Chemistry in the Upper Atmosphere
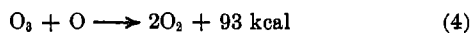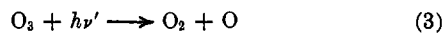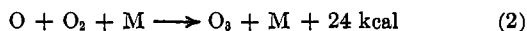
MURRAY J. MCEWAN AND LEON F. PHILLIPS

Chemistry Department, University of Canterbury, Christchurch, New Zealand

The chemistry of the upper atmosphere can be investigated in a variety of ways, including ground-based observation of airglow emission, the use of rocket-borne photometers and mass spectrometers, ground observations of "seeding" experiments in which chemicals are released from a rocket at a high altitude, and laboratory studies of the atomic, molecular, and ionic species shown to be present by field experiments. The present article is concerned almost entirely with the last type of investigation—in particular, we shall describe current laboratory studies of reactions involving electronically excited atoms or molecules and some recent work on ion–molecule reactions. More comprehensive accounts covering the whole area of aeronomy may be found in several books and in the proceedings of some recent conferences.[1-5] As an aid to the general reader the next few paragraphs comprise an introductory survey of the field.

The structure of an idealized model of the atmosphere is shown in Figure 1. In practice the details of the structure vary in a predictable way with latitude, time of day, season, and position in the 11-year cycle of solar activity. Absorption of sunlight at wavelengths below 1760 Å causes the dissociation of O_2 to be virtually complete during the day at altitudes greater than about 120 km and provides a reservoir of energy for the various processes that occur at night. A weaker absorption continuum below 2420 Å produces a large rate of O_2 dissociation, with consequent formation of an important ozone-containing layer, between 30 and 40 km altitude. It is this ozone layer which prevents light of wavelengths shorter than 2900 Å from reaching the Earth's surface. In addition, the light absorbed in this region is converted to heat by the reaction sequence

$$O_2 + h\nu \longrightarrow 2O \tag{1}$$
$$O + O_2 + M \longrightarrow O_3 + M + 24 \text{ kcal} \tag{2}$$
$$O_3 + h\nu' \longrightarrow O_2 + O \tag{3}$$
$$O_3 + O \longrightarrow 2O_2 + 93 \text{ kcal} \tag{4}$$

and is responsible for the steady increase of temperature with altitude that occurs in the stratosphere.

Above about 100 km the gas pressure is low enough (10^{-4} Torr or less) for diffusion to be an important mode of mass transport. During the day stable species such as O_2 diffuse upward until photodissociation occurs, whereupon the resulting fragments diffuse downward until they are removed by reaction or three-body recombination. Between 85 and 100 km the presence of significant amounts of such reactive species as O, H, OH, O_3, and NO leads to the occurrence of a variety of chemiluminescent reactions. The light emission from these reactions is visible from the ground at night (the night glow) and from rockets in the day (the day glow). Interesting emission spectra, including resonance scattering from traces of sodium and other metals, are also visible in the twilight glow, which is observed when the sun appears to be below the horizon at ground level but is still in view from an altitude of 50–150 km.

The strongest features in the night glow are listed in Table I, together with the reactions that are thought to give rise to the excited species. This table is derived from the review by Young,[6] where further discussion may be found. Of particular interest at present are weak emission features arising from long-lived species, such as $O(^1D)$ (radiative lifetime 110 sec) or $O_2(^1\Delta_g)$ (radiative lifetime ca. 45 min), since such species would be expected to have a good chance of taking part in further reactions before losing their energy. Indeed the red emission from $O(^1D)$ is only observed at high altitudes (ca. 200 km and above) where the pressure is very low, because this state is efficiently quenched by O_2 and N_2. The relatively strong green line of atomic oxygen, which has the ^1D level as its lower state, has its maximum intensity near 100 km where the red line is not observed at all. The $^1\Delta_g$ state of O_2 has a lifetime much greater than that of $O(^1D)$, but is only weakly quenched by O_2 and N_2, so that the infrared atmospheric bands are emitted at 100 km and below. The weak nightglow emissions include scattered Lyman-α (1216 Å) radiation of atomic hydrogen. Scattered Lyman-α is observed very strongly in the day glow at altitudes down to about 100 km; solar Lyman-α can be detected down to 70 km, its penetration to this depth being the fortuitous results of the presence of a window at 1216 Å in the absorption spectrum of O_2. During the day, under steady illumination, the usual night-glow emission features appear greatly enhanced, and some new features appear.

A significant proportion of the solar radiation that is

(1) J. W. Chamberlain, "Physics of the Aurora and Airglow," Academic Press, New York, N. Y., 1961.

(2) J. A. Ratcliffe, Ed., "Physics of the Upper Atmosphere," Academic Press, New York, N. Y., 1960.

(3) B. M. McCormac, Ed., "Aurora and Airglow," Reinhold Publishing Corp., New York, N. Y., 1967.

(4) I.A.G.A. Symposium, Berkeley, 1963 (published in *Ann. Geophys.*, **20**, 47 (1964)).

(5) I.A.G.A. Symposium on Laboratory Measurements of Aeronomic Interest, York University, Toronto, 1968; *Can. J. Chem.*, **47**, 1703 (1969).

(6) R. A. Young, *ibid.*, **47**, 1927 (1969).

Table I

Nightglow Emission Features

λ, Å	Emitter	Height of emitting layer, km	Intensity, rayleighs[a]	Probable excitation process
5893	$Na(^2P)$	Ca. 85	100	$Na + O_2{}^* \rightarrow Na^* + O_2$
6300	$O(^1D)$	Above 200	100	$O_3{}^+ + e \rightarrow O^* + O$
5577	$O(^1S)$	Ca. 85	250	$O + O_2{}^* \rightarrow O^* + O_2$
Continuum 4000–15,000	$NO_2(?)$	Ca. 85	1000	$NO + O + M \rightarrow NO_2{}^* + M$
Herzberg bands 3000–4000	$O_2(A^3\Sigma_u{}^+)$	Ca. 85	1000	Complex, but based on $O + O + M \rightarrow O_2{}^* + M$ (and $H + O_3 \rightarrow OH + O_2{}^*$)
Atmospheric bands 7000–9000	$O_2(b^1\Sigma_u{}^+)$	Ca. 85	3×10^4	Complex, but based on $O + O + M \rightarrow O_2{}^* + M$ (also $O(^1D) + O_2 \rightarrow O + O_2(^1\Sigma)$)
Infrared atmospheric bands 1.27 μ, 1.58 μ	$O_2(a^1\Delta_g)$	Ca. 85	5×10^4	$O + O + M \rightarrow O_2{}^* + M$ $O_2{}^* + M \rightarrow O_2(^1\Delta) + M$ (also from ozone photolysis)
Meinel bands 5000 Å–5 μ	$OH (v \leqslant 9)$	Ca. 85	4.5×10^6	$H + O_3 \rightarrow OH^* + O_2$

[a] 1 rayleigh = 10^6 photons per second from a 1-cm^2 column of atmosphere.
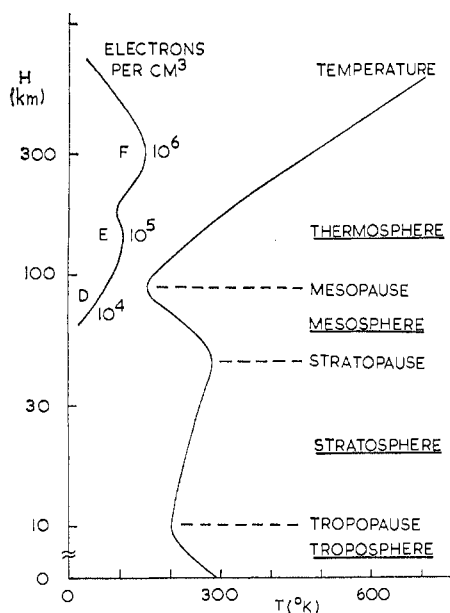

Figure 1. Atmospheric structure and nomenclature. The troposphere contains the weather; the stratosphere is the region of increasing temperature with height immediately above the troposphere; the mesosphere is the region of decreasing temperature with height between stratosphere and thermosphere; the thermosphere is the outer region of temperature increasing with height which ultimately merges with the outermost layer of the sun's atmosphere.

absorbed during the day is at sufficiently short wavelengths to produce photoionization. Thus there is a region of the atmosphere, known as the ionosphere, in which the gas comprises a dilute plasma of ions and electrons. The various regions of the ionosphere are characterized by their altitude and electron density, which ranges from less than $10^4/cm^3$ in the D layer, at about 70 km altitude, to $10^6/cm^3$ in the F_2 layer, at about 300 km. Several of the more abundant ions, notably NO^+, are thought not to be formed by direct photoionization above 100 km, but rather by fast ion-molecule reactions such as

$$N_2{}^+ + O \longrightarrow NO^+ + N \qquad (5)$$
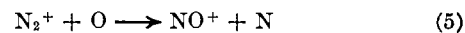
Recently evidence has been obtained to suggest that many of the ions in the D region may exist primarily as hydrated clusters of the type $[M(H_2O)_n]^+$. This completes our introductory survey; we turn next to some specific topics, of which the first is ion–molecule reactions.

Ion–Molecule Reactions

Reactions between ions and neutral species are expected to be important processes in the ionosphere. Primary positive ions are produced by photoionization; primary negative ions by electron attachment. Among the reactions available to primary ions are charge transfer (eq 6) and ion–atom interchange (eq 7).

$$A^{\pm} + BC \longrightarrow A + BC^{\pm} \qquad (6)$$

$$A^{\pm} + BC \longrightarrow AB^{\pm} + C \qquad (7)$$
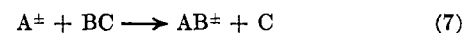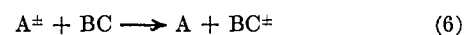
We do not intend to give a comprehensive review of all the ion–molecule reactions of aeronomic interest; for this the reader is referred to papers presented at the I.A.G.A. Aeronomy Symposium (Toronto, 1968) by Biondi,[7] Fite,[8] Phelps,[9] and Ferguson.[10] Instead we shall discuss some current studies relating to processes 6 and 7.

Until about 5 years ago the majority of ion–neutral reactions of interest to aeronomy had not had their rates measured in the laboratory in the energy range relevant to ionospheric conditions. Only in the past 5 years, and largely by the application of the *flowing afterglow* (FA) technique, have the rates of many of these reactions been measured. Because of the success of the FA technique, it is appropriate to describe it briefly here.

(7) M. A. Biondi, *Can. J. Chem.*, **47**, 1711 (1969).
(8) W. Fite, *ibid.*, **47**, 1797 (1969).
(9) A. V. Phelps, *ibid.*, **47**, 1783 (1969).
(10) E. E. Ferguson, *ibid.*, **47**, 1815 (1969).

Table II
Approximate Ionospheric Conditions[a]

Region	Height	Principal ions	[M]	[A]	Temp
D	60	NO^+, $H(H_2O)_2^+$, H_3O^+, NO_2^-	15	10	350
E	110	NO^+, O_2^+, e	13	11	250
Sporadic E	110	Mg^+, Fe^+, Si^+, Ca^+, e	13	11	250
F1	170	NO^+, O_2^+, O^+, e	10	10	700
F2	300	O^+, N^+, O_2^+, NO^+, e	8	9	1500
Magnetosphere	1000	H^+, He^+ (?)		5	1500

[a] Quiet, daytime, midsolar cycle. Heights are in kilometers, temperatures in °K, and molecular [M] and atomic [A] are given as log [N cm^{-3}].

The FA technique developed by Ferguson, Fehsenfeld, Schmeltekopf, and their collaborators[11] is an extension of the mass spectrometric discharge flow method used in studying reactions between neutral species.[12] Essentially the method is to observe the attenuation of a steady stream of ions flowing rapidly down a reaction tube in company with an excess of the second reactant. The rate of disappearance of primary ions and appearance of secondary ions is monitored as a function of either the neutral reactant flow or the inlet–sample port distance (i.e., reaction time). The ions are analyzed with a differentially pumped mass spectrometer which monitors samples withdrawn through an aperture on the axis of the reaction tube. Flow speeds within a reaction tube 1 m long and 8 cm in diameter are of the order of 10^4 cm sec^{-1} at pressures between 0.1 and 1 Torr. Because the neutral reactants are normally present in a large excess, the concentrations of primary ions decrease exponentially as either time or reactant pressure increases. This decrease can commonly be observed quantitatively over a range of several decades. In favorable cases, it is possible to achieve rate constants that are accurate to within ±10% by this method.[10] Therefore aeronomical calculations are more likely to be limited by uncertainties in critical neutral constituent concentrations than by uncertainties in these rate constants.

Table II, which shows the variation of principal ion species with altitude, is derived from the review by Biondi.[7]

Atmospheric Positive Ions. Because many direct rocket-borne mass spectrometer measurements have been made for atmospheric positive ions, their concentrations are much better established than those of negative ions. The relative importance of NO^+ arises because the low ionization potential of NO (9.3 eV) causes reactions removing NO^+ to be endothermic and therefore slow. Thus its loss is due almost entirely to dissociative recombination rather than ion–molecule reaction.

Positive ions not shown in Table II, but which are also present in the ionosphere, include N_2^+ and the metal ions Na^+, Ni^+, and Al^+ observed in the E region in rocket flights of Narcisi[13] and Young, et al.[14] It is generally assumed that a large fraction of the metal ions arise from meteor ablation. N^+, which has a small number density below 150 km ($<10^2$ cm^{-3}), becomes one of the more abundant ions around 300 km.[15]

At night, in the absence of the sun's ionizing radiation, there is a steady decrease in the positive ion and electron densities. One of the problems remaining is that the persistence at night of many atmospheric ions, such as N_2^+ and O_2^+, appears to imply the presence of an ionizing source. The origin and energy of this source have yet to be ascertained.[16,17]

Atmospheric Negative Ions. The presence of negative ions in the ionosphere is a consequence of electron attachment processes and negative ion–molecule reactions. Negative ions that are expected to be important in the D region are NO_2^-, NO_3^-, and CO_3^-, probably with lower concentrations of O^-, O_2^-, and O_3^-.[10,18]

Undoubtedly the two most interesting current problems related to ion–molecule reactions and aeronomy are (i) reactions involving excited species and (ii) molecule–ion clusters.

Reactions of Excited Species. The airglow is the result of light emission by electronically excited atoms, molecules, and ions. Clearly these excited species influence the chemistry of the upper atmosphere, and it therefore becomes important to know how the rates of ion–molecule reactions are altered by either the neutral or charged species possessing electronic and/or vibrational energy. Very little has been published on ion reaction rates with excited neutral species, mainly because of experimental difficulties in obtaining the excited neutral reactant free from other reactive species.

Schmeltekopf, et al.,[19] have measured the ion–atom interchange reaction of atomic oxygen ions with vibra-

(11) F. C. Fehsenfeld, A. L. Schmeltekopf, P. D. Goldan, H. I. Schiff, and E. E. Ferguson, J. Chem. Phys., 44, 4087 (1965).

(12) (a) L. F. Phillips and H. I. Schiff, ibid., 36, 3283, 1509 (1962); (b) J. T. Herron, ibid., 35, 1138 (1961).

(13) R. S. Narcisi, Space Res., 8, 360 (1967).

(14) J. M. Young, C. Y. Johnson, and J. C. Holmes, J. Geophys. Res., 72, 1473 (1967).

(15) M. B. McElroy, Planet. Space Sci., 15, 457 (1966).

(16) T. M. Donahue, ibid., 14, 33 (1966).

(17) E. E. Ferguson, F. C. Fehsenfeld, P. D. Goldan, and A. L. Schmeltekopf, J. Geophys. Res., 70, 4323 (1965).

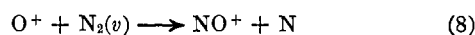(18) F. C. Fehsenfeld, A. L. Schmeltekopf, H. I. Schiff, and E. E. Ferguson, Planet. Space Sci., 15, 373 (1967).

(19) A. L. Schmeltekopf, F. C. Fehsenfeld, G. I. Gilman, and E. E. Ferguson, ibid., 15, 401 (1967).

tionally excited nitrogen (eq 8). They found that at a

$$O^+ + N_2(v) \longrightarrow NO^+ + N \tag{8}$$

$$k_8 = (2 \pm 1) \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \text{ at } 300°K$$

vibrational temperature of 4000°K the rate increases by a factor of 20 over $N_2(v = 0)$. Vibrationally excited nitrogen is believed to be produced at E region altitudes mainly by the quenching of $O(^1D)$ by N_2, and at higher altitudes by photoelectron impact on N_2. An alternative source is reaction 9.

$$N + NO \longrightarrow N_2(v \leqslant 12) + N \tag{9}$$
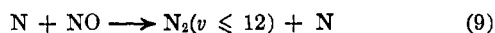
The enhanced reaction rate of O^+ with vibrationally excited N_2 may account for the decrease in electron density in the F region during magnetic storms and auroras.[20] Similarly, the enhanced vibrational temperatures of N_2, believed to give rise to the high electron temperatures observed in the E region, should increase the rate of removal of O^+ ions by about a factor of 10.[21]

The metastable $O_2(^1\Delta_g)$ is a prime choice for an electronically excited neutral reactant for laboratory studies, especially in view of the observation of the highly forbidden $a^1\Delta_g \rightarrow X^3\Sigma_g^-$ infrared atmospheric bands in the airglow.[22] To date Fehsenfeld, et al.,[23] appear to have made the only laboratory measurements of an ion-molecule reaction of $O_2(^1\Delta_g)$. The rates for the electron detachment reactions

$$O_2(^1\Delta_g) + O_2^- \longrightarrow 2O_2 + e \tag{10}$$

$$O_2(^1\Delta_g) + O^- \longrightarrow O_3 + e \tag{11}$$
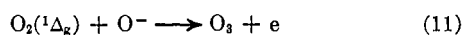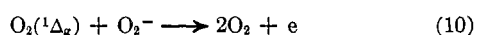
are 2×10^{-10} and 3×10^{-10} cm³ sec⁻¹, respectively, which makes them fast enough to be important in the D region.

Molecule–Ion Clusters. Narcisi,[24] in a series of rocket-borne mass spectrometer measurements of the ions of the D and E regions, observed peaks below 82 km at masses 19 and 37 which he attributed to H_3O^+ and $H_3O^+ \cdot H_2O$, respectively. The repeated observation of these masses in subsequent flights[13] appears to rule out the possibility of rocket contamination and to establish the H_3O^+ ion as one of the dominant ions of the D region, and the polar water molecule as an important clustering agent. This conclusion is substantiated by the similarity of the sharp decrease observed near the mesopause in H_3O^+, $H_5O_2^+$, and neutral water vapor concentrations.[25] In addition, the heavy ions (>45 amu) observed in rocket flights below 82 km could be due to higher hydrates of H_3O^+ or hydrates of other atmospheric ions. Until very recently the origin
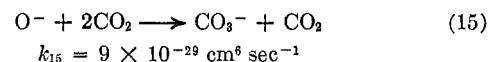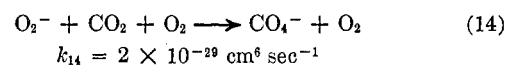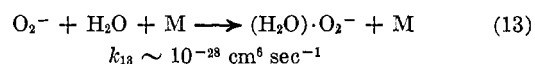
of water cluster ions was unexplained. The suggestion by Hunten and McElroy[26] of an O_2^+ source in the D region arising from photoionization of $O_2(^1\Delta_g)$ enabled Fehsenfeld and Ferguson[27] to suggest a mechanism for clustering involving the intermediate ions $O_2 \cdot O_2^+$ and $O_2^+ \cdot H_2O$. Satisfactory agreement was found between the concentrations of H_3O^+ and $H_3O^+ \cdot H_2O$ observed by Narcisi and those calculated on the basis of $O_2 \cdot O_2^+$ participation.[28]

Turner and Rutherford[29] have measured the laboratory reaction rates of N^+, O^+, N_2^+, NO^+, O_2^+, and Ar^+ with H_2O and of O_2, NO, and H_2O with H_2O^+, in the energy range 1 to 400 eV. They conclude that the major loss mechanisms for H_3O^+ in the atmosphere are clustering, recombination, and charge transfer with metal vapors. It is conceivable, therefore, that many of the ions present in the D region may be hydrated, especially as the majority of exothermic ion–molecule reactions involving the water molecule are fast. For example, Schiff, et al.,[30] using the FA technique, have measured the rate of reaction 12 at thermal energies and

$$H_3^+ + H_2O \longrightarrow H_3O^+ + H_2 \tag{12}$$
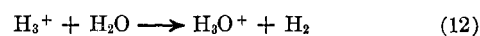
found $k_{12} = 3 \times 10^{-9}$ cm³ sec⁻¹.

Molecular clusters of aeronomic interest are by no means confined to positive ions or, for that matter, to the water molecule. Fite and Rutherford[31] monitored the afterglow of air with a mass spectrometer and found that clustering of up to two water molecules to NO_2^- occurred very readily. Pack and Phelps,[32] in drift tube studies of electron attachment and detachment in CO_2, O_2, H_2O mixtures, observed clustering of CO_2 and H_2O to O_2^- to produce ions such as CO_4^- and $(H_2O)_nO_2^-$. The rate coefficients of these clustering reactions are very large.[33] Consequently it is reasonable to expect

$$O_2^- + H_2O + M \longrightarrow (H_2O) \cdot O_2^- + M \tag{13}$$
$$k_{13} \sim 10^{-28} \text{ cm}^6 \text{ sec}^{-1}$$

$$O_2^- + CO_2 + O_2 \longrightarrow CO_4^- + O_2 \tag{14}$$
$$k_{14} = 2 \times 10^{-29} \text{ cm}^6 \text{ sec}^{-1}$$

$$O^- + 2CO_2 \longrightarrow CO_3^- + CO_2 \tag{15}$$
$$k_{15} = 9 \times 10^{-29} \text{ cm}^6 \text{ sec}^{-1}$$

significant concentrations of hydrated negative ions below 82 km, and future findings of mass spectrometric observations of the negative ion composition of the atmosphere are awaited with great interest.

(20) J. C. G. Walker, *Planet. Space Sci.*, **16**, 321 (1968).

(21) L. Thomas and R. B. Norton, *J. Geophys. Res.*, **71**, 227 (1966).

(22) W. F. J. Evans, D. M. Hunten, E. J. Llewellyn, and A. V. Jones, *ibid.*, **73**, 2885 (1968).

(23) F. C. Fehsenfeld, D. L. AlBritton, J. A. Burt, and H. I. Schiff, *Can. J. Chem.*, **47**, 1793 (1969).

(24) R. S. Narcisi, *Space Res.*, **7**, 186 (1967).

(25) R. S. Narcisi, *Ann. Geophys.*, **22**, 224 (1966).

(26) D. M. Hunten and M. B. McElroy, *J. Geophys. Res.*, **73**, 2421 (1968).

(27) F. C. Fehsenfeld and E. E. Ferguson, *ibid.*, **74**, 2217 (1969).

(28) F. C. Fehsenfeld and E. E. Ferguson, *ibid.*, in press.

(29) B. R. Turner and J. A. Rutherford, *ibid.*, **73**, 6751 (1968).

(30) J. Burt, J. L. Dunn, M. J. McEwan, and H. I. Schiff, submitted for publication.

(31) W. L. Fite and J. A. Rutherford, *Discussions Faraday Soc.*, **37**, 192 (1964).

(32) J. L. Pack and A. V. Phelps, *J. Chem. Phys.*, **45**, 4316 (1966).

(33) J. L. Moruzzi and A. V. Phelps, *ibid.*, **45**, 4617 (1966).

Table III

Electronically Excited Species of Importance in the Atmosphere

Ground state	Excited species	Excitation energy, eV	Lifetime, sec	Ref (lifetime)
$O(^3P)$	^1D	1.96	110	1
	^1S	4.17	0.74	1
$O_2(^3\Sigma_g^-)$	$a^1\Delta_g$	0.98	2.7×10^3	35
	$b^1\Sigma_g^+$	1.63	12	36
	$A^3\Sigma_u^+$	4.53	Metastable	
$N(^4S)$	^2D	2.37	9×10^4	1
$N_2(^1\Sigma_g^+)$	$A^3\Sigma_u^+$	6.17	10, 1.4 ($v = 0$)	37, 38
	$^3\Delta_u$	7.1	Metastable	
	$^5\Sigma_g^+$	9.63	Metastable	
	$C^3\Pi_u$	11.03	4.7×10^{-8}	37, 39
$N_2^+(^2\Sigma_g^+)$	$A^2\Pi_u$	1.12	3×10^{-6}	40
	$B^2\Sigma_u^+$	3.17	6×10^{-8}	37, 39
$H(^2P)$	^2P	10.20	1.6×10^{-9}	41

Summary of Excited Neutral Species

Electronically excited species that are expected to be important in the upper atmosphere are listed in Table III. All of these species except $N_2(^3\Delta_u)$ have been observed in emission in the airglow. Some short-lived or highly excited states which contribute to the airglow, for example, $O(^3S)$ at 9.52 eV, $\tau = 1.7 \times 10^{-9}$ sec,[34] are not included in the list. Only relatively long-lived species, with lifetimes greater than about 10^{-3} sec, are likely to participate in chemical reactions, although the possibility of radiation trapping may alter this view slightly for $H(^2P)$.

Reactions Involving N_2 and N

Although nitrogen is the most abundant constitutent of the atmosphere except at very high altitudes, neutral nitrogen compounds play a relatively minor part in upper atmosphere chemistry. This is because, in contrast to O_2, N_2 is not readily dissociated by light in any spectral region. Apart from a weak predissociation[42] in the $a^1\Pi_g \rightarrow X^1\Sigma_g^+$ (Lyman–Birge–Hopfield) system below 1250 Å, and possibly stronger predissociations in the 800–1000-Å region,[43] the production of atomic nitrogen depends on a primary photoionization process (eq 16) followed by dissociative recombination (eq 17)

$$N_2 + h\nu \ (\lambda < 800 \ \text{Å}) \longrightarrow N_2^+ + e \qquad (16)$$

$$N_2^+ + e \longrightarrow N + N \qquad (17)$$
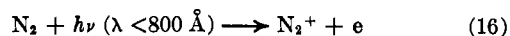
or by ion–molecule reactions such as eq 18. Bands

$$N_2^+ + O \longrightarrow NO^+ + N \qquad (18)$$

of N_2 and N_2^+ and lines of N and N^+ are very common features of auroral spectra, but are almost entirely absent from the normal night glow. The 0,0 band of the first negative system of N_2^+ at 3914 Å is present in the twilight glow and day glow as a result of fluorescent scattering. The aurora is believed to arise from bombardment of the outer layers of the atmosphere with energetic particles, mainly protons, emitted by the sun and constrained by the earth's magnetic field to enter near the poles. Comparable spectra are observed when air is bombarded with ions in the laboratory. The broad continuum which underlies nightglow spectra probably has as its major source the association reaction of NO with atomic oxygen,[6] the partial pressure of NO being fixed at about $10^{-5}[O_2]$ by the steady state of reactions 19 and 20. It might be

$$N + O_2 \longrightarrow NO + O \qquad (19)$$
$$k_{19} = 1 \times 10^{-15} \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{sec}^{-1} \ [44]$$
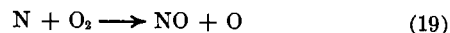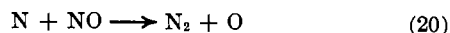
$$N + NO \longrightarrow N_2 + O \qquad (20)$$
$$k_{20} = 2 \times 10^{-11} \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{sec}^{-1} \ [12]$$

expected that a significantly higher steady-state NO concentration would result if reaction 19 were to involve an oxygen molecule in the metastable $^1\Delta_g$ state. However, it appears that this reaction is not markedly faster with $O_2(^1\Delta_g)$ than with ground state O_2.[45]

Many studies with some relevance to the upper atmosphere have been carried out using active nitrogen, i.e., nitrogen pumped from an electric discharge, as a source of nitrogen atoms and/or excited molecules. A comprehensive review of such work prior to 1966 is contained in the book by Wright and Winkler.[46] Some recent studies have thrown light on the relaxation behavior of systems containing a mixture of electronically and vibrationally excited molecules with ground-state atoms, and this we now discuss in detail.

(34) (a) G. M. Lawrence, Bull. Am. Phys. Soc., 13, 424 (1968); (b) M. Gaillard and J. E. Hesser, Astrophys. J., 152, 695 (1968).
(35) R. M. Badger, A. C. Wright, and R. F. Whitlock, J. Chem. Phys., 43, 4345 (1965).
(36) E. C. Zipf, Can. J. Chem., 47, 1863 (1969).
(37) R. W. Nicholls, ibid., 47, 1847 (1969).
(38) D. E. Shemansky and N. P. Carleton, J. Chem. Phys., in press.
(39) J. E. Hesser, ibid., 48, 2519 (1968).
(40) R. W. Nicholls, Ann. Geophys., 20, 144 (1964).
(41) H. A. Bethe and E. E. Salpeter, "Handbuch der Physik," Vol. 35, S. Flugge, Ed., Springer-Verlag, Berlin, 1957, p 352.
(42) A. E. Douglas and G. Herzberg, Can. J. Phys., 29, 294 (1951).
(43) R. D. Hudson and V. L. Carter, J. Geophys. Res., 74, 393 (1969).

(44) K. Schofield, Planet. Space Sci., 15, 643 (1967).
(45) I. D. Clark and R. P. Wayne, Chem. Phys. Letters, 3, 405 (1969).
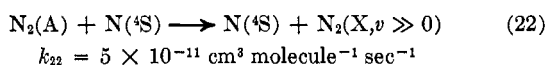(46) A. N. Wright and C. A. Winkler, "Active Nitrogen," Academic Press, New York, N. Y., 1968.

The yellow Lewis–Rayleigh afterglow of active nitrogen consists of selected bands of the first positive $B^3\Pi_g \rightarrow A^3\Sigma_u^+$ system of N_2 and is emitted with intensity proportional to $[N]^2$ from a gaseous system containing atomic nitrogen. The B state is usually considered to be populated by inverse predissociation (possibly collision induced) from the barely stable $^5\Sigma_g^+$ state, although crossing from higher levels of the A state has also been postulated.[47] As a result of the association of two ^4S nitrogen atoms in the presence of a third body it is theoretically possible to form a stable molecule in the $^5\Sigma_g^+$ state or in high vibrational levels of the $A^3\Sigma_u^+$ or $X^1\Sigma_g^+$ states. The potential energy curves for the B and X states do not cross below the dissociation limit, but both of the other two states do cross the B-state curve close to the limit,[48] and thus a radiationless transition is possible (though forbidden by selection rules in the first approximation).

Some time ago it was suggested by Bates,[49] for the case of O_2, that atom interchange reactions of the type
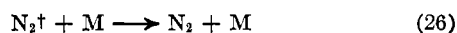
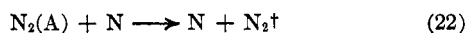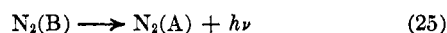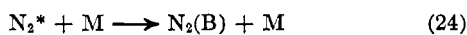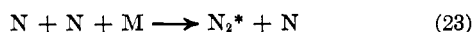$$N_2^* + N \longrightarrow N + N_2\dagger \qquad (21)$$
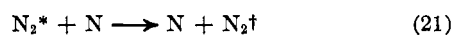
might provide an efficient means of relaxing populations of electronically excited molecules. In reaction 21 $N_2\dagger$ represents a vibrationally excited molecule in a lower electronic level than N_2^*. On the basis of his inability to observe the predicted intensity of Vegard–Kaplan $(A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+)$ bands from active nitrogen Young[50] deduced a high rate for reaction 22. Wray[51] observed

$$N_2(A) + N(^4S) \longrightarrow N(^4S) + N_2(X, v \gg 0) \qquad (22)$$
$$k_{22} = 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

the reverse of reaction 22 to occur in a shock-heated mixture of atomic and molecular nitrogen. Thus it would appear that, in a mixture with ground-state atoms, molecules in different electronic states in the vicinity of the dissociation limit should be readily interconverted by reactions such as (22).

With the inclusion of reaction 22 it is easy to construct a mechanism which leads to a steady state in which A-state molecules in active nitrogen have their concentration proportional to [N], namely
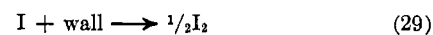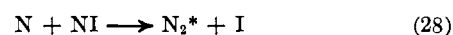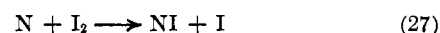
$$N + N + M \longrightarrow N_2^* + N \qquad (23)$$
$$N_2^* + M \longrightarrow N_2(B) + M \qquad (24)$$
$$N_2(B) \longrightarrow N_2(A) + h\nu \qquad (25)$$
$$N_2(A) + N \longrightarrow N + N_2\dagger \qquad (22)$$
$$N_2\dagger + M \longrightarrow N_2 + M \qquad (26)$$

where M is any gas molecule and process 25 is responsible for the first-positive band emission. Thrush[52] has

shown that this mechanism accounts for observations by Noxon[53] of Vegard–Kaplan bands in emission from discharged nitrogen over a wide pressure range.

In the sequence of reactions 22–26, process 25 is sufficiently fast $(k_{25} = 1.5 \times 10^5 \text{ sec}^{-1})$[54] that depopulation of the B state by a reaction similar to (22) is not normally significant. Thus the population of the B state is proportional to $[N]^2$. In contrast, the lifetime of the A state with $v = 0$ is in the range 1–10 sec,[37,38,55] so reaction 22 experiences little competition from the radiative process provided $[N] > 10^{11}$ cm^{-3}. In high vibrational levels of the A state, however, vibrational relaxation by a process similar to (26) and/or radiation to lower levels of the B state could be fast enough to compete effectively with (22) and thus ensure that the population of these levels is proportional to $[N]^2$. This is required if the A state is to be a candidate for the position of N_2^* in reactions 23 and 24. In its zeroth vibrational level a metastable state is not invariably quenched efficiently by ground-state atoms, as shown by the example of the $^1\Delta_g$ state of O_2,[56] for which the low rate of deactivation by $O(^3P)$ may reflect the paucity of available vibrational levels in the O_2 ground state.

Other excited states of N_2 below the first dissociation limit at 9.76 eV (see ref 48) should also be able to be populated *via* reaction 21 and thus to take part in active nitrogen chemistry. Of particular interest is the $^3\Delta_u$ state, recently located spectroscopically by Wu and Benesch,[57] in which higher vibrational levels can undergo allowed transitions to the B state and should therefore be short-lived with population proportional to $[N]^2$. Lower vibrational levels, on the other hand, become progressively more metastable as v decreases, because of the v^3 factor in the transition probability. The state is completely metastable at $v = 0$, with population expected to be proportional to [N].

The reaction flames of metal halides with active nitrogen consist of metallic emission lines[58] for which the excitation processes require energies that are a large fraction of the N_2 dissociation energy, and whose intensities are proportional to $[N]^2$. The same is true of most emission lines of halogen atoms excited by active nitrogen.[59] Emission lines of iodine requiring less than 185 kcal/mole of excitation energy have intensity proportional to [N], but in this case the kinetics of the reaction imply that excited nitrogen molecules are generated by the fast bimolecular mechanism

$$N + I_2 \longrightarrow NI + I \qquad (27)$$
$$N + NI \longrightarrow N_2^* + I \qquad (28)$$
$$I + \text{wall} \longrightarrow \tfrac{1}{2}I_2 \qquad (29)$$

(47) I. M. Campbell and B. A. Thrush, *Proc. Roy. Soc.* (London), A296, 201 (1967).
(48) F. R. Gilmore, *J. Quant. Spectr. Radiative Transfer*, 5, 369 (1965).
(49) D. R. Bates, *J. Atmospheric Terrest. Phys.*, 6, 171 (1955).
(50) R. A. Young, *Can. J. Chem.*, 44, 1171 (1966).
(51) K. L. Wray, *J. Chem. Phys.*, 44, 623 (1966).
(52) B. A. Thrush, *ibid.*, 47, 3691 (1967).

(53) J. F. Noxon, *ibid.*, 36, 926 (1962).
(54) M. Jeunehomme, *ibid.*, 45, 1805 (1966).
(55) H. H. Bromer and E. Spieweck, *Planet. Space Sci.*, 15, 689 (1967).
(56) I. D. Clark and R. P. Wayne, *Chem. Phys. Letters*, 3, 93 (1969).
(57) H. L. Wu and W. Benesch, *Phys. Rev.*, 172, 31 (1968).
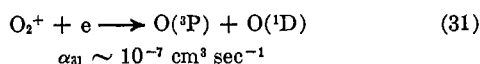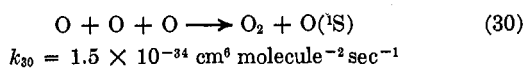(58) L. F. Phillips, *Can. J. Chem.*, 41, 732, 2060 (1963).
(59) L. F. Phillips, *ibid.*, 45, 1429 (1967).
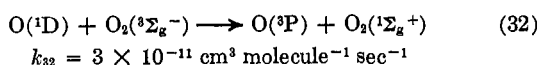
rather than by termolecular recombination of N atoms.

Recently A-state nitrogen molecules have been generated by a weak Tesla discharge in N_2,[60] by mercury photosensitization,[61] and, most effectively, by adding nitrogen downstream from a discharge through flowing argon.[62] Emission spectra have been observed as a result of energy transfer from the A-state molecules to a variety of added species, including mercury (2537-Å line), nitric oxide (γ bands), and SO_2 (both singlet and triplet emission), while other molecules, including O_2 and N_2O, rapidly deactivate the A state without subsequent luminescence. It is interesting to note that the γ bands of NO have been observed to occur weakly in the airglow spectrum[63] without the β bands which accompany the γ bands in the radiation produced by the association reaction of N and O atoms.

Reactions Involving O_2 and O

As Table I shows, emission from excited atomic and molecular oxygen is a major feature of the night glow. Reactions which produce excited atoms at night are

$$O + O + O \longrightarrow O_2 + O(^1S) \qquad (30)$$
$$k_{30} = 1.5 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$$

$$O_2^+ + e \longrightarrow O(^3P) + O(^1D) \qquad (31)$$
$$\alpha_{31} \sim 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$$

During the day reactions 30 and 31 are augmented by photodissociation of O_2 and photoelectron excitation of O.[64,65] Atom recombination and the quenching reaction 32 produce excited molecules at night and are

$$O(^1D) + O_2(^3\Sigma_g^-) \longrightarrow O(^3P) + O_2(^1\Sigma_g^+) \qquad (32)$$
$$k_{32} = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

assisted in the daytime by resonance scattering and by ozone photolysis.[36,66]

$$O_3 + h\nu \longrightarrow O_2(^1\Delta_g) + O(^1D) \qquad (33)$$

Reactions of atomic and molecular oxygen were recently reviewed by Schiff,[67] who emphasized reactions of the ground-state species, and by Zipf,[36] who discussed quenching. Several groups[68] have studied the quenching of $O(^1S)$ by observing the effect of added quenchers on the intensity of emission of the 5577-Å line. The $O(^1S)$ has been generated by photolysis of N_2O, by atom recombination in discharge-flow systems, and by dissociative recombination of O_2^+. Very few studies have been made in which the rates of specific reaction

paths, as opposed to overall quenching, have been measured.

A number of investigations of $O(^1D)$ reactions have been carried out with excited atoms produced by photolysis of gaseous O_2, O_3, N_2O, H_2O, CO, or CO_2;[69] some reactions have also been studied in liquid argon at 87°K.[70] $O(^1D)$ is very reactive by comparison with $O(^3P)$; for example, it rapidly attacks N_2O, which is almost inert to ground-state atoms.[71] The rapid quenching reactions with O_2 to produce $O_2(^1\Sigma_g^+)$ and with N_2 to produce vibrationally excited nitrogen ($k = 2 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}) are important processes in the atmosphere. Unfortunately, laboratory measurements of quenching rates of $O(^1D)$ have differed by up to a factor of 5.

An interesting problem has arisen in connection with the reaction of $O(^1D)$ with CO_2. Its solution may help to explain why the atmospheres of Venus and Mars consist mainly of CO_2, with almost no CO or O_2, despite photolysis of the CO_2 by sunlight. Katakis and Taube[72] observed the exchange reaction 34 to occur when ozone

$$OC^{18}O + O(^1D) \longrightarrow CO_2 + {}^{18}O \qquad (34)$$

was photolyzed with 2537-Å radiation in the presence of labeled CO_2, and they assumed the exchange reaction to proceed through an intermediate CO_3 molecule. Warneck[73] found the products of photolysis of CO_2 at 1470 Å to be deficient in O_2 and attributed the deficiency to CO_3 formation. The loss of oxygen was attributed by Slanger[74] to a wall reaction; he found that the deficiency could be reduced by careful cleaning of the walls of the reaction vessel to remove carbonaceous impurities. A new infrared absorption, developed after the photolysis of ozone in a matrix of CO_2, has been attributed to a stable CO_3 radical.[75] However, Taylor[76] has proposed that the oxygen loss observed during CO_2 photolysis occurs as a result of a direct attack by $O(^1D)$ on the walls and that no stable CO_3 species is involved. The existence of a long-lived CO_3 radical, formed by reaction of $O(^1D)$ with CO_2, would help account for the stability of the atmospheres of Mars and Venus,[77] since except at very short wavelengths the photolysis of CO_2 gives $O(^1D)$ as a product. The most probable fate of the $O(^1D)$, at least on Venus, would be reaction with CO_2 rather than quenching by N_2, and the CO produced in the primary process could then be removed by reaction 35.

$$CO_3 + CO \longrightarrow 2CO_2 \qquad (35)$$
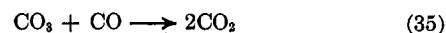
When O_2 is passed through an electrical discharge the

(60) R. A. Young and G. A. St. John, J. Chem. Phys., 48, 895, 898 (1968).

(61) A. Granzow, M. Z. Hoffman, N. N. Lichtin, and S. K. Wason, J. Phys. Chem., 72, 1402 (1968).

(62) (a) D. H. Stedman and D. W. Setser, Chem. Phys. Letters, 2, 542 (1968); (b) D. H. Stedman, J. A. Meryer, and D. W. Setser, J. Am. Chem. Soc., 90, 6856 (1968).

(63) (a) C. A. Barth, J. Geophys. Res., 69, 3301 (1964); (b) C. A. Barth, Ann. Geophys., 22, 198 (1966).

(64) J. F. Noxon, Space Sci. Rev., 8, 92 (1968).

(65) D. M. Hunten, ibid., 6, 493 (1967).

(66) R. L. Gattinger, Can. J. Phys., 46, 1613 (1968).

(67) H. I. Schiff, Can. J. Chem., 47, 1903 (1969).

(68) (a) R. A. Young and G. Black, J. Chem. Phys., 44, 3741 (1966); (b) R. A. Young, G. Black, and T. G. Slanger, ibid., 50, 309 (1969); (c) E. C. Zipf, Bull. Am. Phys. Soc., 12, 225 (1967).

(69) R. A. Young, G. Black, and T. G. Slanger, J. Chem. Phys., 49, 4758 (1968).

(70) W. B. DeMore and O. F. Raper, ibid., 46, 2500 (1967).

(71) W. D. McGrath and J. J. McGervey, Planet. Space Sci., 15, 427 (1967).

(72) D. Katakis and H. Taube, J. Chem. Phys., 36, 416 (1962).

(73) P. Warneck, Discussions Faraday Soc., 37, 57 (1964).

(74) T. G. Slanger, J. Chem. Phys., 49, 3669 (1968).

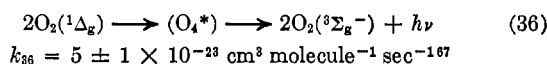(75) N. G. Moll, D. R. Clutter, and W. E. Thompson, ibid., 45, 4469 (1966).
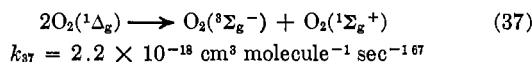
(76) D. S. Sehthi and H. A. Taylor, ibid., 49, 3669 (1968).

(77) D. M. Hunten, Can. J. Chem., 47, 1875 (1969).

metastables $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$ are produced in amounts 5–20% and <1%, respectively, of the total O_2.[78] $O_2(^1\Delta_g)$ reacts readily with unsaturated hydrocarbons and can dissociate O_3 by energy transfer; otherwise it is rather inert chemically. Quenching rates for $^1\Delta_g$ are an order of magnitude smaller than corresponding rates for $^1\Sigma_g^+$.[36] Because of this low reactivity the $^1\Delta_g$ state is able to live out its long radiative lifetime at altitudes below 100 km and to build up to a concentration (ca. 3×10^9 cm^{-3}) which is greater than that of either ozone or nitric oxide. Photoionization of $O_2(^1\Delta_g)$ has recently been suggested as a major source of O_2^+ in the D region.[26]

Perhaps the most interesting reaction reported for O_2 $(^1\Delta_g)$ is the energy-pooling process in which two molecules together can emit a single light quantum[77,79] (eq 36). The light emission consists of bands at 6340 (both

$$2O_2(^1\Delta_g) \longrightarrow (O_4^*) \longrightarrow 2O_2(^3\Sigma_g^-) + h\nu \qquad (36)$$
$$k_{36} = 5 \pm 1 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}[67]$$

ground-state molecules left with $v = 0$) and 7640 Å (one with $v = 0$, one with $v = 1$). Alternatively the products can be one ground-state and one $^1\Sigma_g^+$ molecule (eq 37). The radiative lifetime of the (O_4^*) inter-

$$2O_2(^1\Delta_g) \longrightarrow O_2(^3\Sigma_g^-) + O_2(^1\Sigma_g^+) \qquad (37)$$
$$k_{37} = 2.2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}[67]$$

mediate is estimated to be about 3 sec.

Reaction 37 is probably too slow to be an important source of $O_2(^1\Sigma)$ in the atmosphere, but it is sufficiently fast to be a problem in discharge-flow studies of this species, because of the unavoidable presence of O_2 $(^1\Delta)$. The method of generating $O_2(^1\Sigma)$ by photolysis of O_2 to give $O(^1D)$, followed by reaction 32. does not suffer from this problem.[80] Because of the difficulties of working with these excited species, quenching rates given in the literature differ in some cases by more than a factor of 10.

Studies with H(^{2}P)

The Lyman-α line at 1216 Å, arising from the transition $^2P \rightarrow ^2S$ of atomic hydrogen, is one of the most prominent features of the solar emission spectrum. As it arrives in the E region the line is very broad, due to the high temperature of the emitting atoms, and shows an interesting double reversal. At the bottom of a broad absorption "crater," attributed to absorption by hydrogen in the solar atmosphere, there is a narrow core absorption, due to cool hydrogen atoms between the sun and the point of observation (at about 150 km). At the time the line profile was measured, Purcell and Tousey[81] found the total solar Lyman-α intensity to be 6 erg cm^{-2} sec^{-1} and the amount absorbed in the central core to be about 0.1 erg cm^{-2} sec^{-1}. Assuming

the cool hydrogen to be located near the Earth this corresponds to about 2×10^{12} atoms in a 1-cm^2 column. The peak concentration of atomic hydrogen in the Earth's atmosphere is about 10^7 cm^{-3} near 100-km altitude.[82,83] The absence of polarization of scattered Lyman-α in the day glow indicates that multiple resonance scattering is important,[84] so that, despite the extremely short lifetime of H(^{2}P), it might be possible for Lyman-α photons to spend enough time lodged in atomic hydrogen for reactions of H(^{2}P) to be significant during the day.

In laboratory studies at pressures near 1 Torr Tanaka and McNesby[85] showed that ammonia was formed when atomic hydrogen was irradiated with Lyman-α in the presence of N_2, and Broida and Tanaka[86] observed emission from electronically excited NH which they suggested was most likely produced by reaction 38.

$$H(^2P) + N_2(^1\Sigma_g^+) \longrightarrow NH(^3\Pi) + N(^4S) \qquad (38)$$

Koyano and Tanaka[87] confirmed that H(^{2}P) was required for the reaction with N_2 by showing that no ammonia was formed if the hydrogen atoms were irradiated with Lyman-α from a deuterium-filled lamp.

In a series of extensions of this work we have observed the formation of electronically excited products in reactions of H(^{2}P) with various gases and have measured the rates of deactivation of H(^{2}P) by observing the effect of the added gases on Lyman-α fluorescence. In our first experiment[88] oxygen was mixed with partially dissociated hydrogen flowing from a microwave discharge in an argon–hydrogen mixture and then irradiated with Lyman-α from a mains-operated hydrogen–neon lamp similar to that described by Tanaka and McNesby. The output of the lamp was modulated at twice the mains frequency, and our observation of similarly modulated 100-Hz emission at 3064 Å from excited OH demonstrated the occurrence of the reaction

$$H(^2P) + O_2(^3\Sigma_g^-) \longrightarrow OH(^2\Sigma) + O(^3P) \qquad (39)$$
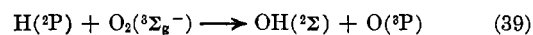
The modulated emission depended on the presence of both ground-state hydrogen atoms and O_2. The $A^2\Sigma \rightarrow X^2\Pi$ bands of OH were observed only with $v' = 0$ in the modulated emission. An alternative source of excited OH in this system[89]

$$O(^3P) + H(^2S) + M \longrightarrow OH(^2\Sigma, v = 0, 1) + M \qquad (40)$$
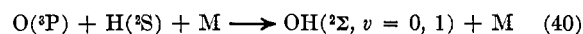
should not contribute to the modulated emission because of the long kinetic lifetime of atomic oxygen at

(78) A. M. Falik and B. H. Mahan, *J. Chem. Phys.*, **47**, 4778 (1967); F. J. McNeal and G. R. Cook, *ibid.*, **47**, 5385 (1967).
(79) L. Bader and E. A. Ogryzlo, *Discussions Faraday Soc.*, **37**, 46 (1964).
(80) T. P. J. Izod and R. P. Wayne, *Proc. Roy. Soc.* (London), **A308**, 81 (1968).
(81) J. D. Purcell and R. Tousey, *J. Geophys. Res.*, **65**, 370 (1960).
(82) T. N. L. Patterson, *Planet. Space Sci.*, **14**, 417 (1966).
(83) B. A. Tinsley, *ibid.*, **17**, 769 (1969).
(84) D. F. Heath, *Astrophys. J.*, **148**, 97 (1967).
(85) I. Tanaka and J. R. McNesby, *J. Chem. Phys.*, **36**, 3170 (1962).
(86) H. P. Broida and I. Tanaka, unpublished results quoted in ref 85.
(87) I. Koyano and I. Tanaka, *J. Chem. Phys.*, **40**, 895 (1964).
(88) T. S. Wauchop and L. F. Phillips, *ibid.*, **47**, 4281 (1967).
(89) S. Tiktin, G. Spindler, and H. I. Schiff, *Discussions Faraday Soc.*, **44**, 218 (1967).

pressures near 1 Torr. In further experiments[90] we detected both modulated and unmodulated emission from excited species formed in the reactions of $H(^2P)$ with O_2, N_2, N_2O, NO, CO, CO_2, and SO_2 and have determined relative emission intensities for the different reactants.

From measurements of the intensity of scattered Lyman-α radiation in the presence of these same reactants[91] a series of relative quenching cross sections was obtained. To convert from relative to absolute cross sections it was necessary to know the "trapping time," i.e., the average time of imprisonment, of the Lyman-α photons in the atomic hydrogen gas. Trapping times were calculated using the theory of Holstein[92] on the basis of atomic hydrogen pressures determined with an isothermal calorimeter probe. Holstein's theory has given good agreement with experiments on the trapping of resonance radiation of mercury[93] and potassium.[94] In the present case the quenching

cross sections obtained were about an order of magnitude smaller than would be expected, e.g., by comparison with the recent results for potassium.[94] Current experiments in our laboratory, in which the trapping time for Lyman-α radiation is measured directly, suggest that the calculated times were too large, as a result either of our overestimating the atomic hydrogen pressure or of the early onset of pressure broadening.

Several conclusions can be drawn from a survey of upper atmosphere chemistry at this time. Perhaps the most obvious is that a remarkably fruitful interaction has occurred between laboratory and field workers. A second conclusion is that a considerable body of experimental and theoretical results has already been obtained, but, especially on the laboratory side, much more is to come. Finally, as investigations are extended to other planets, and possibly as our own atmosphere becomes more contaminated at high altitudes, an unexpectedly large variety of materials are likely to become eligible for study as a part of upper atmosphere chemistry.

(90) T. S. Wauchop and L. F. Phillips, J. Chem. Phys., 51, 1167 (1969).
(91) T. S. Wauchop, M. J. McEwan, and L. F. Phillips, ibid., in press.
(92) (a) T. Holstein, Phys. Rev., 72, 1212 (1947); 83, 1159 (1951); (b) P. J. Walsh, ibid., 116, 511 (1959).
(93) D. Alpert, A. C. McCoubrey, and T. Holstein, ibid., 76, 1257 (1949).
(94) G. Copley and L. Krause, Can. J. Phys., 47, 533 (1969).

Photoelectron Spectroscopy

ARTHUR D. BAKER

Chemistry Department, University College of Swansea, Singleton Park, Swansea, United Kingdom

Photoelectron spectroscopy (PES) is a relatively new technique which permits the direct measurement of the energies required to remove valence shell electrons from atoms and molecules. It can also provide information on the bonding characteristics of orbitals, and in conjunction with other techniques can yield data concerning direct ionization, autoionization, and ion fragmentation processes. PES is thus of importance in fields such as molecular physics and theoretical chemistry, and it is also being developed as an analytical tool in a number of laboratories. Its potential for studying the orbitals involved in bonding adsorbed layers onto surfaces has also been demonstrated.[1]

Technique

Ionizing photons (frequency ν in the vacuum ultraviolet) are directed onto a sample, generally in the gas phase. Electrons may then be ejected from orbitals within the sample molecules. The energy, E, that an

ejected electron possesses depends upon the difference in the energy imparted to the irradiated molecule by the photon, i.e., $h\nu$, and the energy required to eject the electron (i.e., the ionization potential, I, characterizing the orbital which the electron occupied in the molecule). This is the Einstein photoelectric law and is summarized in eq 1.

$$E = h\nu - I \qquad (1)$$

In a photoelectron spectrometer, electrons ejected in this way are separated according to their kinetic energies, and are recorded. A photoelectron spectrum simply shows the relative numbers of electrons collected over the kinetic energy range from 0 up to $(h\nu - I_1)$ where I_1 is the lowest ionization potential of the compound being examined. Different bands in the spectrum thus relate to the ionization of electrons from different orbitals in the irradiated substance.

The expulsion of an electron from a molecule involves the simultaneous formation of an ion which may be in its ground or an excited electronic state,

(1) W. T. Bordass and J. W. Linnett, Nature, 222, 660 (1969).