

Review of Amedro et al

This manuscript presents the first study of the effectiveness of H<sub>2</sub>O as a third body on the recombination of OH with NO<sub>2</sub>. This careful experimental study shows that water vapor is much more effective than N<sub>2</sub> or O<sub>2</sub> in causing recombination. It also presents a global modeling study of a new parameterization of the OH + NO<sub>2</sub> reaction as compared to the IUPAC and JPL recommendations; this parameterization uses the results of a previous study showing that O<sub>2</sub> and N<sub>2</sub> have different efficiencies in quenching the products of OH + NO<sub>2</sub>. The modeling suggests that HOONO could be a non-negligible reservoir of NO<sub>x</sub> 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.

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 N<sub>2</sub> vs O<sub>2</sub> as colliders. This should be made clear.

The enhancement of the quenching of the energized HNO<sub>3</sub> intermediate (HNO<sub>3</sub>\*) due to H<sub>2</sub>O vapor is presumably due to the strong hydrogen bonding between the two (stronger than OH-H<sub>2</sub>O or NO<sub>2</sub>-H<sub>2</sub>O). It would be good to make this explicit and add some references to the literature on the HONO<sub>2</sub>-HOH complex.

There must be previous field work measuring [NO<sub>2</sub>]/[HONO<sub>2</sub>] 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.

Minor Issues:

Line 12: "molecule" is missing an "l"

Line 45: "being" should be "is"

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.

line 68 "prevented" should be "preventing"

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

It might help orient readers if the manuscript provided some idea of the conditions under which the OH + NO<sub>2</sub> → HONO<sub>2</sub> is nearly in the low-pressure limit and high-pressure limit.

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.

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  $k(P_i, T)$ , where  $i = \text{H}_2\text{O}$  or  $\text{N}_2$ . 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.

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.

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

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.

Lines 432-433: Are the H-OONO and H-OONO<sub>2</sub> bond energies known from computational chemistry (well enough to determine which is stronger)?

Figure 3 lacks error bars.

Table 2: The caption lists the range of  $[\text{HOOH}]$  used for the He- $\text{H}_2\text{O}$  experiments twice. I suspect one of these is for the  $\text{N}_2$ - $\text{H}_2\text{O}$  experiments.