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

A. J. C. Varandas*

Departamento de Quimica, Universidade de Coimbra,
3004-535 Coimbra, Portugal

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Concerning the Comment by Smith and Copeland[1] (SC) on my recent paper,[2] I note the following. First, I address their remark that I have taken the input H-atom concentrations from Figure 15.2 of the textbook by Steinfeld, Francisco, and Hase.[3] This is an excellent textbook, and I trusted that any quantitative differences from other measurements should not be of the utmost concern. In fact, despite the commented[1] two-orders-of-magnitude difference with other measured H amounts,[4−8] the general conclusions then reported[2] will be shown to remain largely unaffected. Moreover, the SC point of view may not be shared by other atmospheric researchers. For example, Takahashi et al.[9] report H amounts derived from simultaneous measurements of the vertical profiles of upper atmospheric airglow emissions and atmospheric sodium that vary from 10^9 cm^{-3} at 85 km to 10^8 cm^{-3} at 100 km. Besides remarking on satellite data taken in the equatorial region[7] that show both [H] and [O_3] to have strong semiannual variations, they emphasize[9] that their rocket experiments point to much higher values than those determined from other rocket observations at middle and high latitudes. The observed and fitted profiles are shown in Figure 1; see also Figure 5 of ref 9, where values up to near 10^{10} cm^{-3} are inferred at 82−85 km, and Figure 7.10 of Wayne’s[10] specialized textbook where H concentrations from the same authors inferred from the O_2 atmospheric band are also selected.

In ref 2, I have also assumed that the H + O_3 reaction is the key source of vibrationally “hot” OH. In fact, although other sources of OH(v') are well-established,[1] the H + O_3 reaction is known to play a crucial role in the mesosphere since the correct assignment by Meinel[11] of the near-IR nighttime airglow in the mesopause to such radicals. Moreover, the inclusion of further OH sources such as the O(^{1}D) + H_2O reaction or the water-vapor photolysis would complicate and probably unbalance (by omission of other relevant reactions) the model, thence forbidding an analysis that aims at capturing the essentials of mesospheric chemistry. Of course, if included, this reaction contributes at low altitudes both to OH and OH($v' \leq 4$) production, being difficult to anticipate how it may affect the final ratio of additional OH production, F^{OH}.

I now turn to the double-counting of the oxygen mole fraction in air. I agree with SC that the factor of $^1/_5$ is not necessary in eq 47 of ref 2. For the same reason, the downscale factor for the $F_{ij}^{O_3}$ ratios in Figure 10 of ref 2 should be ∼0.4. Another remark concerns the SC suggestion[1] that I have used a rate constant k_{33} on p 766 of ref 2 that is 250 times too large. It would be true if compared with the rate constant for the reaction OH(v') + O_3 with $v' = 0$. However, k_{33} accounts for vibrational states of OH that do not form hydroperoxyl radicals with an average vibrational energy content exceeding the H + O_2 dissociation asymptote, which occurs for $v' \leq 4$. This explains the decision of choosing a value of k_{33} that corresponds to $v' = 4$. Indeed, as pointed out elsewhere,[2] the use of a smaller value of k_{33} may only enhance the ratio of additional HO_2 production, F^{HO_2}, thence further emphasizing the major results. For this reason, I use the same value of k_{33} in replying to their Comment.

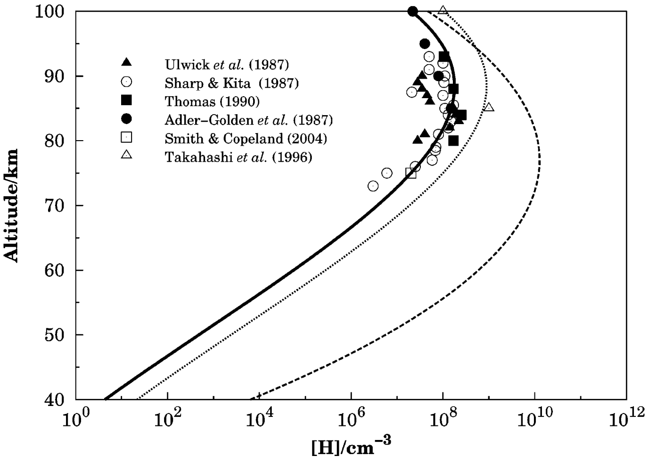

Figure 1. Absolute densities of atomic hydrogen as a function of altitude z. The dots show data extracted by eye from various sources.[4,5,7−9] The lines indicate the fit employed in ref 2 (dashed line), the fit now used (solid line), $\log[H] = -3.7813 + 3.0766 \times 10^{-3}z^2 - 1.9667 \times 10^{-7}z^4$, and the latter upscaled by 5. Shown by the open square is the point recommended by SC.[1] Note that the data of Takahashi et al.[9] has not been included in the least-squares fit. For the error bars, see the original papers.

It has also been remarked[1] that no allowance is made in ref 2 for the relaxation of vibrationally excited O_2. It turns out that I have used steady-state (ss) populations[12] for $O_2(v'')$, and hence, relaxation is assumed to have been taken into account. It should be pointed out that we have most recently[13] analyzed the fact that the efficiency of the triplet-state channel of O_3 photodissociation may decrease with altitude. Although quantitative differences are observed in the ratio of additional O_3 production when compared to the results of ref 2, the essential qualitative trends remain unaltered. Note that other sources of vibrationally hot O_2 may come into play in the upper middle atmosphere. First, relatively large densities of atomic oxygen exist there, and hence, the three-body recombination process O(^{3}P) + O(^{3}P) + M → O_2* + M appears as a natural candidate; M is, in principle, N_2, O_2, or O(^{3}P), and O_2* is any of the seven electronic states of molecular oxygen lying below the first dissociation limit, namely $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$, $c^1\Sigma_u^-$, $A^3\Delta_u$, $A^3\Sigma_g^+$, and $^5\Pi_g$. Although pure statistics would predict the state $^3\Sigma_g^-$ to be formed in only 12% of the collisions, it is recognized[14] that the nascent distribution may not be closely linked to actual observations. Note also that advances in nightglow observations and laboratory experiments suggest that the lowest states contain broad distributions of vibrational states, some corresponding to fairly high values of v''.[14] Thus, if energetics is also taken into account, it seems plausible that the ground electronic state may be at least similarly populated. Additionally, we have shown[15−17] that the O + OH(v') and O + HO_2(v) reactions may under LTD yield appreciable fractions of $O_2(v'')$ with excitations up to $v'' = 25$. Because LTD may be of concern in the upper stratosphere and mesosphere where O atoms (most determinations[10] support the view that [O] ≫ [O_3] at such

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* E-mail: varandas@qtvsl1.qui.uc.pt.

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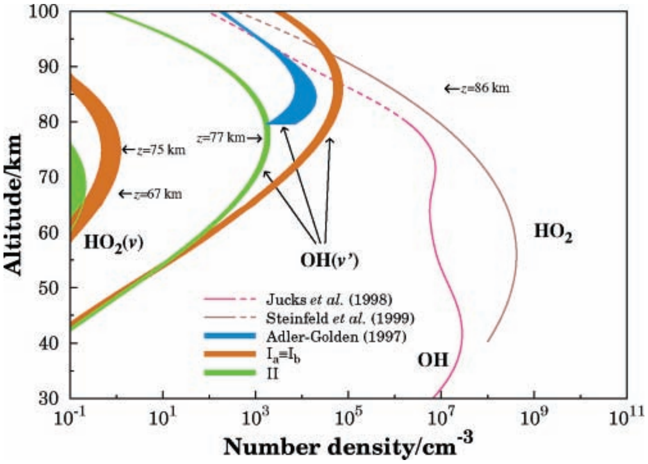

Figure 2. Newly determined dependences on altitude of $[OH(v')]_{ss}$ and $[HO_2(v)]_{ss}$. In this and the following plots, the curves have been labeled as in ref 2, with the shaded areas delimiting the minimum and maximum values and the arrows indicating the positions of the maxima. Also shown are the profiles for the total concentrations of OH,[20] HO_2,[3] and $OH(v')$ from ref 19. The extrapolated curves are shown as dashed lines; see the text.

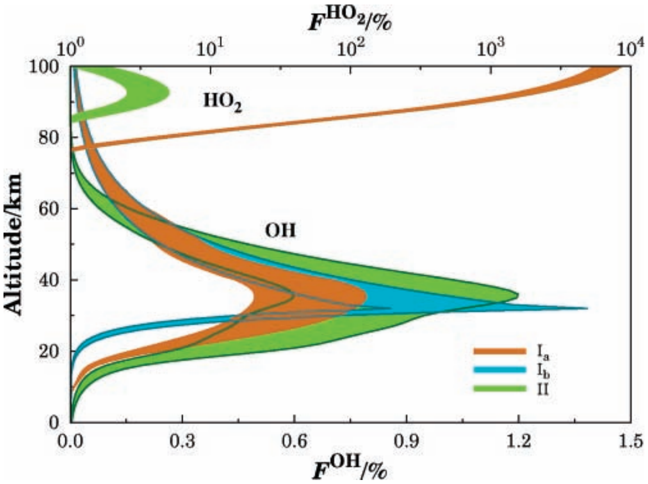

Figure 3. Newly determined dependences on altitude of the ratios F^{OH} and F^{HO_2}.

altitudes) and vibrationally excited OH and HO_2 are likely to be abundant, the assumption that the rate of $O_2(v'')$ production is significant is probably a fair one.

Besides the changes reported in the preceding paragraph, I have satisfied the SC remark of not considering the stoichiometric factors in the steady-state analysis. Being a legitimate proposition under the assumption of a competitive set of elementary reactions, it provides an additional test on the model predictions. It should be emphasized that this by no means implies that the remaining uncertainties in the parameters cannot compensate at least in part the downscaling hereby introduced in $[OH(v')]_{ss}$ and F^{OH}. In particular, the value of[2] $\xi = 0.095$ obtained from the steady-state distribution may be overestimated, because the vibrational relaxation rate constants calculated from trajectory studies[12,18] are at room temperature more than threefold larger than the ones inferred from experiment. The results now obtained are displayed in Figures 2−4. As expected, significant differences are visible when comparing with the plots originally reported,[2] which is largely because of the drastically smaller H densities now employed. Note that no attempt has been made in ref 2 to reduce the excessive amount of $OH(v')$ predicted by the model, although the formulas clearly indicate that $[OH(v')]_{ss}$ is strongly dependent on the input [H] values.

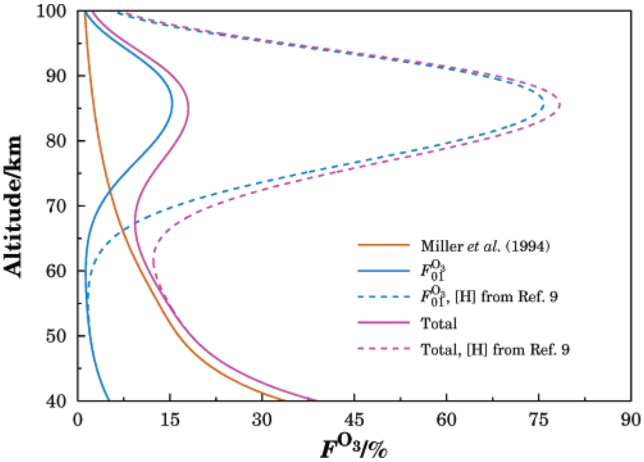

Figure 4. A comparison of the new $F_{01}^{O_3}$ ratios (downscaled by a factor of 0.36) for the HO_x mechanisms with the Wodtke[22] O_x results obtained from the input data used in the present work. Shown by the solid magenta line is their sum (i.e., the total ratio of additional O_3 production). The dashed lines indicate the results obtained by using the [H] vs z curve that matches the points of Takahashi et al;[9] see Figure 1.

Thus, the predictions are genuine in the sense that no attempt has been made[2] to fit any available estimates[19] for the dependence with altitude of $[OH(v')]$. Indeed, I was unaware of such data at the time of publication. Similarly, the H density now used is obtained from a least-squares fitting procedure to (1) the data points of the various profiles,[4,5,7,8] each being assigned a unit weight except if the point corresponds to the maximum [H] value or to an altitude of 100 km, in which case the assigned weight was 10 or 100 (this value has only been considered for the maximum of the more recent set[8]), (2) an extra point of 2×10^7 cm^{-3} at 75 km carrying a weight of 10 to satisfy the SC requirement[1] that most empirical and photochemical transport models and review articles point to such a result. The fit so obtained predicts at 75 km an H density of 2.0×10^7 cm^{-3}, while at 40 km, it yields a value 3 orders of magnitude smaller than that of ref 3! Thus, it provides a very stringent test of the model, having in mind that the more recent rocket measurements of Takahashi et al.[9] cast some doubt on the low [H] profiles now employed (Figure 1 shows that the numerical data taken from the abstract of their paper is fivefold larger).

Figure 2 shows that the results for $[OH(v')]_{ss}$ and $[HO_2(v)]_{ss}$ follow general trends qualitatively similar to those previously reported.[2] Interestingly, the newly predicted densities of $OH(v')$ are found to bracket the values reported by Adler-Golden.[19] He has constructed a state-to-state kinetic model for the Meinel bands of OH from experimental rate constants and Einstein A coefficients jointly with an empirical parametrization of $OH(v')$ quenching by O_2, having predicted the $OH(v')$ densities shown in Figure 2; the bottom and top lines indicate the total densities for $v' \geq 3$ and $v' \geq 1$, respectively. To my knowledge, no estimates of the $[HO_2(\boldsymbol{v})]$ profile have been reported thus far. As expected, the new $HO_2(\boldsymbol{v})$ densities are drastically smaller than those of ref 2, which is also partly due to the smallness of $[O_3]$/ppmv above 70 km as predicted from the fitted curve.[2] Note that the maximum in the $[OH(v')]_{ss}$ profile is correctly displaced to higher altitudes, $77 \leq z/\text{km} \leq 86$, which correlates with the shift in the location of the [H] maximum. A similar upward shift is observed for $[HO_2(\boldsymbol{v})]_{ss}$, with the maximum being located at $67 \leq z/\text{km} \leq 75$. Recall[2] that the [OH] profile is, strictly speaking, valid only up to 80 km, while the O_3 mixing ratio is rather uncertain above that altitude where it probably dies off too suddenly. As a result, the predicted $HO_2(v)$ densities are likely to be underestimated, with the maximum possibly occurring at a somewhat too low altitude. Note also that the extrapolation of the [OH] profile of Jucks et al.[20] crosses those of method I and Adler-Golden[19] for $[OH(v')]$ above 95 km, which may reflect the previously discussed difficulties, besides inaccuracies in the [OH] fit. In turn, Figure 3 shows the newly predicted ratios of additional OH and HO_2 production with respect to the conventional mechanisms. It is seen that the peak in F^{OH} reduces to $1.1 \pm 0.3\%$ which is at least a factor of 5 smaller than observed (i.e., $16 \pm 10\%$, as estimated from the shaded area and model A in Figure 2 of ref 21) but remains centered[2] near 40 km. However, a value of $\xi = 0.02$ would suffice to make the prediction fall within the error bar of the observed peak. A further remark to note that F^{HO_2} under the present conditions is significant only above 80 km.

From a corresponding analysis, the fraction of additional odd oxygen production relative to the rate of O_3 formation in the conventional mechanism ($O_2 + h\nu \rightarrow O + O$) now assumes the form

$$F_{01}^{O_3} = \left\{ \frac{k}{2k_D} \left(R_{v'' \geq v''_0} R_{\lambda_0} J_{O_3 \rightarrow O(^3P)} + k_{16}[H] \right) + 2\left(\frac{k_{22}}{k'_D} - \frac{k}{4k_D} \right) k_{17}[OH] \right\} \frac{[O_3]}{2J_{O_2}[O_2]}$$

where the symbols and numerical values used are as in ref 2. Note that there is now no need to divide by 4 to obtain the rate per photon, because only one such photon is now involved. Figure 4 shows that the sum of the Wodtke[22] and $F_{01}^{O_3}$ ratios reaches a maximum of 19% at 87 km. This will be enhanced over four times if the [H] profile is chosen to mimic the more recent data.[9] Such results appear consistent with other suggestions[23] and may provide evidence corroborating the observed[9,24,25] wide ozone peak(s) in the upper mesosphere.

I finally turn to the results reported by SC. They have carried out box model simulations of the local photochemistry taken from outputs of the Lawrence Livermore National Laboratory 2-D diurnally varying model of the atmosphere[26] by including the reactions involving vibrationally excited species suggested elsewhere.[2] By fixing a series of input requirements and simulation parameters, SC conclude[1] that their method “is the simple and sure way to examine effects”. Without wishing to criticize such a strong statement or descend into the complexities of understanding how their simulation works, I make a few observations. First, the authors base the rate of $O_2(v'')$ production on the O_3 photolysis by solar radiation at 73 km which, as noted already, may seriously underpredict the true (to our knowledge, unknown) value at such altitudes.[15,17] Moreover, SC consider only $O_2(v'')$ species with $v'' \geq 25$, whereas a more correct simulation should employ[17,27] combinations with ($v' \geq 3$; $v'' \geq 13$). Additionally, it is not clear what input $[O_2(v'')]$ and $[OH(v')]$ profiles have been used in the simulation, nor the sources and magnitudes of some of the rate constants employed for the reactions involving vibrationally hot species. In fact, it is not obvious whether a full treatment of the involved chemistry under LTD has been considered rather than equilibrated Boltzmann distributions. Finally, if the authors take vibrational relaxation into account, they should have utilized nascent distributions and the corresponding rate constants rather than steady-state ones.

In summary, it appears fair to claim that the model described elsewhere[2] still pinpoints the basic features of the title ozone-related issues: the peak in F^{OH} at about 40 km and the O_3 surplus in the mesosphere. Clearly, as happens in most schemes, this may partly be due to the assumed simplifications, particularly in the calculation of the steady-state distributions. However, it seems too soon to know an answer prior to improved altitude profiles of the O_3 and H (this is possibly the most difficult one to measure directly[9]) densities, and also box simulations that include a more realistic description of the chemistry of vibrationally excited OH and O_2, both in relaxation and reactive processes. In this context, I restate the belief[17] that LTD should be considered in such simulations, as it may help to unfold the title mesospheric mysteries.

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