-DFT}$ is computed at the TD-BHandHLYP/aug-cc-pVTZ//BHandHLYP/aug-cc-pVTZ level.^{42,30} The MRCI/aug-cc-pVTZ computations employ a CAS reference,³³ in which only the orbitals correlating to the 3d shell of Al are excluded.

emission band versus the experimental one, and probably cannot account for the whole of it.

Perhaps, the first option for an alternative explanation could be the effect of hydration. The presence of additional water molecules, possibly due to collisions of Al with water dimers, would produce a blue shift of the emission spectrum relative to that of the Al + H₂O reaction. As one can see in Figure 7, hydration brings M2 (i.e., the M2-*n*H₂O water adducts) very much below the energy level of Al + (*n* + 1) H₂O and even Al + (H₂O)_{*n*+1}. However, under single collision conditions,² the partial pressure of water dimers is very low; for instance, for $p_{H_2O} = 10^{-3}$ Torr, we should have approximately $p_{(H_2O)_2} = 7 \times 10^{-11}$ Torr^{40,41} for 300 K. Even if the reaction cross section for the Al-(H₂O)₂ interaction would be much larger than that of the Al-H₂O one, and the dynamics of the two-water system more complex than that of Al-H₂O, the water dimer pressure is probably too low. Besides, the Al(H₂O)_{*n*+1} adducts might not react but dissociate; i.e., Al(H₂O)_{*n*+1} → Al(H₂O)_{*n*} + H₂O would be a competitive process.

Our computed *T*-averaged lifetimes for M2 are on the order of 600 fs, while the M2-H₂O collision frequency of one M2 molecule with H₂O would be approximately 10^4 s⁻¹ for $T = 300$ K ($p_{H_2O} = 10^{-3}$ Torr and taking the collision diameter of $d = 3.2$ Å). Excited M2 (M2*) should be even less likely to undergo collisions. That lifetime value cannot be properly compared to former RRKM⁸ or RRK⁹ estimations because of the different conditions and because the system might not behave in an ergodic manner in such fast a process; still those estimations (0.1⁸ to 3 ps⁹) also point to a very fast fragmentation of M2. We cannot accurately compute the lifetime of M1 by the present computations; although for $T = 300$ K we have estimated it to be of the order of 5 ps by RRKM theory,⁸ while

the M1-H₂O collision frequency would also be about 10^4 s⁻¹ (300 K, 10^{-3} Torr and $d = 3.2$ Å). These data show that the interaction of M1 or M2 with a further water molecule has a negligible probability.

The experimental spectrum shows that a small amount of aluminum atoms in the first excited ²S state are present (emission doublet⁴³ at 25236 and 25348 cm⁻¹). While we could not explain presence of the Al(²S) species in the beam (although one could think of some mechanism connected with the beam generation procedure), we performed preliminary calculations that showed the possibility of an Al(²S)-water exciplex with strong emission in the 35000–11500 cm⁻¹ region. The radiative lifetime of Al(²S) is 6.8 ns,⁴⁴ so only a very small fraction of it would undergo complex formation. Since the observed molecular emission is much stronger than the atomic one, we could, in principle, rule out this mechanism too. However, if there would be a mechanism for slow formation of the Al(²S)-water exciplex, that emission could still be meaningful. The lowest quartet term, Al(⁴P), is by 29020–29142 cm⁻¹ above Al(X²P_{1/2}) and would decay only very slowly to Al(X²P) or Al(²S); in other words, that quartet must be a long-lived species. The Al(⁴P)-OH₂ interaction generates three PES (two of ⁴A'' symmetry and one of ⁴A' symmetry for C_s geometries). Figure 8 presents two sets of energy profiles computed at the MRCI/aVTZ+Ry(2) level; they both employ structures optimized for a set fixed Al-O distances for the Al(²S)-OH₂ state (first set) and for the AlOH₂(1⁴A'') state (second set). The basis set includes two shells of Rydberg-type functions (spd for Al and O⁴⁵). The states which correlate with Al(X²P/²S/⁴P)+OH₂ have been displayed. It is readily seen that the lowest quartet term is neatly attractive and even has a very short Al-O equilibrium distance, coming very close in energy

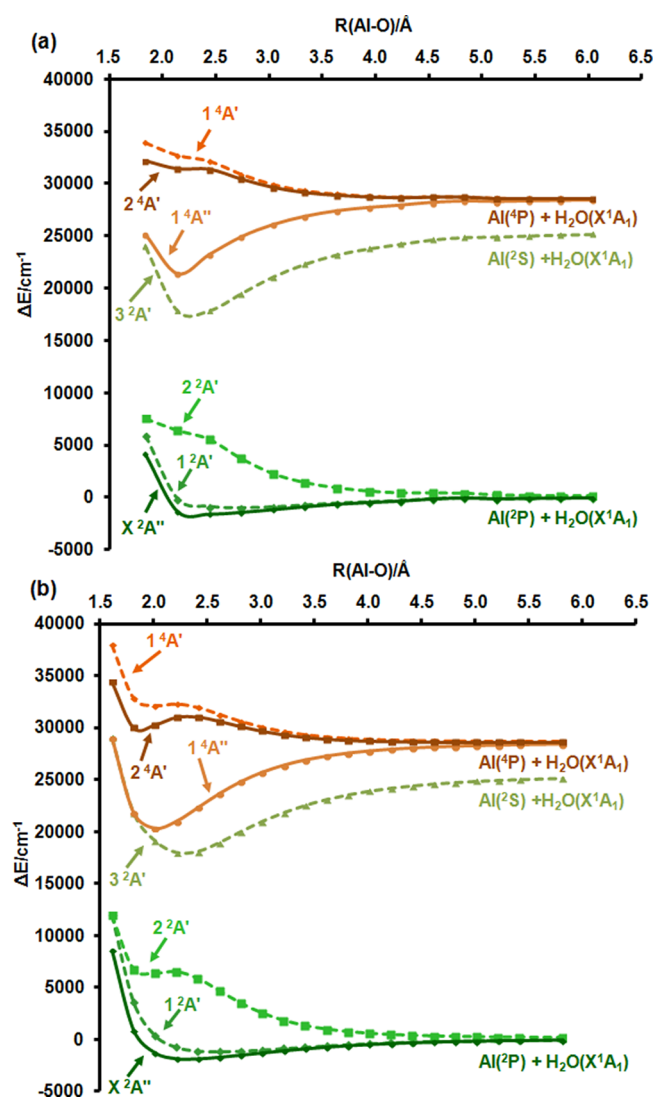
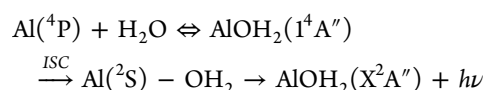


Figure 8. (a) MRCI/aVTZ+Ry(2) energy profiles computed of M1 as a function of the Al–O distance for the states which correlate with $\text{Al}(^2\text{P}/^2\text{S}/^4\text{P})\text{--H}_2\text{O}$. The structures have been optimized for a set of fixed Al–O distances for the $\text{Al}(^2\text{S})\text{--OH}_2$ state ($3^2\text{A}'$) by TDDFT-(BHHLYP)/6-311++G**+Ry(2) computations. (b) Same profiles using BHHLYP/6-311++G** structures determined for the $1^4\text{A}''$ state. The energy gap between $\text{Al}(^2\text{P})\text{--OH}_2$ and $\text{Al}(^4\text{P})\text{--OH}_2$ has been computed at the CCSD(T)/aug-cc-pCVTZ level, correlating all electrons.

to the $\text{Al}(^2\text{S})\text{--OH}_2$ minimum in the second set of energy profiles. For decreasing Al–O distances the corresponding curves cross (as usual, the spin–orbit interaction is not taken into account), what means there could be a high probability of a spin-changing transition. The $\text{Al}(^2\text{S})\text{--OH}_2$ complex formed in this way could decay by emission to the ground or the first excited state (high frequency) or to the dissociative $2^2\text{A}'$ state (low frequency). As said, the band caused by $\text{Al}(^2\text{S})\text{--OH}_2$ could easily extend to frequencies higher than $25\,000\text{ cm}^{-1}$. In other words we would have:



where the emission could take place to the other two lower-lying doublets of M1 as well. By means of transition moment

calculations we have verified that the $\text{Al}(^2\text{S})\text{--OH}_2$ complex should emit at least as strongly as $\text{Al}(^2\text{S})$. Although dissociation ($\text{Al}(^2\text{S})\text{--OH}_2 \rightarrow \text{Al}(^2\text{S}) + \text{H}_2\text{O}$) could be a competing process, one cannot rule out that the dissociation time could be long enough as to allow emission to be a likely outcome. Note that both $\text{Al}(^2\text{S})\text{--OH}_2$ and $\text{AlOH}_2(1^4\text{A}')$, contrary to $\text{AlOH}_2(\text{X}^2\text{A}'')$, are rather deep minima on their respective PES; a long dissociation time is not impossible.

The high-temperature conditions of the oven where the Al beam is generated^{1,2} should allow for a small population of the $\text{Al}(^4\text{P})$ term; at 1700 K, for instance, the equilibrium $\text{Al}(^4\text{P})/\text{Al}(^2\text{P})$ ratio should be $\sim 0.4 \times 10^{-10}$. Even if that number is very small, it should be considered that the atomic $\text{Al}(^2\text{S})$ emission is clearly visible in the spectrum (the $\text{Al}(^2\text{S})/\text{Al}(^2\text{P})$ ratio would be 1.6×10^{-10}) and also that, according to our TSH simulations, M2* accumulates emission probability during very short times (tens of fs). That means, in our view, that some contribution to the spectrum from the quartet term of Al through the exciplex formation process described above cannot be ruled out.

4. CONCLUSIONS

The collisions of Al atoms in a beam at 1700 K with water molecules in the gas phase produce a chemiluminescence due to an unknown species, previously hypothesized to be HALOH .^{1,2} In this work we investigate theoretically the collisions of Al atoms with water molecules. Surface hopping simulations with directly computed semiempirical PES confirm that the emitter can be HALOH . This species is not formed directly in an excited state, which is instead populated by nonadiabatic transitions from the hot ground state. The latter has a lifetime of about 0.6 ps, before dissociating to $\text{AlOH} + \text{H}$. Both the reaction and the total photoemission cross sections are small ($6.3 \times 10^{-3}\text{ Å}^2$ and $2.7 \times 10^{-8}\text{ Å}^2$ respectively), therefore the simulation of the chemiluminescence spectrum required to run about 1.7×10^5 trajectories, a task that would not be easily performed by ab initio methods.

The computed spectrum exhibits two bands. One is in the near-infrared, beyond the wavelength range experimentally investigated, and is due to an excited $\text{Al}\text{--H}_2\text{O}$ complex. The other one is in the visible and is red-shifted with respect to the experimental one, with two maxima at $15\,000$ and $17\,500\text{ cm}^{-1}$, instead of one at $22\,000\text{ cm}^{-1}$. This is partly due to a small inaccuracy of the PES's in the region of the HALOH minimum and perhaps also to artifacts of the surface hopping method. Other explanations of this discrepancy have been explored by accurate ab initio calculations, being beyond the scope of our simulations of the dynamics. One is the effect of interactions with more than one water molecule or reaction with water dimers, that would differently stabilize the ground and the excited state of the emitting species, causing a blue shift of the emission band. Another possibility is the formation of $\text{Al}(^4\text{P},^2\text{S})\text{--H}_2\text{O}$ exciplexes, that would contribute to the short wavelength emission according to the computed potential energy curves. Both processes are far from being demonstrated, but they are worth further theoretical and experimental investigation.

■ ASSOCIATED CONTENT

Supporting Information

Information about the reparametrization of the AM1 semiempirical method and about the analytical corrections (state-specific and geometry dependent corrections) applied and data

about the geometry of some minima and transition states. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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