The Excited State in Atmospheric Chemistry

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1 Introduction

In recent years, the chemistry of the Earth's atmosphere has provided a focus for much scientific activity. Interest has been stimulated by concerns about the environmental consequences of Man's activities in general, and phenomena such as Global Warming, Acid Rain and the Antarctic Ozone Hole in particular. Of course, any attempt to understand the causes of these effects necessarily requires a detailed knowledge of the chemistry of the unpolluted atmosphere, and the result is that significant advances in our knowledge of atmospheric chemistry have been made in the last two decades. To a reasonable extent, it is possible to discuss the chemistry of the atmosphere in terms of the behaviour of its components in thermal equilibrium with their surroundings; *i.e.* for a given chemical species, relative populations of a particular energy level can be calculated using the Boltzmann equation:

$$n_i/n_0 = g_i\exp(-\epsilon_i/kT) \qquad \text{(I)}$$

where n_i and n_0 are the concentrations of the ith energy level and ground energy level, g_i is the degeneracy of the ith level, ϵ_i is its energy, k is the Boltzmann constant and T is the temperature. However, just as the atmosphere is not in chemical equilibrium, there are many examples of excited atoms, molecules, radicals and ions that are present in the atmosphere in concentrations far greater than would be expected on the basis of equation (I). It is towards the chemistry of these excited states that this review addresses itself. Much of the discussion will centre on vibrationally and electronically excited species; at typical atmospheric temperatures, the energy required to access these states is, as a general rule, too great to be achieved in thermal processes. For translational energy and rotational energy, the separations of the energy levels are small compared to kT and at thermal equilibrium, a range of levels is excited. However, we shall see that circumstances exist where translational and rotational temperatures of a particular species may be very much greater than the thermodynamic temperature of the surroundings.

Ultimately, the energy for excitation within the atmosphere comes from the Sun, either in the form of solar radiation or charged particles (the solar wind). Excitation mechanisms include direct absorption of radiation, photodissociation, product formation in exothermic reactions and the interaction of molecules with charged particles. Once formed, these species can influence atmospheric chemistry in many ways. As we shall see in Section 2, O(^{1}D) plays a fundamentally important role in the chemistry of both the troposphere and the stratosphere. The reactivity of O(^{1}D) is significantly different from that of the ground state, O(^{3}P), and other examples of this behaviour also exist. Excited atomic oxygen is also important in the aurorae and airglow and these phenomena are discussed. Radiation emitted from vibrationally excited molecules can be detected in space, allowing remote sensing of many species, while chemical reactions leading to vibrationally excited products can lead to significant problems in the retrieval of concentrations from such measurements. Infrared raditation emitted from the Earth's surface can excite vibrations in a number of trace gases in the atmosphere leading to radiation trapping and the greenhouse effect; in the middle atmosphere, emission from vibrationally excited molecules provides a mechanism for atmospheric cooling. The role of nitric oxide in the thermosphere is a very interesting one; mechanisms for its formation seem to involve translational, rotational, vibrational and electronic excitation.

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It is not possible in a review of this length to cover all aspects of the chemistry of excited states in the atmosphere with the detail that they deserve. In particular, it should be noted that almost all atmospheric chemistry is driven by photochemical processes and that such processes involve the promotion of molecules to excited states. The dynamics of the reorganisation of atoms following these excitations are not considered in this article. Similarly, there is not room to discuss the notation used to describe electronically excited states [*e.g.* O(^{1}D) and O$_2$(a$^1\Delta_g$)] and the interested reader is referred to an introductory text on spectroscopy.[1] I do not intend to give a detailed description of the chemistry of the atmosphere or its structure; some of the standard chemistry[2] is dealt with in Section 2, and the atmosphere is divided into regions according to temperature gradient. These regions are (with very rough altitude ranges): the troposphere (< 18 km); the stratosphere (18—50 km); the mesophere (50—90 km); and the thermosphere (> 90 km).[2]

2 The Importance of O(^{1}D)

The first excited state of atomic oxygen, O(^{1}D), is one of the most important trace constituents in the Earth's atmosphere, playing critical roles in many areas of atmospheric chemistry. In this section, its importance in the troposphere and stratosphere is discussed. In chemical terms, the troposphere can be thought of as a low-temperature combustion system. One of the most important overall processes in this region is the conversion of methane, a by-product of many natural processes, to carbon dioxide and water by a reaction that, stoichiometrically, can be represented very simply:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (1)$$

However, just as in the case of a methane flame, the mechanism for this process is complex and involves a number of radical species. In a combustion system, the energy for the formation of radicals is thermal, while in the troposphere, the energy source for radical formation is solar radiation and the oxidation is photochemical. The critical process is the photolysis of ozone at wavelengths between 290 and 310 nm:

$$O_3 + h\nu \rightarrow O_2(a^1\Delta_g) + O(^1D) \qquad (2a)$$

The atomic fragment, $O(^1D)$, then goes on to generate the important radical species OH in the reaction

$$O(^1D) + H_2O \rightarrow OH + OH \tag{3}$$

The OH radicals thus formed can then abstract a hydrogen atom from methane molecules

$$OH + CH_4 \rightarrow H_2O + CH_3 \tag{4}$$

Once this reaction occurs, the rest of the oxidation can proceed It is outside the scope of this article to discuss in detail this mechanism, but the important point is that the oxidation of methane (and other hydrocarbons) in the troposphere only occurs after the formation of an excited oxygen atom If excited atomic oxygen were not formed in reaction (2a), hydrocarbon oxidation in the troposphere would occur by a very different mechanism What should also be clear is that the oxidising capacity of the troposphere is strongly dependent on the rate at which photolysis of ozone occurs The rate of photolysis depends on the absorption cross-section, quantum yield and the solar flux in the troposphere Because of the absorption of solar UV radiation by ozone in the stratosphere, the absorption cross-section for ozone photolysis at the wavelengths that reach the troposphere is very small The solar flux increases as wavelength increases, but above $\lambda = 310$ nm, energy restrictions do not allow formation of $O(^1D)$ in a spin-allowed process Nevertheless, experiments carried out by Hancock and coworkers[3] indicate that in this region of the spectrum, $O(^1D)$ may be generated with a significant quantum yield and the information obtained from these experiments may have important implications for our understanding of tropospheric chemistry

The chemistry of the stratosphere is also strongly influenced by $O(^1D)$ In this region of the atmosphere, the dominant chemical species is ozone, the formation and destruction of this molecule can be described by a set of oxygen-only reactions known as the Chapman scheme

$$O_2 + h\nu \rightarrow O + O \tag{5}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{6}$$

$$O_3 + h\nu \rightarrow O_2 + O \tag{2}$$

$$O + O_3 \rightarrow O_2 + O_2 \tag{7}$$

Qualitatively, this scheme describes the layered structure of ozone in this region quite well, but predicts ozone concentrations that are greater than those actually observed The origin of the discrepancy is that catalytic cycles of the type

$$X + O_3 \rightarrow XO + O_2 \tag{8}$$

$$XO + O \rightarrow X + O_2 \tag{9}$$

allow trace constituents to control the concentration of ozone because the net effect of reactions (8) and (9) is to convert one oxygen atom and one ozone molecule into two oxygen molcules, while regenerating the species X These trace species are reactive radicals such as Cl, OH and NO Chlorine atoms have a direct photochemical source, being formed in the photolysis of chlorinated organic compounds that reach the stratosphere

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl \tag{10}$$

However, another minor source involves reaction with $O(^1D)$

$$CF_2Cl_2 + O(^1D) \rightarrow ClO + CF_2Cl \tag{11}$$

followed by reaction of ClO with O atoms Furthermore, the strongest source of stratospheric NO is the reaction

$$O(^1D) + N_2O \rightarrow NO + NO \tag{12}$$

and the only sources of OH also involve $O(^1D)$

$$O(^1D) + H_2O \rightarrow OH + OH \tag{3}$$

$$O(^1D) + CH_4 \rightarrow OH + CH_3 \tag{13}$$

The effect of these active chlorine, nitrogen and hydrogen species in the natural atmosphere is to reduce stratospheric O_3 levels by a factor of two and we see that, just as in the troposphere, $O(^1D)$ plays a central role in the chemistry of the region

3 The Troposphere

Aside from the chemical change brought about by $O(^1D)$ described in the previous section, excited states do not play a very important part in the chemistry of troposphere, although they are of critical importance in determining the temperature of the atmosphere and chemical reactions can be strongly temperature-dependent Quenching of excited species by O_2 and N_2 competes effectively with unimolecular processes such as radiative decay in this region More importantly, the high-energy photons and charged particles that cause excitation in the upper atmosphere have been absorbed and there are few processes with sufficient energy to generate excited states in the troposphere One of the reasons that excited states are important in the atmosphere is that those that are accessible from the ground state in an allowed transition determine the radiation field throughout the atmosphere In the optical region of the spectrum, excited states can be located using conventional techniques,[1] while in the far-ultraviolet, electron energy loss spectroscopy[4 5] has proved useful

The main excitation mechanism in the troposphere is, as we have seen, the photolysis of ozone to generate $O(^1D)$ and $O_2(a^1\Delta_g)$ The excited atomic fragment is rapidly quenched, but generates ground-state O atoms that in turn react with molecular oxygen to form ozone and thus start the cycle again, *i e* quenching removes $O(^1D)$ from the atmosphere only temporarily The molecular product of the dissociation, $O_2(a^1\Delta_g)$, is quenched only slowly at atmospheric pressure, and is present in the troposphere at relatively high concentrations It was thought[6] that this species could contribute to the oxidation of hydrocarbons, particularly alkenes, but quantitative studies have shown it to be very unreactive $O_2(a^1\Delta_g)$ in solution is known to be important in, for example, biological systems,[7 8] and recent evidence suggests that it may play a minor role in atmospheric oxidation in cloud droplets [9]

Ozone may also lead to excited state formation *via* reaction with alkenes These reactions are 1,3-dipolar cycloadditions and the adduct falls apart to give a carbonyl and a carbonyl oxide known as a Criegee intermediate, $R^1R^2C{-}O{-}O$ In the gas phase, the intermediate is believed to be generated with significant vibrational excitation and may either decompose or be stabilised and take part in bimolecular reactions Atkinson and coworkers[10] have measured OH yields from these reactions and it seems that the OH is generated in the decomposition of the Criegee intermediate A correlation exists between the fractional yield of OH and the standard enthalpy changes for the reactions[11] of ozone with a series of alkenes The more energy released, the greater the OH yield, as might be expected if the OH is generated from a Criegee intermediate with vibrational excitation However, Hatakeyama *et al* [12] have shown that, although the yield of stabilised Criegee intermediates is pressure dependent, the yield at the high-pressure limit for (*E*)-but-2-ene is significantly less than unity They have suggested that the Criegee intermediate is generated not only with vibrational excitation, but that some is formed on an unbound electronically excited surface It is clear that much experimental and theoretical work is still required to understand the detailed mechanism of these reactions

4 The Aurorae and Airglow

The most spectacular manifestation of the existence of excited states in the Earth's atmosphere comes in the form of the Aurora Borealis (The Northern Lights) and the Aurora Australis (The Southern Lights) These phenomena appear in the polar night as shimmering flames that light up the sky, with electronically excited states of atomic oxygen playing key roles. These dramatic features result from the interaction of the solar wind with atmospheric constituents at altitudes greater than 100 km, the solar wind having been deflected by the magnetic field of the Earth. Indeed, the Earth's magnetosphere has been described as a gigantic cathode-ray tube that focuses solar electrons onto the Earth's poles, with the atmosphere behaving as a fluorescent screen.[13] It might be better, in this context, to describe the atmosphere as a phosphorescent screen, because, as will be described, the major transitions giving rise to the emitted radiation are forbidden by the electric dipole selection rules.

Incoming solar electrons with energies in the region of 10 000 eV interact with molecules in the upper atmosphere of the polar regions, leading to processes such as electron impact ionization, dissociative electron attachment and energy transfer.[14] The products of these interactions may emit radiation themselves, or take part in reactions leading to excited entities. Although a number of excited species are generated during aurorae, the most prominent visible features arise from atomic oxygen. The strongest observed emission comes from the $O(^1S) \rightarrow O(^1D)$ transition, the so-called 'auroral green line' at $\lambda = 557$ nm, but a weaker emission in the red occurs from the $O(^1D) \rightarrow O(^3P)$ transition at $\lambda = 630$ nm. These excited states are believed to be generated in the dissociative recombination process:[14]

$$O_2^+ + e \rightarrow O(^1S) + O(^3P) \qquad (14a)$$

$$O_2^+ + e \rightarrow O(^1S) + O(^1D) \qquad (14b)$$

Many of the transitions that give rise to the aurorae are formally forbidden by the electric dipole selection rules, and the extent to which they are forbidden can have a significant effect on the location of auroral features. For example, the origin of the auroral green line is at an altitude of approximately 100 km, while emission from $O(^1D)$ occurs at altitudes up to about 400 km. Part of the reason for this difference lies in the different radiative lifetimes of the two states. In order for emission to be observed, the emission rate must compete with the rate of quenching by atmospheric molecules. Emission from $O(^1S)$, with a radiative lifetime of 0.7 seconds, can compete with quenching at much lower altitudes (higher pressures) than can $O(^1D)$, with a radiative lifetime of 200 seconds. The quenching rates of the two species are also important, $O(^1S)$ being quenched much more slowly than $O(^1D)$.

Emission from $O(^1S)$ is also a strong feature of the airglow, variously called the dayglow, twilightglow or nightglow depending on when it is observed. The airglow and the aurorae share many common emission features, but the aurorae are sporadic, intense and concentrated in the polar regions, while the airglow is continuous, very weak and can be observed at all latitudes. Excitation mechanisms for particular species in the airglow often differ from those in the aurora. For example, the auroral green line is excited by energy transfer from electronically excited molecular oxygen in the nightglow. A much-simplified mechanism for its formation is:

$$O + O + M \rightarrow O_2^* + M \qquad (15)$$

$$O_2^* + O \rightarrow O_2 + O(^1S) \qquad (16)$$

where O_2^* is an electronically excited state of molecular oxygen. This two-step process is known as the Barth mechanism[15] for excitation of the green line.

Other emitters in the airglow are primarily electronically excited species, although the hydroxyl radical, OH, with vibrational excitation up to $v = 9$ makes a significant contribution to the nightglow.[2] The reaction between H atoms and ozone:

$$H + O_3 \rightarrow OH + O_2 \qquad (17)$$

has just sufficient energy to populate the 9th vibrational level[16] and is the dominant source of $OH(v)$ at night. The reaction:

$$O + HO_2 \rightarrow OH + O_2 \qquad (18)$$

which has enough energy to populate OH ($v = 6$), has been considered and rejected by Kaye[17] as a secondary source of vibrationally excited OH. However, laboratory evidence has shown that the reaction can give rise to emission from OH ($v \leqslant 6$). Figure 1 shows a discharge-flow apparatus coupled to a Fourier transform infrared spectrometer that has been used to study airglow mechanisms in the laboratory in the near-infrared region of the spectrum.[18] Using this apparatus, Lunt *et al.* detected emission from vibrationally excited OH formed in reaction 18, and an emission spectrum recorded from the products of reaction 18 is illustrated in Figure 2. A quantitative laboratory study, comparing the strength of this emission to that produced by reaction 17, is required to assess the importance of reaction 18 to the nightglow.

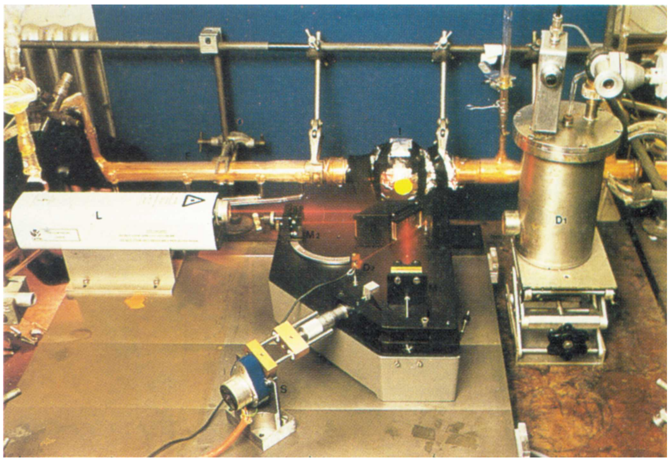

Figure 1 Discharge flow-Fourier transform spectrometer apparatus. B, beamsplitter; D_1, germanium detector; D_2, laser detector; F, flow tube; I, observation region; L, laser; M_1, moving mirror; M_2, fixed mirror; S, stepper motor. The orange glow emanating from the flow tube is the Lewis–Rayleigh afterglow produced from discharged N_2. The major contributor to the glow is from the $N_2(B^3\Pi_g \rightarrow A^3\Sigma_u^+)$ transition, which is observed in aurorae.

Not only does vibrationally excited OH contribute to the airglow, but it can also take part in chemical reactions that are not possible for ground-state hydroxyl radicals. The reaction between O atoms and OH to give $O_2(a^1\Delta_g)$ as a product is only energetically possible if the OH radical possesses at least one quantum of vibrational energy.

$$O + OH(v \geqslant 1) \rightarrow H + O_2(a^1\Delta_g) \qquad (19)$$

$O_2(a^1\Delta_g)$ is one of the strongest airglow emitters, despite the fact that the transition to the ground state $O_2(X^3\Sigma_g^-)$ is forbidden by three electric dipole selection rules; its emission spectrum[19] (measured in the laboratory) is illustrated in Figure 3 at medium resolution (*ca.* 8 cm^{-1}).

Evidence that reaction 19 occurs comes from field, modelling and laboratory investigations. Gattinger and Vallance-Jones[20] have observed correlations in rocket-borne experiments between $O_2(a^1\Delta_g)$ emissions and emissions from vibrationally excited OH, while, on the basis of a modelling study, Krasnopolsky[21] suggested that if 20% of the overall process generated $O_2(a^1\Delta_g)$, the observed altitude–concentration profiles for $O_2(a^1\Delta_g)$ could be explained. In the laboratory, Lunt *et al.*[18] have shown that reaction 19 does occur, but with an efficiency of only *ca.* 2.5%. Their results seem to indicate that reaction 2 can make only a small contribution to the night time emission, but uncertainties in calibration and the difficulties of modelling a reaction system with OH in a range of vibrational levels mean that further experiments are needed on this reaction. Current interest in $O_2(a^1\Delta_g)$ nightglow is centred on O-atom recombination followed by energy transfer,[22] in a mechanism that is closely related to the Barth mechanism for the formation of $O(^1S)$ referred to above.

It is worth mentioning at this point a recent study by Miller *et al.*,[23] following from work by Slanger,[24] that illustrates again how vibrational excitation can lead to enhanced reactivity.

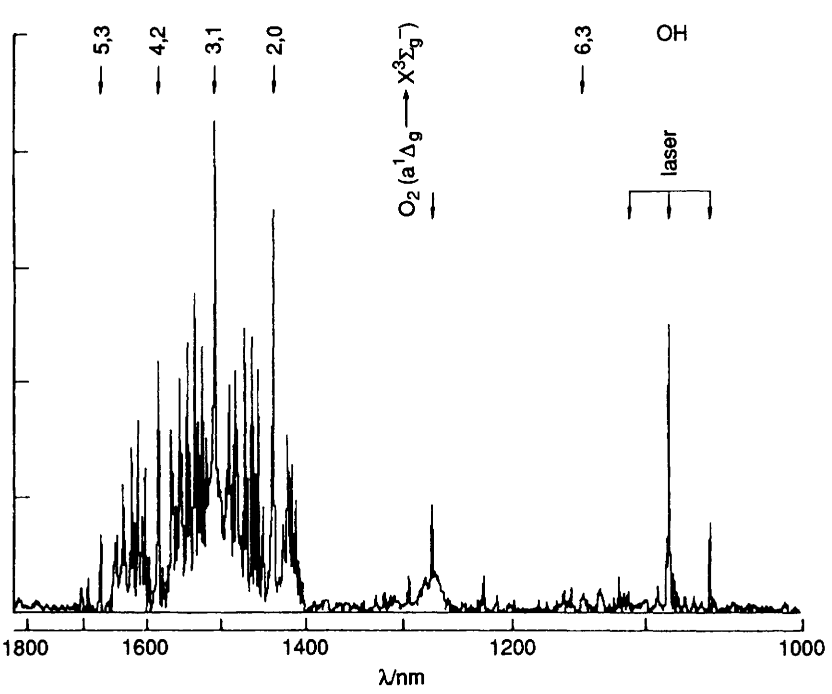

Figure 2 Vibrational emission from OH formed in the reaction of O atoms with HO_2. The numbers identify the upper and lower vibrational quantum numbers involved in the transition and the arrows locate the positions of the Q branches. The laser lines are from scattered light from the HeNe laser shown in Figure 1. Resolution, 8 cm^{-1}.

(Reproduced with permission from *J. Chem. Soc., Faraday Trans. 2*, 1988, **84**, 899)

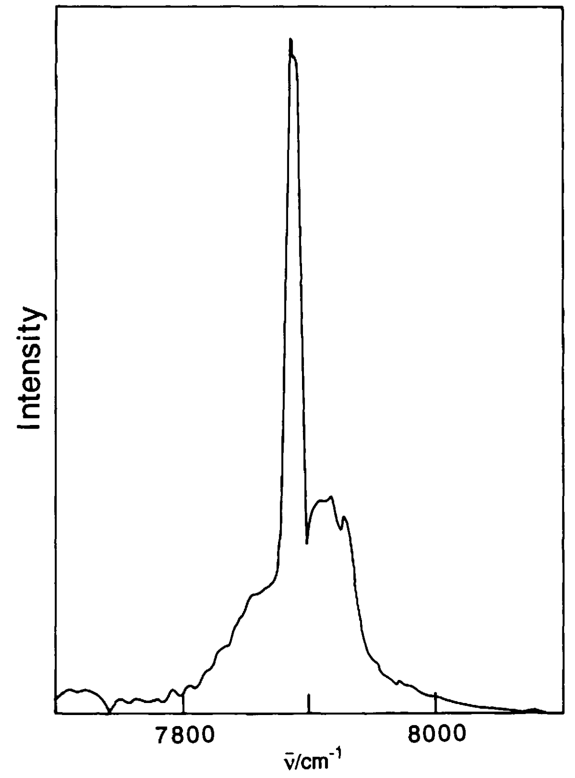

Figure 3 Emission from the transition $O_2(a^1\Delta_g \rightarrow X^3\Sigma_g^-)$. Resolution, 8 cm^{-1}.

Approximately 10% of the photolysis of ozone between 200 and 310 nm occurs to give O and O_2 in their electronic ground states:

$$O_3 + h\nu \rightarrow O_2(X^3\Sigma_g^-) + O(^3P) \qquad (2b)$$

the remaining 90% leading to excited singlets (reaction 2a). In reaction 2b, a significant fraction of the residual energy is channelled into vibrational excitation in the molecular fragment. Vibrationally excited O_2 cannot contribute to the airglow as O_2 does not possess a dipole moment, but reaction with O_2 to give O_3 is energetically feasible:

$$O_2(v \geqslant 26) + O_2 \rightarrow O + O_3 \qquad (20)$$

As yet, evidence is circumstantial, but the reaction may affect ozone concentrations by as much as 10% at some altitudes, and further laboratory investigation is urgently required.

Continuing for the moment with the subject of ozone photolysis, the major daytime contributor to the airglow is $O_2(a^1\Delta_g)$, formed in reaction 2a:

$$O_3 + h\nu \rightarrow O_2(a^1\Delta_g) + O(^1D) \qquad (2a)$$

As discussed in Section 2, there are some uncertainties in the wavelength dependence of the quantum yield for this process.[3] Nevertheless, the broad features of $O_2(a^1\Delta_g)$ formation and quenching rates are sufficiently well understood in the daytime atmosphere that measurements of emission from $O_2(a^1\Delta_g)$ made by rocket-borne instruments have been used successfully to generate $[O_3]$–altitude profiles.[25] These measurements are a slightly unusual example of how emission from excited states can be used to detect species in the atmosphere and this topic makes up the next section of this review.

5 Remote Sensing

A number of satellite-borne instruments have measured the concentrations of atmospheric constituents by observing emission from their vibrationally excited states. For example, the Limb Monitor of the Stratosphere (LIMS) instrument onboard the Nimbus 7 satellite obtained vertically-resolved concentration profiles with almost global coverage for O_3, NO_2, H_2O and HNO_3. More recently, the Improved Stratospheric and Mesopheric Sounder (ISAMS) and the Cryogenic Limb Array Etalon Spectrometer (CLAES) on the Upper Atmosphere Research Satellite (UARS) made observations on a range of molecules using this method. Concentrations are retrieved from measured radiances in appropriate regions of the spectrum and it is assumed that the species of interest is in thermal equilibrium, *i.e.* that Boltzmann's

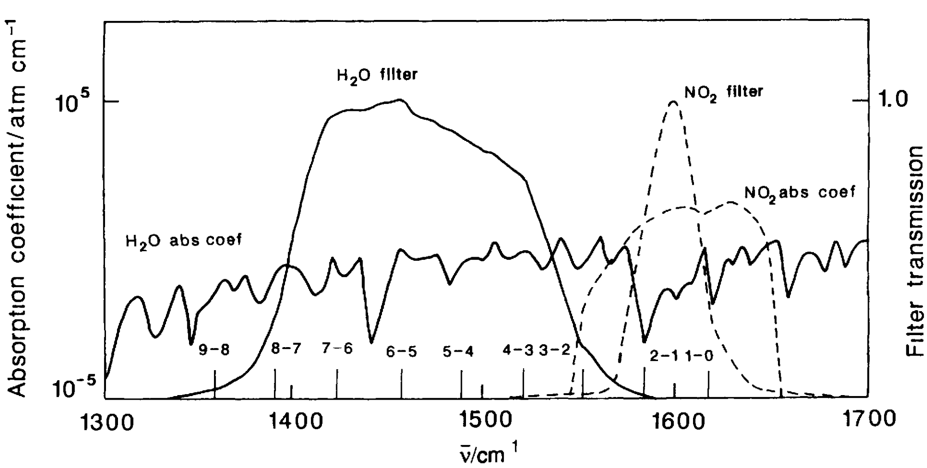

Figure 4 Spectral responses of LIMS 6.2 μm (NO_2) and 6.9 μm (H_2O) filters and absorption coefficients of H_2O ν_2 and NO_2 ν_3 fundamental bands. (Reproduced with permission from B. J. Kerridge and E. E. Remsberg, *J. Geophys. Res.*, 1989, **94**, 16323)

equation is obeyed. This assumption is known as the Local Thermodynamic Equilibrium (LTE) approximation. Absolute concentrations can be obtained for the vibrationally excited molecule if the instrument is accurately calibrated in the spectral region of interest and the Einstein *A* factor is known for the vibrational transition.

Unfortunately, the LTE approximation can break down if mechanisms other than thermal excitation exist for the formation of the vibrationally excited state that is being observed. For example, Solomon *et al.*[26] have considered whether Nonlocal Thermodynamic Equilibrium (NLTE) effects could influence the retrieval of ozone concentrations from radiance measurements by the LIMS instrument at 9.6 μm. The ν_3 fundamental band of ozone emits in this region of the spectrum, but laboratory studies showed that an appreciable fraction of the reaction

$$O + O_2 + M \rightarrow O_3 + M \qquad (21)$$

leads to excitation of ozone in this mode. In addition, the $\nu_3 = 1$ vibrational level can be excited directly by absorption of infrared radiation emitted from the Earth's surface. From a detailed modelling study using laboratory data on the kinetics of the formation and quenching of vibrationally excited ozone, Solomon *et al.* came to the conclusion that reaction 21 had a substantial effect on ozone retrievals at altitudes above 50 km. While these interferences certainly increase the difficulty of determining ozone concentrations, these authors point out that the measurements also provide information about nonthermal processes in the atmosphere.

Kerridge and Remsberg[27] have considered the possibility that NLTE in the ν_3 mode of NO_2 may affect both NO_2 and H_2O retrievals from the LIMS instrument. Figure 4 shows the spectral responses of the LIMS filters for H_2O and NO_2 along with spectra for these species between 1300 and 1700 cm^{-1}. The figure shows that direct excitation to NO_2 ($\nu_3 = 1$) by absorption of infrared radiation followed by re-radiation might affect the NO_2 measurements, but could only have a minimal effect on the water retrievals, because the overlap between the NO_2 ($\nu_3 = 1$) emission spectrum and the H_2O filter is very small. However, processes leading to the excitation of higher vibrational levels of NO_2 could lead to emission in the region of the water filter. For example the $\nu_3 = 6$ to $\nu_3 = 5$ transition occurs at the peak transmission of the H_2O filter. Kerridge and Remsberg considered two possible mechanisms for the formation of highly vibrationally-excited NO_2. Absorption of visible solar radiation at wavelengths greater than the dissociation threshold for NO_2 (400 nm) leads to excitation to the first excited state of NO_2. Very strong coupling exists between the ground (X^2A_1) and first excited state ($\tilde{A}^2B_2$) leading to vibrational excitation in the molecular ground state. The reaction of NO with O_3

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (22)$$

is known to form both electronically and vibrationally excited NO_2. Clough and Thrush published emission spectra of the $\Delta\nu_1 = \Delta\nu_3 = -1$ combination bands at 3.7 μm, and detected some emission at 6.2 μm, but did not publish the spectrum.[28]

Laboratory evidence supporting the role of reaction 22 comes from work carried out at the Rutherford Appleton Laboratory, where emission resulting from products of the reaction was recorded using a high-resolution Fourier transform spectrometer.[29] Figure 5 shows a spectrum of the emission observed on reaction of NO with O_3. The position and structure of the band reveal that it corresponds to the $\nu_3 = 1$ to $\nu_3 = 0$ transition of NO_2, showing that reaction 22 could well affect the retrieval of NO_2 from the LIMS data. Furthermore, at lower resolution, emission can be detected at slightly lower energy, as is illustrated in Figure 6. This emission appears to come from $\Delta\nu_3 = -1$ transitions of NO_2 with significant amounts of vibrational energy, providing evidence for Kerridge and Remsberg's suggestion that reaction 22 could influence the retrieval of H_2O data.

There is one further point regarding the formation of excited state products in the reaction of NO with O_3 that is of some importance. The reaction was once considered as a possible source of nighttime $O_2(a^1\Delta_g)$ in the mesosphere, thus contributing to the nightglow. However, laboratory evidence[19] indicates an upper limit of 3×10^{-5} for the fraction of reaction 22 that forms $O_2(a^1\Delta_g)$. At the same time, electronically excited $NO_2(\tilde{A}^2B_2)$ appears to be formed in the reaction. These two observations are, at first sight, contradictory. The reaction of NO with O_3 can, as a result of the degeneracy of NO, proceed on two reaction surfaces and the two lowest-lying sets of products are $NO_2(X^2A_1) + O_2(X^3\Sigma_g)$ and $NO_2(X^2A_1) + O_2(a^1\Delta_g)$. Even if we restrict the transition state to a planar configuration, these two sets of products correlate with reactants, and it is difficult to see how $NO_2(\tilde{A}^2B_2)$ can be accessed. Redpath *et al.*[30] have tried to reconcile the problem by suggesting that the reaction proceeds through a transition state where the NO approaches the central O atom of the ozone molecule, maintaining C_s symmetry. Under these circumstances, $O_2(a^1\Delta_g)$ does not correlate with reactants, whereas an excited state of NO_2 (but not the $\tilde{A}^2B_2$ state) does. However, this explanation suggests that the reaction proceeds through a transition state with a very restricted geometry. Adler-Golden[31] has suggested that NO_2 is actually generated in the ground electronic state, but with high vibrational excitation. The vibrationally excited NO_2 can then cross onto the $\tilde{A}^2B_2$ state, thus explaining how this state can be formed while $O_2(a^1\Delta_g)$ is not.

Adler-Golden's description of the reaction mechanism also explains some work carried out by Clough and Thrush,[28] who discovered that the temperature dependences of the emission from vibrationally and electronically excited NO_2 formed in reaction 22 were identical. These authors proposed that vibrationally excited NO_2 was formed *via* the electronically excited state, rather than the other way around. The difficulty with this mechanism is that it implies that none of the excess energy in the ground-state channel

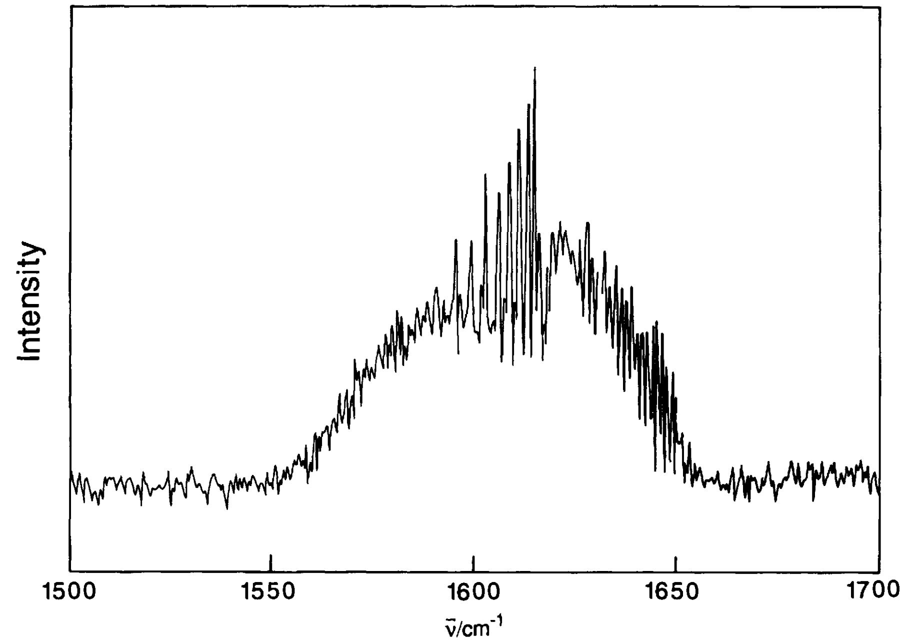

Figure 5 Spectrum showing emission from vibrationally excited NO_2 generated in the reaction of NO with O_3. Resolution, 1 cm^{-1}.

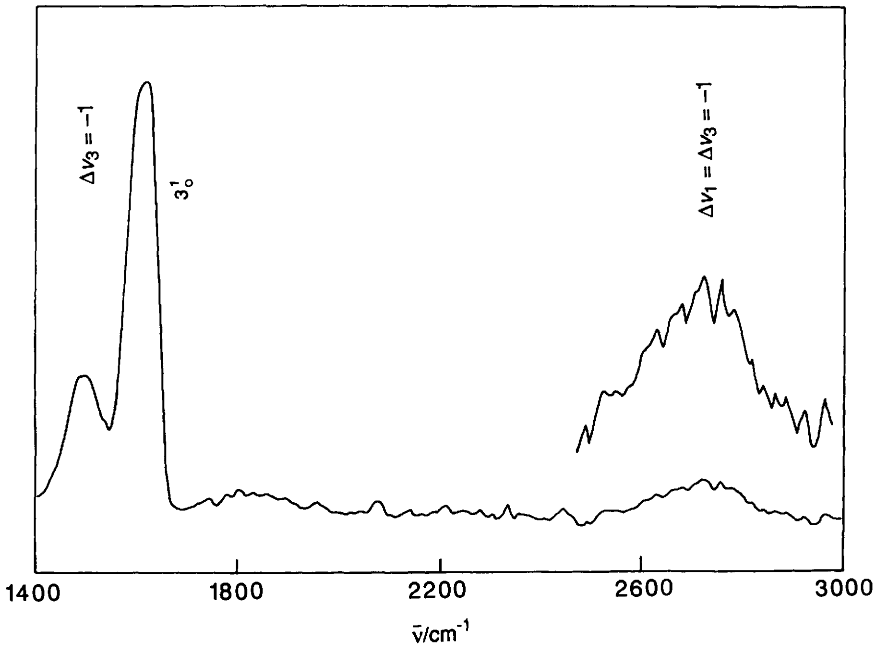

Figure 6 Spectrum showing emission from vibrationally excited NO_2 generated in the reaction of NO with O_3. Resolution, 8 cm^{-1}.

is released into the vibrational modes of NO_2; because NO_2 contains the newly formed bond in the reaction, this description of the reaction is unconvincing. From the point of view of the LIMS retrievals, the details of the mechanism are very important; only a small fraction of the reaction generates electronically excited NO_2 and Clough and Thrush's mechanism would suggest that reaction 22 could not significantly affect vibrational populations in the atmosphere. In Adler-Golden's interpretation, the experimental evidence allows a significant fraction of the reaction to generate vibrationally excited NO_2 in the atmosphere.

6 Heat Balance in the Atmosphere

In order that satellite instruments such as LIMS and ISAMS are able to measure concentrations of atmospheric constituents, energy, in the form of infrared radiation, must be transferred from the atmosphere to space. Excited states are clearly linked to this process and have an important part to play in both the heating and the cooling of the atmosphere. In the lower atmosphere, absorption of infrared radiation emitted from the Earth's surface excites vibrations and leads to warming of the atmosphere. At higher altitudes, vibrationally or electronically excited species may be generated by a number of mechanisms, and the subsequently-emitted radiation can escape this optically-thin region of the atmosphere and lead to cooling or reduced heating efficiency.

It is possible to calculate the temperature of the Earth assuming that it is in thermal equilibrium with the Sun and that both behave as black bodies.[2] The calculated temperature is approximately 256 K, in reasonable agreement with the temperature measured from space on the basis of the total thermal radiation emitted by the

Earth. However, surface temperatures on Earth are on average around 288 K, significantly higher than both the calculation and measurement from space. The origin of this discrepancy is that while the Earth may be treated, at least approximately, as a black body, the Earth and the atmosphere combined may not. Viewed from space, the total amount of radiation emitted by the Earth gives a temperature of 256 K according to Stefan's Law, but the frequency distribution of radiation is closer to that of a black body with a temperature of 288 K with radiation at certain wavelengths not present. These wavelength regions with no radiation result from the absorption of radiation by infrared-active molecules such as CO_2 and H_2O, the greenhouse gases. These molecules are excited into one of their vibrational modes and this energy is ultimately converted into heat, thus increasing the temperature of the lower atmosphere. At high altitudes, collisions can excite vibrations in infrared-active molecules (mainly CO_2), which can then emit radiation. If the atmosphere is optically thin, trapping will not occur and the radiation can escape to space, causing atmospheric cooling.

The ultimate source of heat for the Earth and its atmosphere is the Sun. While in the lower atmosphere, atmospheric heating occurs mainly indirectly, following warming of the Earth's surface, at higher altitudes heating occurs directly. A good example of the results of direct heating is the temperature inversion observed in the stratosphere.[2] This inversion occurs because ozone is present in relatively high concentrations in this part of the atmosphere, and absorbs solar UV radiation which causes a warming effect. The resultant temperature gradient, with warm air above cold, is extremely stable to vertical motion and thus has a very important effect on the atmospheric dynamics of the region. At altitudes below the stratosphere, the efficiency of conversion of solar radiation to heat is very close to unity, but it should be borne in mind that the mechanism for the conversion is complex and at higher altitudes, the efficiency may be very much reduced.

Absorption converts solar radiation into atomic and molecular internal energy, and, if bonds are broken, chemical potential energy. Mlynczak and Solomon[32] have considered the mechanism of middle atmosphere heating following the photolysis of ozone. As we have already seen, this process occurs through more than one channel:

$$O_3 + h\nu \rightarrow O_2(a^1\Delta_g) + O(^1D) \qquad (2a)$$

$$O_3 + h\nu \rightarrow O_2(X^3\Sigma_g^-) + O(^3P) \qquad (2b)$$

Rate constants for quenching of $O_2(a^1\Delta_g)$ by atmospheric gases are very small (*ca.* 10^{-20} cm^3 molecule^{-1} s^{-1}) and emission at λ = 1270 nm can transfer energy from the atmosphere; above 40 km, virtually all photons emitted in the upward direction escape and many photons emitted in the opposite direction will heat parts of the atmosphere far removed from the photolysis event. Mlynczak and Solomon make the point that this process does not constitute atmospheric cooling because the energy has not been converted to heat when it is released; rather, the escape leads to a reduction in heating efficiency of the absorbed radiation. Quenching of $O(^1D)$ by N_2 is very rapid and emission from atomic oxygen does not affect heating efficiencies in the lower thermosphere. However, vibrationally excited N_2 formed in the quenching collision can transfer its energy to CO_2 in the ν_3 mode which can then emit at λ = 4.3 μm. Mlynczak and Solomon used a detailed model to conclude that below about 50 km the heating efficiency of the singlet channel was virtually 100%, but may drop to as low as 65% at 100 km. The triplet channel could also have a reduced efficiency if the vibrationally excited O_2 were not completely converted to heat. These authors concluded that quenching was efficient, but did not consider the possibility of the reaction of vibrationally excited O_2 (Section 3, reaction 20).

The effect of chemical potential energy on the heating of the atmosphere was also considered[32] by Mlynczak and Solomon. This energy is released following exothermic chemical reaction and such reactions may occur a long way removed from where the photolysis happened, thus providing a way of transferring energy through the atmosphere; warm polar winters in the mesosphere have been attributed to this behaviour. Mlynczak and Solomon presented evidence to show that the reaction of H atoms with O_3 is an important source of heat in the middle atmosphere, although their analysis was hampered by uncertainties in the radiative and quenching lifetimes of vibrationally excited OH. It has been assumed that the reaction of O atoms with HO_2 efficiently converts chemical potential energy into heat. However, as we saw in Section 4, this reaction appears to generate vibrationally excited OH and its heating efficiency may be reduced by radiative emission from these species.

Cooling by emission from vibrationally excited CO_2 is the most important mechanism for disposing of heat from the middle atmosphere. However, at very high altitudes, this process becomes increasingly inefficient and a more important mechanism is *via* transitions between the fine-structure components of ground-state atomic oxygen, $O(^3P)$. $O(^3P)$ is made up of three components with different values of J, the quantum number for total (orbital plus spin) electronic angular momentum; the components are, in increasing energy, $^3P_2$, $^3P_1$ and $^3P_0$, with degeneracies of 5, 3 and 1, respectively. The transition:

$$O(^3P_1) \rightarrow O(^3P_2) + h\nu(\lambda = 63\ \mu m) \qquad (23)$$

is believed to make a significant contribution to the cooling of the thermosphere, at least for as long as the fine-structure components exist in thermal equilibrium. The sparsity of collisions in the upper thermosphere is such that local thermodynamic equilibrium is not maintained[33] (for $z > 400$–600 km depending on solar activity), and this cooling mechanism is lost as the $J = 2$ level becomes overpopulated relative to the other components. This effect is an interesting example as it shows that the excited state can be important because it is not occupied when, on the basis of the Boltzmann distribution, it should be.

7 Nitric Oxide in the Thermosphere

Another species that contributes to the dissipation of energy from the thermosphere is nitric oxide, NO, which appears to moderate the temperature during periods of high solar and geomagnetic activity. A discussion of the behaviour of this molecule in the thermosphere is particularly pertinent to this review because we must consider translational, rotational, vibrational and electronic excitation! Thermospheric nitric oxide is of great importance because during the long polar winter it is transported down through the atmosphere and affects stratospheric ozone concentrations.[34] The molecule is formed in the reaction of ground-state $N(^4S)$ atoms with O_2:

$$N(^4S) + O_2 \rightarrow NO + O \qquad (24)$$

This reaction is slow at room temperature,[35] and even at thermospheric temperatures is not a major source because NO can be destroyed in the 'cannibalistic' reaction:

$$N(^4S) + NO \rightarrow N_2 + O \qquad (25)$$

A more important source of NO[34] involves the reaction of the first electronically excited state of N atoms, $N(^2D)$, with O_2:

$$N(^2D) + O_2 \rightarrow NO + O \qquad (26)$$

This species is generated in a number of processes, the main lower thermospheric source[34] being the dissociative electron attachment of NO^+:

$$NO^+ + e \rightarrow N(^2D) + O \qquad (27)$$

while electron impact dissociation of N_2 is also important:

$$N_2 + e \rightarrow N(^4S) + N(^2D) + e \qquad (28)$$

The electrons involved in reaction 28 must possess a significant amount of energy in order to effect the dissociation and are either photoelectrons or secondary auroral electrons. A second excited state of atomic nitrogen, $N(^2P)$, is also formed[36] in the electron-impact dissociation of N_2, but is quickly quenched to $N(^2D)$ Barth[34] concluded in a modelling study that NO concentrations in the lower thermosphere were highly sensitive to the branching ratio for $N(^2D)$ in reactions 27 and 28

However, there are other uncertainties associated with thermospheric NO production It has been suggested that one channel of reaction 26 may lead to the formation of $O(^1D)$ and thus contribute to auroral or dayglow emission at 630 nm Gérard[36] suggests that there is no evidence one way or the other for this supposition and that the problem will not be resolved until direct laboratory evidence is obtained Recent measurements indicate that NO is present in the thermosphere in high vibrational states, but also with rotational energy significantly greater than expected from thermal processes [37] Reaction 26 is *energetically* capable of accessing the observed levels, but angular momentum constraints seem to require significant translational energy in the reactants [37] Theoretical calculations on the dynamics of reaction 24 suggest that translationally hot ground-state $N(^4S)$ atoms may react with O_2 significantly faster than N atoms with a thermal velocity distribution and be an important source of NO, particularly in the daytime thermosphere [38]

Emission from electronically excited NO is also detected in the thermosphere,[39] one source being the recombination of N and O atoms

$$N + O \rightarrow NO^* \qquad (29)$$

The δ and γ bands of NO have been detected by rocket-borne spectrometers[39] and used to derive nighttime $N(^4S)$ altitude–concentration profiles (during the day, fluorescent emission from electronically excited NO interferes with such measurements, but has been used to determine NO concentrations) Emission from $NO(b^4\Sigma\ )$ generated in reaction 29 has been detected in the near-infrared,[40] and it can be assumed that a considerable fraction of the reaction leads to $NO(a^4\Pi)$ formation, as only this state and the ground state correlate with the reactant atoms It is likely that these states have some role to play in the heating efficiency of reaction 29, doublets formed in the reaction will emit radiation to space, ultimately giving ground-state $NO(X^2\Pi)$, emission from $NO(a^4\Pi)$ is forbidden by the electronic dipole selection rules, and so energy stored in this state should be efficiently converted to heat

8 Concluding Remarks

In this paper the role of the excited state in the atmosphere has been reviewed It is clear that excited states are important in many aspects of atmospheric chemistry and physics Some parts of the science are quite well understood, the chemistry of $O(^1D)$ in the troposphere is a good example, although it should be remembered that there are uncertainties in the quantum yield for its formation from ozone photolysis at wavelengths that are important in the lower atmosphere Advances in satellite technology allow excited species to be observed in the remotest regions of the atmosphere and enormously fast digital computers can be used to interpret the measurements through modelling studies These models require a detailed knowledge of the fundamental physical and chemical processes that occur in the atmosphere and such knowledge comes from laboratory experiments Many questions concerning these fundamental processes remain unanswered and even details from well-studied systems (*e g* ozone photolysis) can prove to have important consequences Determining quantitative details for the mechanisms of formation of excited species and their losses through quenching, radiative decay and reaction require sophisticated experimental methods and still provide a significant challenge for laboratory scientists

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