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Wave-modified mean exothermic heating in the mesopause region

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Abstract. We employ a model of wave-driven OH nightglow fluctuations to calculate the effects of gravity waves on the chemical exothermic heating due to reactions involving odd hydrogen and odd oxygen species in the mesopause region. Using a model based on time means and deviations from those means, it is demonstrated that gravity waves contribute to the time-average exothermic heating. The effect can be significant because the fractional fluctuations in minor species density can be substantially greater than the fractional fluctuation of the major gas density. Our calculations reveal that the waves mitigate the exothermic heating, demonstrating their potential importance in the heat budget of the mesopause region.

INTRODUCTION

Chemical heating due to recombination of atomic oxygen was first shown to be an important component of the thermal budget of the mesopause region by *Kellogg* (1961). *Crutzen* (1971) demonstrated that the chemical heating due to exothermic reactions involving odd hydrogen and odd oxygen species can be substantial in the mesopause region. *Mayr et al.* (1990) have examined how wind-induced diffusion of atomic oxygen away from the polar regions impacts the thermal and momentum budgets of the upper mesosphere and lower thermosphere. More recently, *Mlynczak and Solomon* (1991; 1993) have attempted to derive exothermic heating efficiencies to account for the energy lost through chemiluminescence for some of those reactions, but the analysis was hampered by a lack of accurate sets of reaction rates and branching ratios for the pertinent reactions. They demonstrated that daytime chemical exothermic heating rates, smaller than their nighttime values, are comparable to the ultraviolet heat input to the region.

The set of chemical equations employed by *Mlynczak and Solomon* (1991; 1993) to calculate the exothermic heating are essentially those equations employed by *Walterscheid et al.* (1987), *Hickey* (1988), *Schubert et al.* (1991), and *Hickey et al.* (1992) to determine the effects of internal gravity waves on the OH nightglow. These waves perturb the minor species concentrations involved in the OH nightglow through the effects of transport, divergence and temperature perturbations, and through chemical coupling between species. These airglow perturbation models demonstrate that the minor species fluctuate with different amplitudes and phases with respect to each other under the influence of a gravity wave. Also, minor species fractional density fluctuations can be substantially greater than the major gas fractional density fluctuations.

It is clear that gravity waves will cause significant fluctuations in the exothermic heating if the number densities of the minor species that are responsible for this exothermic heating are also fluctuating. Furthermore, the time-averaged second order heating involving products of first order minor species' density fluctuations will, in general, be non-zero. This implies that the time-averaged effect of the waves may result in heating rates that differ significantly from those previously calculated by *Mlynczak and Solomon* (1991; 1993).

WAVE-MODIFIED MEAN EXOTHERMIC HEATING

A detailed energy budget calculation should include the total wave contribution, $\langle q_w \rangle$, to the mean state heating, where

$$\langle q_w \rangle = \langle q_{we} \rangle + \langle q_{wme} \rangle + \langle q_{whf} \rangle + \langle q_{wef} \rangle \tag{1}$$

and a $\langle\,\rangle$ denotes a time-average. The term q_{we} represents exothermic heating involving products of disturbance concentrations, while the term q_{wme} represents wave-induced exothermic heating involving products of time-averaged constituent concentrations. The latter reflects the wave contribution to the maintenance of the mean state temperature and constituent profiles (*Walterscheid and Schubert*, 1989; *Garcia and Solomon*, 1985). The total exothermic heating calculated for mean state quantities is $\langle q_{me} \rangle = \langle q_{me0} \rangle + \langle q_{wme} \rangle$, where q_{me0} is the exothermic heating in the absence of waves. The terms q_{whf} and q_{wef} are purely dynamical terms representing the sensible heat flux by the wave and the eddy heat flux by wave-induced turbulence, respectively.

In our analysis we emphasize the effects of waves on the chemical exothermic heating as given by $\langle q_{we} \rangle$. The contribution of $\langle q_{we} \rangle$ towards the wave-modified exothermic heating can be viewed simply as a correction to the term $\langle q_{me} \rangle$, providing a more accurate determination of time-averaged exothermic heating when constituents are wave-disturbed. The modification of the mean thermal state by wave transports and wave-induced turbulence, as given by $\langle q_{whf} \rangle$ and $\langle q_{wef} \rangle$, is a different problem. However, we compare $\langle q_{whf} \rangle$ to $\langle q_{we} \rangle$ in the appendix.

Our objective is to assess whether waves can be important in the evaluation of time-mean exothermic heating. The analysis is performed under the following assumptions. First, time scales for changes in mean state quantities are long compared to the time-scale for waves (ω^{-1} = wave period/2π). This is valid for waves that are not too strongly dissipating. Second, wave-driven perturbations in exothermic heating do not significantly affect wave characteristics. This is justified because for ~ hour period waves the energy added to the wave over a wave cycle is small compared to the wave energy (i.e., $Q'/\omega c_p << T'$, where T' is

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Table 1. Reactions, Rate Constants, and Heats of Reaction (ΔE)

#	Reaction	Reaction Rate Constant*	ΔE (kcal/mol)
1	$O+OH \rightarrow H+O_2$	$4\text{x}10^{-17}$	-16.77
2	$H+O_2+M \rightarrow HO_2+M$	$2.1\text{x}10^{-44}\exp(290/T)$	-49.10
3	$H+O_3 \rightarrow OH+O_2$	$1.4\text{x}10^{-16}\exp(-470/T)$	-76.90
4	$O+HO_2 \rightarrow OH+O_2$	$4\text{x}10^{-17}$	-53.27
5	$O+O+M \rightarrow O_2+M$	$4.7\text{x}10^{-45}(300/T)^2$	-119.40
6	$O+O_2+M \rightarrow O_3+M$	$1.0\text{x}10^{-46}\exp(510/T)$	-25.47

* Rate constants are in units of m^6s^{-1} for termolecular reactions and m^3s^{-1} for bimolecular reactions

the temperature perturbation and c_p is the specific heat at constant pressure). Third, linear steady-state theory has quantitative validity for estimating the magnitude of wave effects. This approach is valid for well developed wave fields that are not strongly modified by wave-breakdown, critical levels or wave-wave interactions. Despite its limitations, this approach has been widely used with great success for obtaining first approximations of the sense of the magnitude of wave effects. When this approach indicates that waves are important it is unlikely that a more detailed analysis would negate these indications.

The reactions considered by *Mlynczak and Solomon* (1991; 1993) are summarized in Table 1. Although Reaction (5) of this table isn't included in our OH fluctuation model, its associated exothermic heating is calculated because the atomic oxygen continuity equation is solved in our nightglow fluctuation model with chemical loss being obtained from reactions 1, 4 and 6.

The time-averaged effects of the waves on the exothermic heating are calculated using a perturbation approach. Second order heating is calculated *a posteriori* using the first order perturbations, a standard approach used in a variety of geophysical fluid flow problems (e.g., *Landau and Lifshitz*, 1987). We employ this approach in order to quantify and establish the importance of the gravity wave-driven exothermic heat source.

From *Mlynczak and Solomon* (1991; 1993) and *Mlynczak* (1992) the rate of conversion of chemical potential energy into heat (q) per unit volume is given by $q = \varepsilon \Delta E k n_1 n_2$, where k is the temperature dependent reaction rate, n is the species' number density, and ΔE is the exothermicity of the reaction. Following *Mlynczak and Solomon* (1993), the heating efficiency, ε, is assumed to be constant and equal to 0.6 for the ozone-hydrogen reaction and unity otherwise. A gravity wave will perturb q by perturbing k, n_1 and n_2. We let $k = \bar{k} + k' + k''$, $n_1 = \bar{n}_1 + n_1' + n_1''$, and $n_2 = \bar{n}_2 + n_2' + n_2''$, where a prime and double prime denote a first and second order perturbation about the time-mean state (overbars refer to time-averages of mean state quantities throughout), respectively. Expanding q to second order yields the net exothermic heating rate per unit volume in the presence of a gravity wave, $q = \bar{q} + q' + q''$, where

$$\bar{q} = (\varepsilon \Delta E)\bar{k}\bar{n}_1\bar{n}_2 \tag{2a}$$

$$q' = (\varepsilon \Delta E)\left\{\bar{k}\left(n_1'\bar{n}_2 + \bar{n}_1 n_2'\right) + k'\bar{n}_1\bar{n}_2\right\} \tag{2b}$$

$$\begin{aligned} q'' = (\varepsilon \Delta E)\Big\{&\bar{k} n_1' n_2' + k'\left(n_1'\bar{n}_2 + \bar{n}_1 n_2'\right) + \\ &\bar{k}\left(n_1''\bar{n}_2 + \bar{n}_1 n_2''\right) + k''\bar{n}_1\bar{n}_2\Big\} \end{aligned} \tag{2c}$$

The heating rate per unit mass (Q) is given to second order by:

$$Q = \frac{\bar{q}}{\bar{\rho}}\left\{1 - \frac{\rho'}{\bar{\rho}} - \frac{\rho''}{\bar{\rho}} + \left(\frac{\rho'}{\bar{\rho}}\right)^2\right\} + \frac{q'}{\bar{\rho}}\left\{1 - \frac{\rho'}{\bar{\rho}}\right\} + \frac{q''}{\bar{\rho}} \tag{3}$$

The net time-averaged exothermic heating in the presence of a gravity wave is then given by:

$$\langle Q \rangle = \frac{\bar{q}}{\bar{\rho}}\left\{1 + \left(\rho'/\bar{\rho}\right)^2\right\} - \frac{\langle q'\rho' \rangle}{\bar{\rho}^2} + \frac{\langle q'' \rangle}{\bar{\rho}}, \tag{4}$$

where ρ is the total mass density, and where

$$\langle q'' \rangle = (\varepsilon \Delta E)\left\{\bar{k}\langle n_1' n_2' \rangle + \bar{n}_1\langle k' n_2' \rangle + \bar{n}_2\langle k' n_1' \rangle\right\} \tag{5}$$

and a $\langle\ \rangle$ denotes time-averages over wave disturbed quantities. The fact that the cycle average of a pure sinusoid is identically zero enabled us to write $\langle \rho' \rangle = \langle \rho'' \rangle = \langle q' \rangle = \langle T' \rangle = \langle k' \rangle = \langle k'' \rangle = \langle n_j' \rangle = \langle n_j'' \rangle = 0$, where j = 1 or 2. We write $Q_{net} = Q_0 + Q_2 \geq 0$, where $Q_0 = \bar{q}/\bar{\rho}$, and

$$Q_2 = \frac{\langle q'' \rangle}{\bar{\rho}} - \frac{\langle q'\rho' \rangle}{\bar{\rho}^2} + \frac{\langle \rho'^2 \rangle \bar{q}}{\bar{\rho}^3}. \tag{6}$$

Q_0 represents the mean heating rate calculated by *Mlynczak and Solomon* (1991; 1993) that explicitly involves only products of time-averaged constituent concentrations. Q_{net} involves both Q_0 and heating involving products of disturbance concentrations. Their difference, Q_2, represents the second order effect of the wave on the exothermic heating rate. Q_2 is estimated by noting that the time-average of two complex numbers, say α and β, can be written as $(1/2)|\alpha||\beta|\cos\varphi$, where φ is their phase difference. As mentioned earlier, Q_0 may contain an implicit effect of gravity waves which is different from the effects considered here.

The values of n_1', n_2' and k' required in the above equations are provided from our Eulerian model of minor species density fluctuations (e.g., *Schubert et al.*, 1991; *Hickey et al.*, 1992). The Eulerian analysis is appropriate for examining changes in the altitude profiles of the exothermic heat input and the corresponding temperature change. We compare these Eulerian values of Q_2 with those obtained using a Lagrangian Stokes drift formalism (*Longuet-Higgins*, 1969; *Andrews and McIntyre*, 1978; *Coy et al.*, 1986). The Stokes analysis is appropriate for examining the orbit averaged exothermic heating experienced by a parcel. Any radical difference between the exothermic heating obtained from the two different approaches would be inconsistent with our intuitive understanding of the problem. Reassuringly, the two approaches give quantitatively similar results.

The net heating using the Stokes drift approach is written as

$$\langle Q^s{}_{net} \rangle = Q_0 + Q_2 + \langle \delta Q^s \rangle, \tag{7}$$

where, after neglecting a term involving mean Stokes velocity (see *Walterscheid and Hocking*, 1991), the Stokes correction is

$$\langle \delta Q^s \rangle = \langle \underline{\xi}' . \underline{\nabla Q}' \rangle + \frac{1}{2}\langle \zeta'^2 \rangle \frac{\partial^2 \bar{Q}}{\partial z^2} \tag{8}$$

where $\underline{\xi}' = (\xi', \zeta')$ is the perturbation displacement vector.

The important aspect of our results is that Q_2 can be negative. This is due to the dominance of the first term in equation (6). We emphasize that exothermic heating is always positive. The fact that Q_2 may be negative means that the waves reduce the net exothermic heating; that is to say, $Q_{net} < Q_0$. We formulate our results in terms of Q_2 to facilitate their presentation.

RESULTS

Typically, most power is observed to reside in the long period, long wavelength gravity waves, so we calculate the net exothermic heating in the presence of a wave of horizontal wavelength (λ_x) 500 km (e.g., *Meek et al.*, 1985). The mean state employed here was defined using the model output of *Garcia and Solomon* (1985) for nighttime conditions during December at 18°N, 39°N and 82°N. Calculations are performed for two wave periods (1 and 3 hours) and two altitudes (85 and 90 km) using the model described in *Hickey et al.* (1992).

The total mean daily heating rates (Q_0) at 85 (90) km altitude are 12.48 (12.15), 9.46 (11.51) and 7.42 (10.95) °K/day for latitudes of 18, 39 and 82°N, respectively. These are the potential heating rates for nighttime conditions. The actual daily mean heating rates will be smaller than this because of the reduced exothermic heating during daylight hours (*Mlynczak and Solomon*, 1993). Nonetheless, the total heating rates are large. Although not shown, most of the exothermic heating is produced by the $H+O_3$ and O+OH reactions, with a significant contribution being made by the two odd oxygen reactions. The $H+O_2+M$ and $O+HO_2$ reactions make only a minor contribution to the overall exothermic heating for this mean state.

Typical rms values of $T'/\overline{T}$ inferred from radar data (winds) and falling sphere data (density) over a large range of latitudes during winter are about in the range 5 to 10% (*Theon et al.*, 1967; *Philbrick et al.*, 1980, 1984, 1985; *Zimmerman and Keneshea*, 1986; *Schubert et al.*, 1990; *Walterscheid and Schubert*, 1990; *R.A. Vincent, private communication*, 1987), but larger amplitudes are not uncommon, especially in the high-latitude winter mesopause (*Theon et al.*, 1967; *Philbrick et al.*, 1984, 1985). Since our results show that the most significant effects for a given wave amplitude occur at high latitudes during winter, we employ values of wave amplitude that are on the high side of typical global values. We employ 10% to represent typical rms values; 15% to represent disturbance amplitudes during periods of enhanced wave activity; and 20% to represent extreme amplitudes that can be realized for wave spectra dominated by fast energetic waves (*Orlanski and Bryan*, 1969; *Walterscheid and Schubert*, 1990). We do not give results for the 3-hour wave for wave amplitudes of 15% and 20% because for this wave they imply a large degree of wave overturning.

Table 2 shows the percentage ratios Q_2/Q_0 and $\{Q_2+\langle\delta Q^s\rangle\}/Q_0$ for the various wave amplitudes. The Eulerian and Stokes formalisms produce similar results. Q_2 is dominated by the reaction of O and OH. The effect of the waves is more pronounced at 85 km than it is at 90 km altitude, because the O scale height is appreciably smaller at 85 km altitude, causing $n'/\bar{n}$ for O to be greater there through vertical advection effects. Q_2/Q_0 is always greatest for the longer period wave primarily because w'/T' (w' is the vertical component of velocity) is larger at longer wave periods, increasing vertical advection effects. For a given wave amplitude, the ratio Q_2/Q_0 increases towards higher latitudes. This is due to the decrease of the O scale height and the increase of $\overline{T}$ with increasing latitude, the former increasing $n'/\bar{n}$ for O and the latter increasing $n'/\bar{n}$ for OH through the temperature dependence of reaction 3. The ratio Q_2/Q_0 is modest for the more typical rms amplitudes of 10%, but it becomes large under disturbed conditions for wave amplitudes of 15%. The high latitude results demonstrate that occasionally the chemical energy input to the high latitude winter mesopause region is strongly influenced by wave dynamics. Our calculations reveal that the mean OH nightglow emission peaks near 85 km altitude for the mean state employed here (see Figure 4 of *Hickey et al.*, 1992), suggesting that the wave effects are strongest near the peak of the OH nightglow. If the peak of the emission layer were displaced vertically, we expect a similar displacement would occur in the peak of Q_2. However, the mean exothermic heating does not necessarily peak at the same altitude as that of the OH nightglow emission.

DISCUSSION AND SUMMARY

The reduced exothermic heating results from a reduction in the effective rate of chemical recombination in the presence of a gravity wave. This means that gravity waves will affect the equilibrium minor species density profiles. These effects will be reflected in observations and should be included in models of the chemistry of the mesopause region.

We have shown that gravity waves will affect the exothermic heating in the mesopause region by causing chemically active minor species to fluctuate. Our calculations, performed for fairly energetic waves, indicate that occasionally these waves can have a large mitigating effect on the exothermic heating implied by the mean constituent concentrations alone. To a lesser degree, we expect these effects to be operative often since gravity waves are a ubiquitous feature of the mesopause region. The possibility that less typical waves, radically different from those considered may add to the net exothermic heating requires further study.

Although we have demonstrated the potential importance of these mitigating gravity wave effects on exothermic heating, detailed global energy budget calculations will require that we incorporate values of wave amplitude obtained from either observed and theoretical spectra of gravity waves, or from modeling of breaking gravity waves in the mesopause region. We will eventually require knowledge of the global characteristics of

Table 2. Percent change in exothermic heating for waves of various amplitudes for various latitudes in December. The Stokes drift results [ ] and the absolute ratio $\langle q_{we}\rangle/\langle q_{whf}\rangle$ { } are also shown. See text for details.

Lat/Amp	1 hr (z = 85 km)	3 hr (z = 85 km)	1 hr (z = 90 km)	3 hr (z = 90 km)
18°N: 10%	-9.5 [-10.9] {.02}	-12.6 [-15.0] {.004}	-2.7 [-2.0] {.005}	-4.1 [-3.7] {.001}
15%	-21.3 [-24.5]		-6.1 [-4.4]	
39°N: 10%	-13.6 [-17.9] {.03}	-18.0 [-24.3] {.005}	-3.0 [-2.8] {.007}	-4.3 [-4.6] {.001}
15%	-30.6 [-40.3]		-6.7 [-6.3]	
82°N: 10%	-15.7 [-20.4] {.05}	-20.2 [-26.5] {.008}	-3.0 [-2.1] {.01}	-4.4 [-3.1] {.002}
15%	-35.4 [-45.8]		-6.8 [-4.8]	
20%	-62.9 [-81.4]		-12.0 [-8.5]	

gravity wave spectra, including effects of persistence and localization of wave activity. The data for such an evaluation are not presently available. Furthermore, time-dependent calculations coupling chemistry and dynamics will need to be implemented.

APPENDIX

At typical gravity wave periods, the term $\langle q_{whf} \rangle$ in equation (1) is given approximately by

$$\langle q_{whf} \rangle = c_p \frac{d}{dz} \langle \bar{\rho} w' T' \rangle \qquad (A1)$$

where all symbols are as previously defined. The ratio $\langle q_{we} \rangle / \langle q_{whf} \rangle$, shown in Table 2, is much smaller than unity, indicating that for the waves considered here, the mean exothermic heating involving products of disturbance concentrations is significantly smaller than that due to the divergence of the sensible heat flux. The largest calculated value of $\langle q_{we} \rangle / \langle q_{whf} \rangle$ is 0.05 and occurs at 85 km where $\langle q_{we} \rangle$ maximizes because of basic state conditions and obtains for the 1 hour period wave because faster waves are less affected by dissipation. The quantity $\langle q_{whf} \rangle$ is a sensitive function of wave dissipation (*Walterscheid*, 1981). Therefore the ratio $\langle q_{we} \rangle / \langle q_{whf} \rangle$ is apt to exhibit considerable variability reflecting the commensurate variability in the eddy diffusion coefficients. Decreasing these eddy diffusion coefficients by a factor of ten had no effect on $\langle q_{we} \rangle$ but resulted in a fifteen fold decrease in $\langle q_{whf} \rangle$ and caused the largest calculated value of $\langle q_{we} \rangle / \langle q_{whf} \rangle$ to approach unity. Therefore, future calculations should be performed for a broad range of acceptable eddy diffusion coefficients and gravity wave parameters. Finally, we remark that $\langle q_{whf} \rangle$ represents a redistribution of heat so that its integral over altitude vanishes, but in general the altitude integral of $\langle q_{we} \rangle$ will be non zero.

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