THE PHOTODISSOCIATION OF VIBRATIONALLY EXCITED OZONE IN THE UPPER ATMOSPHERE

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Summary

The photodissociation of vibrationally excited O_3 in the sunlit mesosphere is investigated. Dissociation rate coefficients for specific vibrationally excited states of O_3 are calculated for the conditions of an overhead sun. Possible vibrational enhancements of the $O(^1D)$ and $O_2(a^1\Delta_g)$ production rates are assessed. It is shown that such enhancements should make only minor contributions to the daytime production of these species in the mesosphere and lower thermosphere.

1. Introduction

There is continued interest in attempts to understand the processes which control the concentrations of O_3 in the atmosphere. Although O_3 number densities peak in the stratosphere there is now a considerable body of evidence to indicate that a high altitude secondary maximum also exists. This was first suggested from rocket measurements of $O_2(a^1\Delta_g)$ emission in the dayglow reported by Evans *et al.* [1], was subsequently observed on several occasions using other techniques and has most recently been detected by a near-IR spectrometer experiment on the Solar Mesospheric Explorer satellite [2]. Most photochemical models now predict an upper secondary maximum but it has not yet been established if the apparent maximum in the experimental observations is due to errors in certain basic assumptions made during data reduction (see Thomas *et al.* [2]). The techniques normally used to measure O_3 concentrations above 80 km depend critically on information about the coefficients for O_3 absorption in the Hartley continuum. Solar, lunar and stellar occultation techniques [3 - 5] rely directly on the absorption coefficient data, while the techniques based on observation of the 1.27 μm emission from $O_2(a^1\Delta_g)$ require, in addition, knowledge of the quantum yields of $O_2(a^1\Delta_g)$ and $O(^1D)$ produced during the dissociative absorption process [2]. Recent observations by Rawlins *et al.* [6] have shown that significant populations of vibrationally excited O_3

exist in the 80 - 100 km region of the atmosphere. As vibrational excitation is known to increase dramatically O_3 absorption coefficients in the long wavelength wing of the Hartley continuum [7] and to "red shift" the continuum to wavelengths where the solar flux increases rapidly, vibrational enhancements of the rates of production of the species used to infer O_3 concentrations in the mesosphere have been evaluated.

2. Analysis

The dramatic effect of vibrational excitation on O_3 absorption in the Hartley continuum has been established by a variety of techniques involving thermal excitation [7], chemical excitation [8] and direct IR laser pumping of vibrational levels [9]. Some uncertainty surrounds the extent to which excitation of the bending (ν_2) and asymmetric stretch (ν_3) modes may affect the absorption spectrum [10, 11], but there is a general consensus that the major effect arises from excitation of the symmetric stretch (ν_1) mode [11, 12]. The ground vibrational level, $O_3(000)$, is the only state for which the Hartley continuum can be measured directly [7], but information about the continua arising from the lowest-lying excited states has been extracted from composite spectra observed under various conditions of vibrational excitation [11]. A theoretical understanding of the absorption spectra of specific vibrational components is not yet complete [10, 11] but the experimental observations can be reasonably well reproduced by spectra calculated with the reflection approximation for dissociative absorption continua [8, 11]. For the present analysis Hartley continua arising from specific vibrational levels of O_3 have been calculated using the reflection approximation with the procedure described by Kleindienst and Bair [8]. The Hartley continua calculated for a few selected vibrational levels of O_3 are shown in Fig. 1. Comparison of these spectra with the wavelength dependence of the solar irradiance, shown in Fig. 2, indicates that O_3
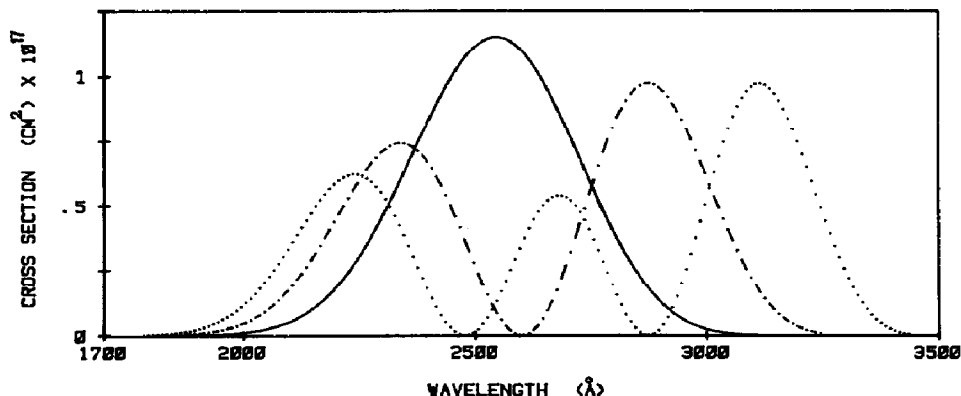

Fig. 1. Hartley absorption continua for $O_3(000)$ (———), $O_3(100)$ (— · —) and $O_3(200)$ (········), calculated as described in the text.
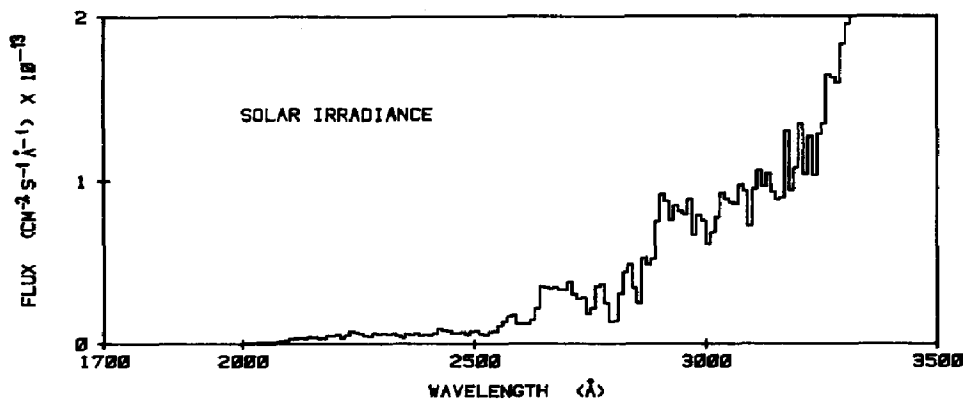
Fig. 2. Unattenuated solar irradiance employed in the present analysis. The data for wavelengths up to 3170 Å are from Mount and Rottman [20]; beyond this wavelength the data of Mentall *et al.* [21] have been adopted.

TABLE 1

Total photolysis coefficients J_∞ and production coefficients for $O(^1D)$ and $O_2(a^1\Delta_g)$

Vibrational level (in increasing order of energy)	J_∞ ($\times 10^{-3}$ s^{-1})	$O(^1D)$ and $O_2(a^1\Delta_g)$ production coefficient ($\times 10^{-3}$ s^{-1})
(000)	8.2	7.3
(010)	10.3	9.3
(001)	11.6	10.4
(100)	18.0	16.0
(020)	13.0	11.7
(011)	14.6	13.1
(110)	21.9	19.5
(002)	16.3	14.6
(030)	16.4	14.7
(101)	24.0	21.3
(200)	29.7	24.3

molecules excited in the ν_1 mode will have atmospheric dissociation coefficients substantially larger than that of ground state O_3.

The photodissociation coefficient for any atmospheric species is the wavelength integral of the product of the relevant absorption cross section and the actinic solar flux at the altitude of interest. Photodissociation coefficients determined for an unattenuated overhead sun with the irradiance of Fig. 2 and the O_3 cross sections, calculated as described above, yield the J_∞ values listed in Table 1.

As the $O_2(a^1\Delta_g)$ and $O(^1D)$ quantum yields resulting from O_3 photolysis depend on both the wavelength and the internal energy of the absorbing molecule [13], further considerations must be made in order to calculate the rates of $O_2(a^1\Delta_g)$ and $O(^1D)$ production from the dissociation of specific

vibrational levels. In the present analysis it has been assumed, on the grounds of spin conservation, that $O_2(a^1\Delta_g)$ formation accompanies that of $O(^1D)$ throughout the entire Hartley continuum. The wavelength dependence of the excited state quantum yields from specific vibrational levels in the "fall-off" region have been calculated using a method similar to that described by Moortgat *et al.* [13] and Adler-Golden *et al.* [10]. For each vibrational level a rotational temperature of 200 K, typical of the 80 - 100 km region, has been adopted and the rotational energy distribution was calculated according to the classical expression for the density of states of a rotor with two degrees of freedom [14]. It has been assumed that the internal energy of the molecule adds fully to the energy of the absorbed photon. This effect may contribute to the apparent spin-disallowed production of $O_2(a^1\Delta_g)$ in some laboratory experiments at wavelengths well beyond the $O(^1D) + O_2(a^1\Delta_g)$ dissociation limit at about 3100 Å [15]. It has also been assumed that for a given total energy the probability of $O(^1D)$ and $O_2(a^1\Delta_g)$ formation varies from zero at an energy threshold, taken to be the $O(^1D) + O_2(a^1\Delta_g)$ dissociation limit, to 0.9 [15] at an energy 800 cm^{-1} above the threshold [13]. Examples of the calculated wavelength dependence of the excited state quantum yields are illustrated in Fig. 3 for $O_3(000)$, $O_3(100)$ and $O_3(200)$. When the wavelength-dependent quantum yields are incorporated into the total photolysis calculation for an overhead sun the $O_2(a^1\Delta_g)$ and $O(^1D)$ production coefficients listed in Table 1 are obtained.
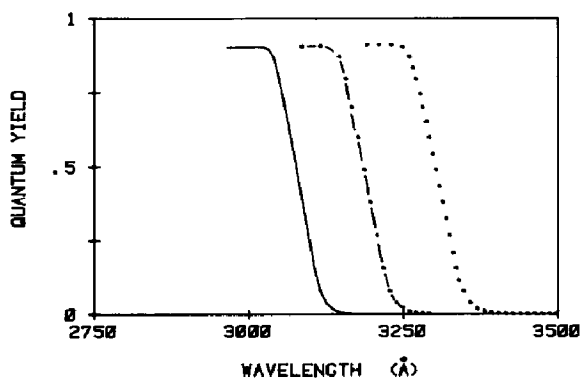

Fig. 3. Wavelength dependence of the $O(^1D)$ and $O_2(a^1\Delta_g)$ quantum yields from the photolysis of $O_3(000)$ (———), $O_3(100)$ (— · —) and $O_3(200)$ (········) calculated as described in the text.

3. Discussion

The foregoing analysis has demonstrated that vibrational excitation, particularly in the ν_1 mode, can enhance the coefficients for photodissociation of O_3 in the upper atmosphere. However, the significance of this effect, and any implications for inversion algorithms used to infer meso-

spheric O_3 concentrations from the airglow measurements referred to in Section 1, depend on the extent to which O_3 is vibrationally excited at the altitudes of interest. Departures of O_3 vibrational populations from local thermodynamic equilibrium in the mesosphere can arise because of two major sources of excitation; firstly, as a result of excitation during the three-body association of molecular and atomic oxygen and secondly, through absorption of IR earthshine in the fundamental $O_3(001) \leftarrow O_3(000)$ transition at 9.6 μm. To date, the only published observations of vibrationally excited O_3 in the upper atmosphere have been made under nighttime conditions [6, 16, 17]. Although the processes which determine O_3 vibrational distributions in the mesosphere and lower thermosphere are not well understood, it is unlikely that the enhanced dissociation rates calculated above would compete with the processes which are expected to dominate the loss of vibrationally excited states — namely radiation [6] and collisional deactivation by major atmospheric species. As collisional deactivation, and the aforementioned sources of vibrational excitation, should exhibit only minor diurnal variations in the upper mesosphere, the nighttime observations of vibrationally excited O_3 may be used to estimate the daytime excited state concentrations.

Rawlins *et al.* [6] have analysed spectra of IR emission in the ν_3 band of O_3 measured between 80 and 100 km in a rocket experiment reported by Stair *et al.* [17]. Their analysis suggests that the quiescent nighttime vibrational populations in levels *above* the $O_3(000)$ level and below the $O_3(013)$ level may be characterized by a vibrational temperature of about 460 K. The zenith radiances between 80 and 100 km reported by Stair *et al.* [16, 17] may be used to estimate average $O_3(001)$ populations, over this altitude range, of about 10^6 cm^{-3}. For a vibrational temperature of 460 K the populations in the $O_3(010)$ and $O_3(100)$ levels would be about 3×10^6 cm^{-3} and about 8×10^5 cm^{-3} respectively, while the population in the $O_3(200)$ level would be about 3×10^4 cm^{-3}. As total O_3 concentrations in the 80 - 100 km region of the sunlit mesosphere are reported to be in the range (2×10^7) - (1×10^8) cm^{-3} [2, 3], the $O_2(a^1\Delta_g)$ and $O(^1D)$ production rates should be dominated by the photolysis of $O_3(000)$. If the vibrational temperature of 460 K applies to all levels, including the $O_3(000)$ level, the population-weighted coefficient for $O_2(a^1\Delta_g)$ and $O(^1D)$ production would be 7.9×10^{-3} s^{-1} as opposed to the $O_3(000)$ value of 7.3×10^{-3} s^{-1}, and O_3 concentrations inferred from $O_2(a^1\Delta_g)$ emission rates would only be in error by about 10%. Consequently, total O_3 densities inferred from the $O_2(a^1\Delta_g)$ airglow emission should not be significantly distorted by the vibrationally enhanced $O_2(a^1\Delta_g)$ production rates. It should be emphasized that the present analysis has been carried out using Hartley continua calculated according to the reflection approximation described by Kleindienst and Bair [8]. A modification of this approximation [18] suggests that the red shift in the Hartley continua arising from excitation of the ν_2 and ν_3 modes may be considerably smaller, in which case the J_∞ values presented here for molecules excited in these modes represent upper limits.

4. Conclusions

Atmospheric photodissociation rate coefficients for various vibrationally excited states of O_3 have been presented. It has been shown that the coefficients for O_3 molecules excited in the ν_1 mode are substantially larger than that of the ground vibrational state. The enhanced dissociation rates and $O_2(a\,^1\Delta_g)$ and $O(^1D)$ production rates are not large enough to lead to significant errors in mesospheric O_3 concentrations inferred from $O_2(a\,^1\Delta_g)$ airglow emission measurements. However, in the aurora where higher vibrational temperatures have been inferred [6] the enhanced dissociation rates may play a more significant role and contribute to the enhanced $O_2(a\,^1\Delta_g)$ emission rates observed in sunlit aurora [19].

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