

The following contains the comments of the referee (black), our replies (blue) indicating changes that will be made to the revised document (red).

Reviewer #3

This manuscript presents the first study of the effectiveness of H₂O as a third body on the recombination of OH with NO₂. This careful experimental study shows that water vapor is much more effective than N₂ or O₂ in causing recombination. It also presents a global modeling study of a new parameterization of the OH + NO₂ reaction as compared to the IUPAC and JPL recommendations; this parameterization uses the results of a previous study showing that O₂ and N₂ have different efficiencies in quenching the products of OH + NO₂. The modeling suggests that HOONO could be a non-negligible reservoir of NO_x in some parts of the atmosphere. This is a very important paper that is clearly in the scope of ACP. There are no major problems with the manuscript, but a few of points should be clarification or emphasized more strongly before publication in ACP.

We thank the reviewer for the careful review and the positive assessment of our manuscript.

My major concern about this manuscript is actually rather minor: In the global modeling, it is not clear how much of the affects of the new parameterization, occurs due to water vapor and how much due to the use of the results of the author's previous paper on N₂ vs O₂ as colliders. This should be made clear.

As we already mention, the impact of H₂O is limited to the boundary-layer (Fig. 5), above which the H₂O concentration decreases rapidly. We now emphasise this by writing:

The presence of water vapour does not impact on values of k_1 above the boundary layer.

The enhancement of the quenching of the energized HNO₃ intermediate (HNO₃*) due to H₂O vapor is presumably due to the strong hydrogen bonding between the two (stronger than OH-H₂O or NO₂-H₂O). It would be good to make this explicit and add some references to the literature on the HONO₂-HOH complex.

We have added text mentioning the HNO₃ – H₂O complex:

Water vapour is therefore a factor ≈ 8 more efficient than O₂, and a factor ~ 6 more efficient than N₂ as a quencher of the HO-NO₂ intermediate, which is qualitatively consistent with known strong binding (40 kJ mol⁻¹) in the HNO₃-H₂O complex (Tao et al., 1996).

There must be previous field work measuring [NO₂]/[HONO₂] and corresponding modeling work that did or did not find discrepancies. It seems that the authors should refer discuss a few of these, at least briefly.

This is an old problem in atmospheric chemistry. HNO₃ is not formed solely in the reaction between OH and NO₂ but also in heterogeneous processes that hydrolyse N₂O₅, the rate of which depends on poorly constrained factors such as e.g. the aerosol surface area. Uncertainties in modelled OH are large as are uncertainties for HNO₃ measurements, which in the boundary layer reflect deposition to surfaces, again poorly constrained. In short, uncertainties in kinetic parameters are only one factor that influence NO₂ and HNO₃ ratios and this issue is too complex to deal with properly in this manuscript.

Minor Issues:

Line 12: “molecule” is missing an “l” **Corrected**

Line 45: “being” should be “is” **Corrected**

Line 50-52. The sentence beginning “Theoretical calculations...” might better appear immediately after the discussion of the chaperone mechanism, rather than after the introduction of enhanced collider gases.

Corrected as suggested

line 68 “prevented” should be “preventing” **Corrected**

line 75: “in Tables 1 and 2.” might better be phrased as “in the notes to Tables 1 and 2.”

Corrected as suggested

It might help orient readers if the manuscript provided some idea of the conditions under which the $\text{OH} + \text{NO}_2 \rightarrow \text{HONO}_2$ is nearly in the low-pressure limit and high-pressure limit.

We added the following text

Under the conditions of T and p relevant for atmospheric chemistry, the title reaction is in the fall-off regime.

Line 102: The manuscript states that the low vapor pressure of water prevents it from being used as a bath gas by itself, but 5 Torr of water vapor is roughly equivalent of 50 Torr of He. So I think that it would be clearer to say that it is not possible to determine $k_0(\text{H}_2\text{O})$ by using pure water vapor as a bath gas.

This is correct. We prefer to remove this statement completely.

Lines 205 ff. “In other words....” It is not clear to this reader how it follows from the previous text that the total rate constant of a $\text{H}_2\text{O}-\text{N}_2$ bath gas is not the sum of individual rate constants $k_i(P_i, T)$, where $i = \text{H}_2\text{O}$ or N_2 . It seems like a step of the logic has not been made explicit, and that it would help the reader if the manuscript made the logic clearer.

Starting the sentence with “In other words” was indeed confusing.

We have removed this.

In Section 3.2.1, it would be helpful to indicate the pressures at which $k(P, 300)$ deviates by more than 10% from the low-pressure and high-pressure limits. This would help orient the reader.

It is not obvious what insight this brings as there is no physical meaning associated with a 10% deviation. We believe this would be confusing and prefer not to follow this suggestion.

Line 298: the pressures only add up to 990 mbar, not 1 bar.

We now write:

The pressure of water vapour is 34 mbar, those of O_2 and N_2 are then 210 and 756 mbar, respectively

Lines 334 ff. If I understand correctly, the manuscript takes the branching ratio between reactions (1a) and (1b) from previous work. This is equivalent to assuming that water vapor

enhances both rate constants to the same extent. This assumption should be made very explicit in the manuscript.

We have added the following sentence to make this clear.

We assume α is independent of water vapour.

Lines 432-433: Are the H-OONO and H-OONO₂ bond energies known from computational chemistry (well enough to determine which is stronger)?

We are not aware of such calculations and are not in a position to do them ourselves. The text simply introduces the possibility that the OH rate coefficients for H-OONO and H-OONO₂ are different and suggests that theoretical calculations would be useful. Hopefully, someone will conduct such calculations and calculate the relative rate coefficient.

Figure 3 lacks error bars.

The error bars are already on the plot but are in most case smaller than the symbol. We have added to the caption:

With a few exceptions, the error bars (2σ) are generally smaller than the symbols.

Table 2: The caption lists the range of [HOOH] used for the He-H₂O experiments twice. I suspect one of these is for the N₂-H₂O experiments. **Correction made.**