***This document contains supplementary materials (Table of reactions and associated notes such as the rationale for the choice of the reaction rate coefficients and literature references) that were too large to be put in the paper entitled:***

# AN INTRIGUING PHOTOSENSITIZED HETEROGENEOUS SINK OF NITROUS OXIDE:

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The paper is currently under final stages of the Editor's consideration for publication in ***Applied Surface Science***.

*The theme of the paper is summarized by the following abstract extracted from the paper*:

Nitrous oxide ($N_2O$) seems to be efficiently destroyed at the room temperature on surfaces of quartz or Pyrex photolysis cells exposed simultaneously to UV radiation (254 # 8 # 300 nm) and ozone ($O_3$). Compared to the well-known loss of $N_2O$ on various surfaces (including quartz/sand) at high temperatures the new loss process is intriguing. The intriguing aspect is that a combination of UV photons and a gas, rather than the elevated temperature, was instrumental in the surface loss of $N_2O$. Further studies of the loss process might reveal potential useful roles of analogous processes in environmental catalysis and atmospheric chemistry.

Table 1. Listing of the Reactions Used in the Present Study

(Rate Coefficients are in the form $A(300/T)^n \exp(-\varepsilon/T)$ $cm^3s^{-1}$, with T as the temperature)

| | Reactions | | | | A | n | ε |
|---|---|---|---|---|---|---|---|
| 1. | $O_3$ | + hv | P O | + $O_2$v23 | 8.79e-04 | 0.00e 00 | 0.00e 00 |
| 2. | $O_3$ | + hv | P O | + $O_2$v22 | 1.63e-03 | 0.00e 00 | 0.00e 00 |
| 3. | $O_3$ | + hν | 6 O | + $O_2$v21 | 2.53e-03 | 0.00e 00 | 0.00e 00 |
| 4. | $O_3$ | + hν | 6 O | + $O_2$v20 | 3.26e-03 | 0.00e 00 | 0.00e 00 |
| 5. | $O_3$ | + hν | 6 O | + $O_2$v19 | 3.42e-03 | 0.00e 00 | 0.00e 00 |
| 6. | $O_3$ | + hν | 6 O | + $O_2$v18 | 2.89e-03 | 0.00e 00 | 0.00e 00 |
| 7. | $O_3$ | + hν | 6 O | + $O_2$v17 | 1.96e-03 | 0.00e 00 | 0.00e 00 |
| 8. | $O_3$ | + hν | 6 O | + $O_2$v16 | 1.10e-03 | 0.00e 00 | 0.00e 00 |
| 9. | $O_3$ | + hν | 6 O | + $O_2$v15 | 6.57e-04 | 0.00e 00 | 0.00e 00 |
| 10. | $O_3$ | + hν | 6 O | + $O_2$v14 | 6.96e-04 | 0.00e 00 | 0.00e 00 |
| 11. | $O_3$ | + hν | 6 O | + $O_2$v13 | 1.20e-03 | 0.00e 00 | 0.00e 00 |
| 12. | $O_3$ | + hν | 6 O | + $O_2$v12 | 2.21e-03 | 0.00e 00 | 0.00e 00 |
| 13. | $O_3$ | + hν | 6 O | + 3$O_2$v<12 | 7.78e-02 | 0.00e 00 | 0.00e 00 |
| 14. | $O_3$ | + hν | 6 O($^1$D) | + $O_2$ | 9.00e-01 | 0.00e 00 | 0.00e 00 |
| 15. | $O_2$v23 | + $N_2$ | 6 $O_2$v22 | + $N_2$ | 8.00e-15 | 0.00e 00 | 0.00e 00 |
| 16. | $O_2$v22 | + $N_2$ | 6 $O_2$v20 | + $N_2$ | 7.00e-15 | 0.00e 00 | 0.00e 00 |
| 17. | $O_2$v21 | + $N_2$ | 6 $O_2$v19 | + $N_2$ | 1.90e-14 | 0.00e 00 | 0.00e 00 |
| 18. | $O_2$v20 | + $N_2$ | 6 $O_2$v18 | + $N_2$ | 2.30e-14 | 0.00e 00 | 0.00e 00 |
| 19. | $O_2$v19 | + $N_2$ | 6 $O_2$v17 | + $N_2$ | 2.80e-14 | 0.00e 00 | 0.00e 00 |
| 20. | $O_2$v18 | + $N_2$ | 6 $O_2$v16 | + $N_2$ | 2.00e-14 | 0.00e 00 | 0.00e 00 |
| 21. | $O_2$v17 | + $N_2$ | 6 $O_2$v15 | + $N_2$ | 2.00e-14 | 0.00e 00 | 0.00e 00 |
| 22. | $O_2$v16 | + $N_2$ | 6 $O_2$v14 | + $N_2$ | 7.74e-15 | 0.00e 00 | 0.00e 00 |
| 23. | $O_2$v15 | + $N_2$ | 6 $O_2$v14 | + $N_2$ | 8.17e-15 | 0.00e 00 | 0.00e 00 |
| 24. | $O_2$v14 | + $N_2$ | 6 $O_2$v13 | + $N_2$ | 7.50e-15 | 0.00e 00 | 0.00e 00 |
| 25. | $O_2$v13 | + $N_2$ | 6 $O_2$v12 | + $N_2$ | 4.50e-15 | 0.00e 00 | 0.00e 00 |
| 26. | $O_2$v12 | + $N_2$ | 6 $O_2$ | + $N_2$ | 2.20e-15 | 0.00e 00 | 0.00e 00 |
| 27. | $O_2$v23 | + $O_2$ | 6 $O_2$v22 | + $O_2$ | 1.20e-14 | 0.00e 00 | 0.00e 00 |
| 28. | $O_2$v22 | + $O_2$ | 6 $O_2$v21 | + $O_2$ | 5.40e-14 | 0.00e 00 | 0.00e 00 |
| 29. | $O_2$v21 | + $O_2$ | 6 $O_2$v20 | + $O_2$ | 5.80e-15 | 0.00e 00 | 0.00e 00 |
| 30. | $O_2$v20 | + $O_2$ | 6 $O_2$v19 | + $O_2$ | 3.30e-15 | 0.00e 00 | 0.00e 00 |
| 31. | $O_2$v19 | + $O_2$ | 6 $O_2$v18 | + $O_2$ | 4.70e-15 | 0.00e 00 | 0.00e 00 |
| 32. | $O_2$v18 | + $O_2$ | 6 $O_2$v17 | + $O_2$ | 4.00e-15 | 0.00e 00 | 0.00e 00 |
| 33. | $O_2$v17 | + $O_2$ | 6 $O_2$v16 | + $O_2$ | 8.43e-15 | 0.00e 00 | 0.00e 00 |
| 34. | $O_2$v16 | + $O_2$ | 6 $O_2$v15 | + $O_2$ | 9.45e-15 | 0.00e 00 | 0.00e 00 |
| 35. | $O_2$v15 | + $O_2$ | 6 $O_2$v14 | + $O_2$ | 1.34e-15 | 0.00e 00 | 0.00e 00 |

Table 1. Listing of the Reactions Used in the Present Study (cont.)
(Rate Coefficients are in the form $A(300/T)^n \exp(-\varepsilon/T)$ $cm^3 s^{-1}$, with T as the temperature)

| | Reactions | | | | | | A | n | ε |
|---|---|---|---|---|---|---|---|---|---|
| 36. | $O_2$v14 | + $O_2$ | | P $O_2$v13 | + $O_2$ | | 1.30e-14 | 0.00e 00 | 0.00e 00 |
| 37. | $O_2$v13 | + $O_2$ | | P $O_2$v12 | + $O_2$ | | 1.50e-14 | 0.00e 00 | 0.00e 00 |
| 38. | $O_2$v12 | + $O_2$ | | P $O_2$ | + $O_2$ | | 1.60e-14 | 0.00e 00 | 0.00e 00 |
| 39. | $O_2$v23 | + $O_3$ | | P $O_2$ | + $O_2$ | + O | 1.00e-11 | 0.00e 00 | 0.00e 00 |
| 40. | $O_2$v22 | + $O_3$ | | 6 $O_2$ | + $O_2$ | + O | 1.00e-11 | 0.00e 00 | 0.00e 00 |
| 41. | $O_2$v21 | + $O_3$ | | 6 $O_2$ | + $O_2$ | + O | 1.00e-11 | 0.00e 00 | 0.00e 00 |
| 42. | $O_2$v20 | + $O_3$ | | 6 $O_2$ | + $O_2$ | + O | 1.00e-11 | 0.00e 00 | 0.00e 00 |
| 43. | $O_2$v19 | + $O_3$ | | 6 $O_2$ | + $O_2$ | + O | 1.00e-11 | 0.00e 00 | 0.00e 00 |
| 44. | $O_2$v18 | + $O_3$ | | 6 $O_2$ | + $O_2$ | + O | 1.00e-11 | 0.00e 00 | 0.00e 00 |
| 45. | $O_2$v17 | + $O_3$ | | 6 $O_2$ | + $O_2$ | + O | 1.00e-11 | 0.00e 00 | 0.00e 00 |
| 46. | $O_2$v16 | + $O_3$ | | 6 $O_2$ | + $O_2$ | + O | 1.00e-11 | 0.00e 00 | 0.00e 00 |
| 47. | $O_2$v15 | + $O_3$ | | 6 $O_2$ | + $O_2$ | + O | 1.00e-11 | 0.00e 00 | 0.00e 00 |
| 48. | $O_2$v14 | + $O_3$ | | 6 $O_2$ | + $O_2$ | + O | 1.00e-11 | 0.00e 00 | 0.00e 00 |
| 49. | $O_2$v13 | + $O_3$ | | 6 $O_2$ | + $O_2$ | + O | 1.00e-11 | 0.00e 00 | 0.00e 00 |
| 50. | $O_2$v12 | + $O_3$ | | 6 $O_2$ | + $O_2$ | + O | 1.00e-11 | 0.00e 00 | 0.00e 00 |
| 51. | $O_2$v23 | + $N_2O$ | | 6 $NO_2$ | + NO | | 1.80e-14 | 0.00e 00 | 0.00e 00 |
| 52. | $O_2$v22 | + $N_2O$ | | 6 $NO_2$ | + NO | | 1.80e-14 | 0.00e 00 | 0.00e 00 |
| 53. | $O_2$v21 | + $N_2O$ | | 6 $NO_2$ | + NO | | 1.80e-14 | 0.00e 00 | 0.00e 00 |
| 54. | $O_2$v20 | + $N_2O$ | | 6 $NO_2$ | + NO | | 1.80e-14 | 0.00e 00 | 0.00e 00 |
| 55. | $O_2$v19 | + $N_2O$ | | 6 $NO_2$ | + NO | | 1.80e-14 | 0.00e 00 | 0.00e 00 |
| 56. | $O_2$v18 | + $N_2O$ | | 6 $NO_2$ | + NO | | 1.80e-14 | 0.00e 00 | 0.00e 00 |
| 57. | $O_2$v17 | + $N_2O$ | | 6 $NO_2$ | + NO | | 1.80e-14 | 0.00e 00 | 0.00e 00 |
| 58. | $O_2$v16 | + $N_2O$ | | 6 $NO_2$ | + NO | | 1.80e-14 | 0.00e 00 | 0.00e 00 |
| 59. | $O_2$v15 | + $N_2O$ | | 6 $NO_2$ | + NO | | 1.80e-14 | 0.00e 00 | 0.00e 00 |
| 60. | $O_2$v14 | + $N_2O$ | | 6 $NO_2$ | + NO | | 1.80e-14 | 0.00e 00 | 0.00e 00 |
| 61. | $O_2$v13 | + $N_2O$ | | 6 $NO_2$ | + NO | | 1.80e-14 | 0.00e 00 | 0.00e 00 |
| 62. | $O_2$v12 | + $N_2O$ | | 6 $NO_2$ | + NO | | 1.80e-14 | 0.00e 00 | 0.00e 00 |
| 63. | $O_2$ | + O | + $N_2$ | 6 $O_3$ | + $N_2$ | | 6.00e-34 | 2.30e 00 | 0.00e 00 |
| 64. | O | + O | + $N_2$ | 6 $O_2$ | + $N_2$ | | 5.36e-34 | 1.00e 00 | 0.00e 00 |
| 65. | O | + O | + $N_2$ | 6 $O_2(c)$ | + $N_2$ | | 2.82e-34 | 1.00e 00 | 0.00e 00 |
| 66. | $O_3$ | + O | | 6 $O_2$ | + $O_2$ | | 2.00e-12 | 0.00e 00 | 2.06e 03 |
| 67. | $O_3$ | + O | | 6 $O_2$ | + $O_2(\nu=23)$ | | 6.00e-12 | 0.00e 00 | 2.06e 03 |
| 68. | $O_2(^1\Delta)$ | + $N_2$ | | 6 $O_2$ | + $N_2$ | | 1.00e-20 | 0.00e 00 | 0.00e 00 |
| 69. | $O_2(^1\Delta)$ | + $O_2$ | | 6 $O_2$ | + $O_2$ | | 3.60e-18 | 0.00e 00 | 2.20e 03 |
| 70. | $O_2(^1\Delta)$ | + $O_3$ | | 6 $O_2$ | + $O_2$ | + O | 4.00e-15 | 0.00e 00 | 0.00e 00 |
| 71. | $O(^1D)$ | + $N_2$ | | 6 O | + $N_2$ | | 1.80e-11 | 0.00e 00 | -1.10e 02 |
| 72. | $O(^1D)$ | + $O_2$ | | 6 O | + $O_2(b)$ | | 3.20e-11 | 0.00e 00 | -7.00e 01 |

Table 1. Listing of the Reactions Used in the Present Study (cont.)
(Rate Coefficients are in the form $A(300/T)^n\exp(-\varepsilon/T)$ $cm^3s^{-1}$, with T as the temperature)

| | Reactions | | | | | | A | n | ε |
|---|---|---|---|---|---|---|---|---|---|
| 73. | $O(^1D)$ | + $N_2O$ | | 6 $N_2$ | + $O_2$ | | 4.90e-11 | 0.00e 00 | 0.00e 00 |
| 74. | $O(^1D)$ | + $N_2O$ | | 6 NO | + NO | | 6.70e-11 | 0.00e 00 | 0.00e 00 |
| 75. | $O(^1D)$ | + $O_3$ | | 6 $O_2$ | + $O_2$(c) | | 6.00e-11 | 0.00e 00 | 0.00e 00 |
| 76. | $O(^1D)$ | + $O_3$ | | 6 $O_2$ | + $O_2$(b) | | 6.00e-11 | 0.00e 00 | 0.00e 00 |
| 77. | $O(^1D)$ | + $O_3$ | | 6 $O_2$ | + $O_2$ | + O | 1.20e-10 | 0.00e 00 | 0.00e 00 |
| 78. | NO | + $O_3$ | | 6 $NO_2$ | + $O_2$ | | 2.00e-12 | 0.00e 00 | 1.40e 03 |
| 79. | $NO_2$ | + O | | 6 NO | + $O_2$ | | 9.00e-12 | 0.00e 00 | -1.20e 02 |
| 80. | $NO_2$ | + hν | | 6 NO | + O | | 1.70e 00 | 0.00e 00 | 0.00e 00 |
| 81. | NO | + O | + $N_2$ | 6 $NO_2$ | + $N_2$ | | 1.35e-30 | 0.00e 00 | 0.00e 00 |
| 82. | $NO_2$ | + O | + $N_2$ | 6 $NO_3$ | + $N_2$ | | 9.00e-31 | 2.00e 00 | 0.00e 00 |
| 83. | $NO_3$ | + O | | 6 $O_2$ | + $NO_2$ | | 1.00e-11 | 0.00e 00 | 0.00e 00 |
| 84. | $NO_3$ | + NO | | 6 $NO_2$ | + $NO_2$ | | 1.50e-11 | 0.00e 00 | -1.70e 02 |
| 85. | $NO_3$ | + $NO_2$ | + $N_2$ | 6 $N_2O5$ | + $N_2$ | | 2.00e-30 | 3.90e 00 | 0.00e 00 |
| 86. | $N_2O_5$ | + hν | | 6 $NO_3$ | + $NO_2$ | | 2.78e-02 | 0.00e 00 | 0.00e 00 |
| 87. | $O_2$(b) | + $N_2$ | | 6 $O_2$ | + $N_2$ | | 2.00e-15 | 0.00e 00 | 0.00e 00 |
| 88. | $O_2$(b) | + $O_2$ | | 6 $O_2$ | + $O_2$ | | 3.90e-17 | 0.00e 00 | 0.00e 00 |
| 89. | $O_2$(b) | + $O_3$ | | 6 O | + $O_2$ | + $O_2$ | 1.60e-11 | 0.00e 00 | 0.00e 00 |
| 90. | $O_2$(b) | + $O_3$ | | 6 $O_2$ | + $O_3$ | | 6.60e-12 | 0.00e 00 | 0.00e 00 |
| 91. | $O_2$(b) | + O | | 6 $O_2$ | + O | | 8.00e-14 | 0.00e 00 | 0.00e 00 |
| 92. | $O_2$(b) | + $N_2O$ | | 6 $N_2$ | + $O_3$ | | 2.00e-12 | 0.00e 00 | 1.00e 03 |
| 93. | $O_2$(b) | + $N_2O$ | + $N_2$ | 6 $NO_2$ | + NO | + $N_2$ | 5.00e-34 | 0.00e 00 | 0.00e 00 |
| 94. | $O_2$(c) | + $O_3$ | | 6 $O_2$ | + $O_2$ | + O | 1.00e-11 | 0.00e 00 | 0.00e 00 |
| 95. | $O_2$(c) | + $N_2$ | | 6 $O_2$(b) | + $N_2$ | | 1.00e-15 | 0.00e 00 | 0.00e 00 |
| 96. | $O_2$(c) | + $O_2$ | | 6 $O_2$(b) | + $O_2$ | | 3.00e-14 | 0.00e 00 | 0.00e 00 |
| 97. | $O_2$(c) | + $N_2O$ | | 6 $N_2$ | + $O_3$ | | 4.00e-13 | 0.00e 00 | 0.00e 00 |
| 98. | $N_2O$ | + $O_3$ | + $N_2$ | 6 $N_2O.O_3$ | + $N_2$ | | 4.00e-33 | 0.00e 00 | 0.00e 00 |
| 99. | $N_2O.O_3$ | + $N_2$ | | 6 $N_2O$ | + $O_3$ | | 1.00e-11 | 0.00e 00 | 2.44e 03 |
| 100. | $N_2O.O_3$ | +hν | | 6 NO | + NO | + $O_2$ | 5.00e-01 | 0.00e 00 | 0.00e 00 |
| 101. | $N_2O.O_3$ | +hν | | 6 $N_2$ | + $O_2$ | + $O_2$ | 5.00e-01 | 0.00e 00 | 0.00e 00 |
| 102. | $N_2O$ | + O | + $N_2$ | 6 $N_2O.O$ | + $N_2$ | | 4.00e-33 | 0.00e 00 | 0.00e 00 |
| 103. | $N_2O.O$ | + $N_2$ | | 6 $N_2O$ | + O | + $N_2$ | 1.00e-11 | 0.00e 00 | 2.09e 03 |
| 104. | $N_2O.O$ | + O | | 6 $N_2O$ | + $O_2$ | | 1.00e-11 | 0.00e 00 | 0.00e 00 |
| 105. | $N_2O.O$ | + $O_3$ | | 6 $N_2OOO^*$ | + $O_2$ | | 8.00e-12 | 0.00e 00 | 2.06e 03 |
| 106. | $N_2O.O$ | + $O_3$ | | 6 $N_2O$ | + $O_2$ | + $O_2$ | 7.20e-11 | 0.00e 00 | 2.06e 03 |
| 107. | $N_2OOO^*$ | | | 6 $N_2$ | + $O_3$ | | 1.00e 10 | 0.00e 00 | 0.00e 00 |

## Explanatory notes:

The following twenty six species were considered: $N_2O$, $O_3$, $O(^1D)$, O, $O_2(c^1\Sigma)$, $O_2(b^1\Sigma)$, $O_2(^1\Delta)$, $O_2$, $O_2(v)$ with $v$ ranging from 23 to 12, $N_2OCO_3$, $N_2OCO$, NO, $NO_2$, $NO_3$, $N_2O_5$. All photo rates are in the unit of the total photodissociation rate for $O_3$. ***Many of the reactions are purely hypothetical and their rate coefficients have been stretched to the limit.*** This has been done to show that the rapid destruction of $N_2O$ observed by Black et al cannot be explained by conceivable gas phase reactions even after stretching the reaction rate coefficient and products to the limit whenever possible.

**Reactions 1 to 14:** It is assumed that 90% of the $O_3$ photodissociation at 254 nm produce $O(^1D)$ and $O_2(^1\Delta_g)$, while the remaining 10% produce highly vibrationally excited $O_2$ with $v \leq 23$ and $O(^3P)$. Vibrational levels below $v$ =12 were not considered since they may not destroy $N_2O$. It was thus assumed that once $v$ =12 is deactivated it is no different from $O_2$ in the $v$ =0 vibrational state for our purpose. The nascent vibrational state population was based on Patten et al. [25] study. The total J-value ($=2.17\times10^{-3}\ s^{-1}$) was a parameter determined by fitting the experimental data.

**Reactions 15 to 38:** The rate coefficients for the deactivation of $O_2$ vibrational levels ($14\leq v \leq23$) by $N_2$ and $O_2$ via both one and two quantum processes were taken from Mack et al. [19] Two gaps in their data were filled in by pure guesses. The same for the vibrational levels $v$ = 12 and 13 were from Park and Slanger [18].

**Reactions 39 to 50:** Assumed on the basis of Park and Slanger [18].

**Reactions 51 to 62:** The estimates for the rate constants of the reactions (51) through (62) in the Table are based on the following two assumptions. It is assumed that termolecular insertion of $N_2O$ into $O_2$ is possible when $O_2$ is vibrating with a large vibrational quantum number leading to a large internuclear distance between the two O-atoms and approaching $N_2O$ sideways. It is also assumed that species resulting from this termolecular process is the same as the $N_2O_3$ specie formed by the termolecular association between NO and $NO_2$ and it therefore almost immediately collisionally break apart. The rate constant for this termolecular association was assumed to be $10^{-35}\ cm^6\ s^{-1}$. With this assumption the effective rate constant for the reactive removal of $O_2$(high $v$) by $N_2O$ is at the 1% level of the rate constants for removal by the v-v transfer process measured by Mack et al. [19].

**Reaction 63:** From Demore et al. [26]

**Reactions 64 and 65:** The $O_2(c^1\Sigma)$ may be produced in Black et al. experiments by the O, O recombination. The choice for the probability of the $O_2$(c) formation in O, O recombination was based upon the results of airglow studies by Bates [27], and by Lopez-Gonzales et al. [28]

**Reactions 66 and 67:** The reaction between $O_3$ and O leading to the formation of two $O_2$ molecules is highly exothermic by about 4.06 ev. The exothermicity of the bimolecular reactions between a triatomic molecule and an atom usually ends up in the vibrational energy of the newly formed bond. Vibrationally highly excited OH radicals from the $O_3$ + H reaction, or the vibrationally excited ClO radicals from the $O_3$ + Cl reactions are examples of this phenomenon. It is, therefore, logical to speculate that one of the $O_2$ molecule from the $O_3$ + O reaction might be vibrationally highly excited. Here it has been assumed that 75% of the $O_3$ + O reactions lead to one $O_2(v=23)$. This is an extreme assumption, made solely to underscore the key point that highly vibrationally excited $O_2$ could not have caused the significant loss of $N_2O$ in the Black et al experiment.

**Reactions 68 to 91:** Excepting the J-values for the reactions 80 and 86, the rate constants are either directly from or are based on DeMore et al.'s [26] recommendations. The J-values for the reactions 80 and 86 are based on the cross sections tabulated by DeMore et al. [26] and the relative intensity of the lamp-output as a function of the wavelength provided by Dr. R. L. Sharpless [Private communication, 1997]. The relative intensity was put on an absolute scale by requiring the total $O_3$ photodissociation rate at 254 nm to be $2.17\times10^{-3}$ $s^{-1}$ as explained earlier. Note that the results of this study are quite insensitive to the errors in the J-values for the reactions 80 and 86.

**Reactions 92 and 93:** As discussed by Prasad [20].

**Reactions 94 to 97:** The rate coefficients for the deactivation of $O_2$(c) by $O_2$ are from Kenner and Ogryzlo [29]. The same for $N_2$ is, however, an estimate assuming that it is probably similar to the rate constant for the deactivation of $O_2(A^3\Sigma)$ by $N_2$ measured by Kenner and Ogryzlo [30]. It has been also assumed that a reaction between $O_2$(c) and $N_2O$ (i.e., the reaction (97) of the Table 1) occurs and its rate coefficient is the same as the rate coefficient for the quenching of $O_2$(A) by $N_2O$ measured by Kenner and Ogryzlo [29]. These assumptions are extreme. Even so, they were made solely to show that neither $O_2$(high $v$) nor $O_2$(c) can account for the substantive loss of $N_2O$ in the Black et al experiment, even with extremely favorable assumptions.

**Reactions 98 to 101:** The rate constant for the reaction (98) and (99) are pure guesses and are also exaggerated for the reasons already stated. The absorption cross section of the $N_2O.O_3$ species at the 254 nm radiation from the Hg-lamp was assumed to be the same as that of the free $O_3$. Reactions 100 and 101 assume that when created within the $N_2O{\bullet}O_3$ species $O(^1D)$ can react with $N_2O$ in stead of running the great risk of being quenched by the large $N_2$ concentration as would be case with 'free' $O(^1D)$ from the photodissociation of a 'free' $O_3$ molecule (Prasad [20]).

**Reactions 102 to 103:** Remarks similar to those for the reactions 98 and 99 apply.

**Reaction 104:** The rate coefficient is a pure guess designed to show that all conceivable gas phase processes for the destruction of $N_2O$ in Black et al. experiment are inadequate.

**Reactions 105 to 107:** Reactions 105 and 106 assume that when $N_2O.O$ reacts with $O_3$ then a good part of the reaction exothermicity (4.01 ev) stays in the newly formed bond in the excited $N_2OOO^*$ species. Thus, the excited $N_2OOO^{**}$ could have an internal energy of almost 1 ev even if only 25% of the reaction exothermicity remains in the newly formed species. In this case, the reaction (106) may occur, assuming that the excited $N_2OOO^*$ is the same as the transition state involved in the production of $N_2O$ from excited ozone discussed by Prasad [13], Prasad et al [14] and experimentally observed by Zipf and Prasad [15]. It must be emphasized that these reactions are quite unlikely. They have been nevertheless included here due to reasons already stated several times.

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