COMMENTS

Comment on "Are Vibrationally Excited Molecules a Clue for the O_3 Deficit Problem and HO_x Dilemma in the Middle Atmosphere?"

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Received: August 18, 2004

Recent measurements[1] of OH in the mesosphere are overpredicted by standard photochemical models. Coupled with underpredictions of data on HO_2 and O_3, this predictive inconsistency has led to a reexamination of the relatively simple H−O kinetics in the upper atmosphere.[2,3] Varandas[4] has proposed that reactions involving vibrationally excited O_2 and OH can explain this situation, on the basis of what is reported to be a steady-state analysis of rates derived from detailed trajectory calculations.[5] We wish to point out several problems with this analysis.

The predicted concentrations of vibrationally excited OH, $OH(v')$, in Figure 6 of the Varandas manuscript[4] unexpectedly equal or exceed those for thermal OH[6−8] ($\sim 3 \times 10^6$ cm^{-3}) and show an altitude dependence significantly different from rocket and satellite measurements of these vibrationally excited molecules. The altitude profile of vibrationally excited OH in the Earth's atmosphere is well-known through measurements of the emission from these levels in the Meinel bands.[9] The many mesospheric measurements and accompanying kinetic models of such densities,[10−13] none of which is referenced or discussed in the paper, invalidate both this altitude distribution and the amounts of $OH(v')$ by orders of magnitude. Observed maximum $OH(v' \geq 3)$ at 85 km is $<10^4$ cm^{-3}, not $\sim 10^7$ as seen in Figure 6 near 80 km. Significant amounts are found at 80−95 km, not 60−80 km shown in Figure 6. The source of this $OH(v')$ error lies in using H-atom concentrations taken from a textbook graph[14] that are over 2 orders of magnitude too large. Measured H amounts,[15] empirical and photochemical transport models,[6−8,16,17] and review articles[6,10] all point to an H-atom concentration at 75 km near 2×10^7 cm^{-3} rather than the 10^{10} of Varandas[4] and do not reach amounts above 2×10^8 at higher altitude. This error directly propagates into overstating any excited-state concentrations or kinetics effects.

Also, purported steady-state analyses are presented without detailed derivations. It appears the algebra is applied to a selected sequence or envisioned cycle of reaction steps, whereas proper analysis requires full consideration of all competing steps. More critically, multipliers are used without justification, for example applying the $H + O_3$ reaction rate 5 times in generating the $OH(v')$ expression (eq 39 and following). The net result is that the HO_x steady-state values relative to H are overstated by 5. This same general criticism may be applied to computations of the fractional effect of the enhanced mechanism on OH concentrations later in the paper.

TABLE 1: Rate Parameter Additions for the Vibrationally Excited Mechanism of Varandas[4] [a]

reaction ($k = A\,e^{-E/RT}$)	A (cm^3/molec/s)	E (cal/mole)
$H + O_3 \rightarrow OH(v') + O_2$	1.40×10^{-10}	934.
$OH + O_3 \rightarrow H + O_2 + O_2(v)$ [20%]	1.20×10^{-12}	1749.
$O_3 + h\nu \rightarrow O + O + O_2(v'')$ [73 km]	9.75×10^{-4}/s	
$O_3 + h\nu \rightarrow O(^1D) + O_2(v)$ [73 km]	7.35×10^{-3}/s	
$OH(v') + O_3 \rightarrow HO_2(v) + O_2$	1.70×10^{-11}	
$OH(v') + O_3 \rightarrow H + O_2 + O_2$	2.24×10^{-11}	
$OH(v') + M \rightarrow OH + M$	2.43×10^{-11}	
$HO_2(v) + O_3 \rightarrow OH + 2O_2$	2.00×10^{-14}	1351.
$HO_2(v) + M \rightarrow HO_2 + M$	2.43×10^{-11}	
$OH(v') + O_2(v'') \rightarrow H + O + O_2$	8.00×10^{-11}	
$O_2(v'') + O_2(v) \rightarrow O_3 + O$	8.00×10^{-12}	
$O_2(v'') + O_2 \rightarrow O_2(v) + O_2$	3.00×10^{-13}	
$O_2(v) + O_2 \rightarrow 2O_2$	4.00×10^{-15}	

[a] Base photolysis rates from Connell.[18] O_2 relaxation rates estimated from values summarized in Slanger and Copeland.[21] $v'' \geq 25$; $v' \geq 3$; $v \geq 1$.

Rather than descending into the complexities of further analysis, we have included the proposed mechanism modifications into box model simulations of the local photochemistry taken from outputs of the Lawrence Livermore National Laboratory 2-D diurnally varying model of the atmosphere.[18] This method is the simple and sure way to examine effects. The photolysis rates, kinetics rate constants,[19] species concentrations, and temperature are taken from the 2-D model output, and additional excited-state reactions are added. The selected locale is August 15 at noon, 50N latitude, for 43-, 55-, and 73-km altitudes. The added steps and rate constants are shown in Table 1. Kinetics and photolysis rates were then integrated for 5 h using the Senkin code.[20] This time is in large excess of that required to achieve a photochemical steady state. The results of the box model simulation are given in Table 2. (Small changes from the initial concentrations reflect effects of temporally varying radiation and transport in the 2-D model.) No differences in final O_3, OH, or HO_2 concentrations ($<1\%$) were observed with the added excited-state kinetics. The proposed modifications have no effect, nullifying the conclusions reported from the Varandas analysis and casting doubt on the methodology.

In addition to the problems mentioned already, there are other substantive errors. The paper assumed that $H + O_3$ is not just the main but the only source of OH (p 764), but in fact as most models show, the $O(^1D) + H_2O$ reaction dominates below 50 km, and the rapid HO_x recycling reaction $O + HO_2 \rightarrow OH + O_2$ must also be considered. Thus, an important OH-formation step is being ignored in this comparison of an excited-state production mechanism. Second, the "approach I" estimate of vibrational enhancement, which shows the larger effect, is based on eq 47. This equation erroneously double-counts the oxygen mole fraction in air (in both the $^1/_5$ factor and the $[O_2]$ term). The value and enhancement are thus artificially inflated by a factor of 5. Third, no relaxation kinetics for vibrationally excited O_2 can be found in the paper or its mechanisms. Such rate constants (mainly by O_2) are known[21] and necessary to determine the steady-state $O_2(v)$ populations and rates; if excluded from the integrated kinetics modeling, wildly excessive

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10.1021/jp0405613 CCC: $30.25

TABLE 2: Results of 5-Hour Photochemical Model Integration[a]

altitude	start O_3	start OH	start HO_2	reg. O_3	reg. OH	reg. HO_2	excit. O_3	excit. OH	excit. HO_2
km	ppm	ppb	ppb	ppm	ppb	ppb	ppm	ppb	ppb
73	0.167	4.05	1.85	0.186	3.74	1.70	0.186	3.74	1.70
55	1.46	0.867	0.403	1.55	0.827	0.383	1.55	0.827	0.383
43	4.56	0.298	0.190	4.66	0.288	0.185	4.66	0.289	0.184

[a] Last column results use Table 1 vibrationally excited mechanism additions.

amounts of O_3 and HO_x result, especially at the lower altitudes. Finally, the rate constant given for $k(33)$ on p 766 is 250 times too large.

We conclude from these facts and the direct simulations that the analysis which purports to show excited-state HO_x chemistry as a potential solution to the ozone deficit and the HO_x dilemma in upper atmosphere modeling is faulty, and demonstrate that the mechanism rate constants are insufficient to produce significant changes. Other searches for solutions will continue, but great care must be exercised in analyzing effects.

Acknowledgment. Research supported by the NASA ITM Physics Program (grants NAG5-11927, NAG5-10391, and NNG04GG05G) and the NSF Aeronomy Program (grants 99098078 and 0233523). Thanks to Dr. Peter Connell of LLNL for providing his model results.

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