# COMMENT ON "MIDDLE ATMOSPHERE HEATING BY EXOTHERMIC CHEMICAL REACTIONS INVOLVING ODD-HYDROGEN SPECIES"

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In a recent letter *Mlynczak and Solomon* [1991] (hereafter *M&S*) have assessed the atmospheric heating rates associated with the exothermic odd hydrogen reactions

$$O+OH \rightarrow H+O_2$$
$$H+O_2+M \rightarrow HO_2+M$$
$$O+HO_2 \rightarrow OH+O_2$$
$$H+O_3 \rightarrow OH+O_2$$
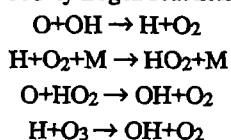
These authors (*M&S*) find that the reactions are a significant source of heat in the middle atmosphere and that the H+O$_3$ reaction makes the single most important contribution. As *M&S* explained, some of the energy released in the H+O$_3$ reaction is radiated from the atmosphere in the OH Meinel band airglow emission and they have used the Meinel band excitation models of *McDade and Llewellyn* [1987] and *Lopez-Moreno et al.* [1987] to calculate the fraction of the exothermicity that is locally degraded into heat. In their letter *M&S* report that the peak nighttime heating rates calculated for the collisional cascade and sudden death models of *McDade and Llewellyn* [1987] are much smaller than those obtained using the collisional cascade coefficients of *Lopez-Moreno et al.* [1987]. *M&S* claim that the lower heating rates calculated using the *McDade and Llewellyn* models can be almost entirely attributed to the OH(v)+O reaction and the 14% of the H+O$_3$ exothermicity that goes directly into heat, and they state that only a small fraction of the heating calculated for these models is due to collisional quenching of vibrationally excited OH. This result is rather surprising since *McDade and Llewellyn* [1987] point out that their models and parameters imply that the vibrationally excited OH radicals must be significantly quenched in the 85 to 90 km region. We would, therefore, have anticipated considerably larger heating rates. We do note that the calculations of *M&S* were performed using the OH Meinel band transition probabilities of *Turnbull and Lowe* [1989] and that the *McDade and Llewellyn* [1987] parameters were obtained from an analysis which employed the relative transition probabilities of *Murphy* [1971]. We also note that *M&S* adopted rate coefficients for the OH(v)+O reaction that are not strictly consistent with the model parameters of either

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McDade and Llewellyn [1987] or *Lopez-Moreno et al.* [1987]. Although this mixing of model parameters should be avoided where possible, the discrepancies arising from this procedure cannot account for the differences between the calculated and anticipated heating rates for the *McDade and Llewellyn* models.

In an attempt to identify the source of these differences we have carried out an independent assessment of the heating rates associated with the H+O$_3$ reaction, for various geophysical conditions, using the *McDade and Llewellyn* [1987] models. These calculations were first performed using the *Murphy* [1971] transition probabilities and were repeated using the transition probabilities of *Turnbull and Lowe* [1989]. The calculations show that, irrespective of the choice of transition probabilities, the heating rates associated with both the collisional cascade and sudden death models of *McDade and Llewellyn* [1987] are much larger than those reported by *M&S*. We also find and that these calculated heating rates are quite similar to those obtained by *M&S* (and us) using the *Lopez-Moreno et al.* [1987] collisional cascade coefficients with the *Turnbull and Lowe* [1989] transition probabilities. For example, if the sudden death parameters of *McDade and Llewellyn* [1987] are used together with the transition probabilities of *Turnbull and Lowe* [1989], our calculations show that, at 90 km under midnight conditions at equinox, 65% of the exothermicity of the H+O$_3$ reaction would go towards atmospheric heating. Similarly, if the collision cascade parameters of *McDade and Llewellyn* [1987] and *Lopez-Moreno et al.* [1987] are adopted in this analysis, we find that 67% and 81% of the energy would be deposited as heat.

It is not clear to us why *M&S* obtained such small heating rates for the *McDade and Llewellyn* [1987] models but it is possible that *M&S* may have misinterpreted the *McDade and Llewellyn* model parameters. These parameters are not absolute rate coefficients; rather they are reduced quantities representing the ratio of the relevant rate coefficients and the total radiative transition probability out of the OH v=9 level, i.e., A(9). Therefore, we suggest that *M&S* may have treated the *McDade and Llewellyn* parameters as absolute rate coefficients and used them together with the *Turnbull and Lowe* [1989] transition probabilities without scaling the parameters up by the appropriate factor of ~275 sec^{-1}, i.e., the *Turnbull and Lowe* A(9) value. This would have caused the calculated collisional loss rates to be insignificant compared to the radiative loss rates and would have resulted in the H+O$_3$ heating rates being seriously underestimated for the *McDade*

and Llewellyn models. The comments made by *M & S* concerning the differences between the *McDade and Llewellyn* collisional cascade parameters and the laboratory measurements of *Rensberger et al.* [1989] and *Dodd et al.* [1990] would seem to support this hypothesis. *M&S* note that the *McDade and Llewellyn* collisional cascade rate coefficients are smaller than the laboratory measured values for OH($v \le 3$). However, if the *Turnbull and Lowe* [1989] OH($v=9$) radiative lifetime is correct then the absolute collisional cascade rate coefficients inferred from the *McDade and Llewellyn* collisional cascade parameters would be much larger than the laboratory measured coefficients reported by *Rensberger et al.* [1989] and *Dodd et al.* [1990]. As discussed by *McDade* [1991] this would imply that the sudden death model should be preferred.

To conclude, therefore, our analysis shows that the H+O$_3$ heating efficiencies calculated using the *McDade and Llewellyn* [1987] and *Lopez-Moreno et al.* [1987] Meinel band models are very similar and this result corroborates the *Mlynczak and Solomon* [1991] thesis that the H+O$_3$ reaction must be a significant source of heat in the middle atmosphere.

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