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ION-MOLECULE COLLISIONS, ELECTRON MOLECULE COLLISIONS, EXCITATION AND IONIZATION OF ATOMS

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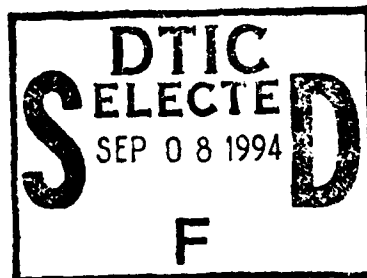
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15 April 1991-14 April 1994

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11. SUPPLEMENTARY NOTES

13. ABSTRACT (Maximum 200 words)

• Corrected values of the dissociative recombination rate coefficient for $N_2^+(v)$ have been deduced from an analysis of published experimental data. The theory of the dissociative recombination of polyatomic ions has been developed with particular reference to the branching ratios of the exothermic channels. The role of single-electron transitions in dissociative recombination has been discussed and it has been shown that the radiationless transition probability is indeed very high. Research on the dissociative recombination of CHO^+, H_3^+ and D_3^+ has led to the discovery of a new mechanism for dissociative recombination, characterized by the radiationless transition being of the single-electron type and by the absence of any crossing. It takes place through a multi-step process and is generally very rapid. Despite having been discovered only recently, it is of common occurrence. • Extensive calculations on tidal termolecular ionic recombination have been performed. • The discrepencies between the various results on $CH_3^+ + H_2$ and $CD_3^+ + D_2$ association have been discussed. • The emission of the 557.7 nm line of O I, the Herzberg I bands of O_2 and the Atmospheric bands of O_2 have been satisfactorily explained. • Rocket results on the emission of the 557.7 nm and 630.0 nm lines of O I from the nocturnal F-region have been analysed. • A new theory of the nightglow's green continuum has been proposed: metastable oxygen molecules collide with the ambient gas molecules to form complexes that dissociate by allowed radiative transitions.

14. SUBJECT TERMS
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CONT OF BLOCK 13:

• A new source of the heavy carbon enhancement in the stratosphere has been advanced. • Monte Carlo computations have been carried out in order to verify that the flip transitions that transform asymmetrical heavy ozone into symmetrical heavy ozone take place at the rate required to explain the observations. Without such transitions, the heavy ozone enrichment would be confined to the asymmetric isomer. • The R-matrix method has been applied to the study of photoionization of the lowest–lying seven states of atomic oxygen and of the lowest–lying seven states of atomic nitrogen. The study of ial cross sections for photoionization of the ground state of atomic oxygen have had significant impact on ospheric studies. • The R-matrix method has been used to study the scattering of electrons by molecular ox for a number of internuclear separations, R, including the equilibrium separation. Results have been obtained or 12 scattering symmetries for impact energies up to 1.0 Ryd. Summed cross sections for elastic scattering from the ground state and for transitions from the ground state to the $a\,^1\Delta_g$, $b\,^1\Sigma_g^+$ and the '6 eV' states are presented and are compared with experimental data. The positions and widths of the resonances in the $^2\Pi_g$ and $^2\Pi_u$ scattering symmetries are tabulated for $1.85\,a_0 \leq R \leq 2.90\,a_0$. The change in polarization of the scattered electrons has also been calculated. For elastic scattering from the ground state, the change was found to be small (confirming a previous result), although some structure is seen due to the $^2\Pi_g$, $^2\Pi_u$ and $^4\Sigma_u^-$ resonance states. Larger changes were found for electronic excitation, with considerable variation in the 8 eV region due to the $^2\Pi_u$ resonance. • Total and single differential cross sections for electron impact ionization of $He\,(1s^2)\,^1S$, $He\,(1s2s)\,^1S$ and $He\,(1s2s)\,^3S$ have been calculated within the R-matrix method for incident projectile energies up to 350 eV. The calculations included the processes which leave the residual ion in an excited state $He^+(nl)$ $(n \leq 3)$. The results have been compared with experiments and other theoretical data.

CONT OF BLOCK 14:

Green continuum
Stratosphere: heavy CO_2, heavy O_3
Photoionization: OI, NI
Electron scattering by molecular oxygen
Electron impact ionization of helium

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1. Publications

The following scientific publications have resulted from the research supported by Grant AFOSR-91-0261:

Competing sources of heavy CO_2 enhancement in the stratosphere and magnitude of heavy O_3 enhancement
Planet. Space Sci. **39**, 945 (1991)
by D. R. Bates.

Rate coefficients for $N_2^+(v)$ dissociative recombination
Planet. Space Sci. **39**, 1297 (1991)
by D. R. Bates and J. B. A. Mitchell.

Dissociative recombination of polyatomic ions
J. Phys. B: At. Mol. Opt. Phys. **24**, 3267 (1991)
by D. R. Bates.

Single-electron transitions and cluster ion super dissociative recombination
J. Phys. B: At. Mol. Opt. Phys. **25**, 3067 (1992)
by D. R. Bates.

Association of CH_3^+ and H_2: conflicting results
Astrophys. J. **375**, 833 (1992)
by D. R. Bates.

Nightglow emissions from oxygen in the lower thermosphere
Planet. Space Sci. **40**, 211 (1992)
by D. R. Bates.

Emission of the forbidden red and green lines of atomic oxygen from the nocturnal F-region

Planet. Space Sci. **40**, 893 (1992)

by D. R. Bates.

Photoionization of excited states of atomic nitrogen

J. Phys. B: At. Mol. Opt. Phys. **25**, 1209 (1992)

by K. L. Bell, K. A Berrington and C. A. Ramsbottom.

R-matrix calculations of low-energy electron scattering by oxygen molecules

Phys. Rev. Lett. **68**, 2011 (1992)

by C. J. Noble and P. G. Burke.

Dissociative recombination when potential energy curves do not cross

J. Phys. B: At. Mol. Opt. Phys. **25**, 5479 (1992)

by D. R. Bates.

Photoionization cross sections for atomic oxygen

Planet. Space Sci. **40**, 1419 (1992)

by K. L. Bell and R. P. Stafford.

Stratospheric heavy ozone: the symmetric isomer

Planet. Space Sci. **40**, 1573 (1992)

by W. L. Morgan and D. R. Bates.

Tidal termolecular ionic recombination

    J. Phys. B: At. Mol. Opt. Phys. **25**, 5421 (1992)

    by W. L. Morgan and D. R. Bates.

Enigma of H_3^+ dissociative recombination

    Planet. Space Sci. **41**, 9 (1993)

    by D. R. Bates, M. F. Guest and R. A. Kendall.

Dissociative recombination: Unexpected twist in a long tale

    Comments on Atomic and Molecular Physics **29**, 53 (1993)

    by D. R. Bates.

Vibrational excitation of products of dissociative recombination

    Mon. Not. R. Astron. Soc. **263**, 369 (1993)

    by D. R. Bates.

Cause of terrestrial nightglow continuum

    Proc. R. Soc. Lond. A **443**, 227 (1993)

    by D. R. Bates.

Prevalence of rapid dissociative recombination in absence of crossing of potentials

    Proc. R. Soc. Lond. A **443**, 257 (1993)

    by D. R. Bates.

The ionosphere

In "Relating Geophysical Structures and Processes", (American Geophysical Union, 1993), pp 11 -18.

by D. R. Bates.

Exchange processes in the scattering of polarized electrons by oxygen molecules

J. Phys. B: At. Mol. Opt. Phys. **27**, 185 (1994)

by C. Fullerton, G. Wöste, D. G. Thompson and K Blum.

Low-energy electron scattering by oxygen molecules

J. Phys. B: At. Mol. Opt. Phys. (in press) (1994)

by K. B. Higgins, C. J. Noble and P. G. Burke.

Ionization and simultaneous excitation of helium atoms by electron impact

J. Phys. B: At. Mol. Opt. Phys. (in press) (1994)

by A. Raeker, K. Bartschat and R. H. G. Reid.

2. Dissociative recombination

Laboratory afterglow measurements of Zipf (1980) that have been presumed to show that the recombination coefficient of $N_2^+(v)$ is independent of the vibrational level v have been analysed (Bates and Mitchell, 1991) to make allowance for the coupling due to symmetrical resonance charge transfer

$$N_2^+(v) + N_2(0) \quad \rightleftharpoons \quad N_2^+(0) + N_2(v) \qquad (1)$$
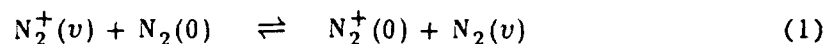
and also for the vibrational deactivation in collisions with Ne atoms present in the afterglow. An experimental value for this vibrational deactivation coefficient that has been reported (Dobler *et al*, 1982) is much higher than would be expected or than can be reconciled with the data of Zipf. It is therefore rejected. The analysis shows that the recombination coefficient for $N_2^+(0)$ is about 2.6×10^{-7} cm^{3}s^{-1} at 300 K and that the recombination coefficients for $N_2^+(1)$ and $N_2^+(2)$ are much smaller. These coefficients conflict with the dissociative recombination cross sections *versus* energy curve obtained by the merged beam method (Noren *et al*, 1989). Reasons were presented for believing that the curve cannot be correct.

Experimental data on products of the dissociative recombination of polyatomic ions have been discussed and rationalized in terms of the valence bonds concerned (Bates, 1991b). By combining the data with theoretical considerations, branching ratios for the various dissociative channels have been derived. There are two main classes of saturated polyatomic ions: those for which the number of valences of the ionized atom is decreased by neutralization, and those for which the number is increased. The hydride ions H_3O^+ and H_4N^+ are simple examples of the valence decrease class. We have reasoned that, while H_3O^+ may shed two H atoms in dissociative recombination with thermal electrons, H_4N^+ cannot do likewise because of a difference in the OH and NH_2 relic radicals. We predict that a bond between a pair of neutral atoms in an ion like $CH_3O^+H_2$ cannot be broken by dissociative recombination. Although the number of valences of an isolated C^+ ion increases on neutralization, we predict that the dissociative recombination of polyatomic ions containing C^+ normally

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takes place through a radiationless transition that causes a decrease. For example, when CH_3^+ sheds an H atom by dissociative recombination the CH_2 relic radical should be mainly in the $^1A_1$ metastable state with the C atom having two paired orbitals (a pure "lone pair") so that it is effectively divalent. In contrast to $CH_3O^+H_2$ dissociative recombination, we expect that $CH_3C^+H_2$ dissociative recombination may break a bond between neutral atoms. In this event ethylene would be formed. From an examination of the distribution of the measured dissociative recombination coefficients of polyatomic ions we have inferred that they are constrained by having an upper limit, and we have shown that this may be understood by application of the maximum cross section theorem of collision theory.

Energy considerations show that dissociative recombination of the proton-bridge ions $H_2O \cdot H^+ \cdot H_2O$ and $NH_3 \cdot H^+ \cdot NH_3$ can occur only through single-electron transitions. The nature of a single-electron transition that leads to dissociative recombination has been discussed. Calculations have demonstrated that the rate of the radiationless transition involved is extremely fast (Bates, 1992a). We have also discussed the recombination of the related cluster ions $H_3O^+(H_2O)_n$ and $H_4N^+(NH_3)_n$ and explained the experimental results.

Direct and indirect dissociative recombination have been compared. If the attractive potential-energy curve of the ground state of the ion is not crossed by a suitable repulsive potential-energy curve of the molecule formed by neutralization, the indirect process can be much faster than the direct process. However, in the case of HCO^+ (for example), its rate-coefficient $\alpha(I)$ is several orders of magnitude less than the measured value even though the radiationless transition involved is of the extremely rapid single-electron type. A new process, multi-step indirect dissociative recombination, that entails the system passing successively through several intermediate states in $\Delta\nu = 1$ steps, has been introduced. Examination of the formula for its rate-coefficient $\alpha(I^*)$, obtained from high-order perturbation theory, shows that the final pre-dissociative step is rate-limiting. Extensive computations have been done on the overlap integrals between the bound vibrational wavefunctions of the ion and the wavefunction for the separating fragments of the molecule. It has been concluded

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from these that multi-step indirect dissociative recombination provides a solution to the enigma posed by the laboratory data on HCO^+ recombination. The multi-step mechanism is the key to understanding dissociative recombination in cases where the relevant potentials do not cross and the transition from the continuum is single-electron (Bates 1992e).

The high dissociative recombination coefficient measured for H_3^+ in its ground vibrational level has appeared irreconcilable with theory, there being no crossing of potential-energy curves favourable to dissociative recombination at low temperature. It has been shown that the new mult-step process can explain the experimental results. Strong support for the multi-step process has been provided by measurements on the D_3^+ recombination coefficient which is comparable in magnitude with the H_3^+ recombination coefficient despite the quantal tunnelling through a substanial potential barrier that is involved. In earlier theory, such tunnelling would be far slower for D_3^+ than for H_3^+ because of the greater reduced mass (Bates, Guest and Kendall 1993).

A straightforward (but hitherto overlooked) argument proves that, for many polyatomic ions, the crossings of potential curves that had been presumed to be instrumental in the dissociative recombination process cannot exist. For instance, in the dissociative recombination of a polyatomic hydride ion leading to the release of an H atom, a single-electron radiationless transition is always involved and this precludes a crossing of potentials. And yet for every such case on which experimental data is available this process is rapid. Thus, rapid dissociative recombination without a crossing of potentials is common. The experimental results may be accounted for by the new multi-step cousin of the original mode of dissociative recombination. This cousin is more common in nature than the curve-crossing form of dissociative recombination (Bates 1993a, 1993d).

A considerable fraction of any molecular product of the dissociative recombination of a polyatomic ion has been proven to be normally vibrationally excited. The usual main source of the excitation is the impulsive force between the products. In the case of a monohydride. the vibrational excitation due to the impulse acting on its heavy

atom is inappreciable, but that due to the much weaker impulse acting on its H atom may be great. Another source is rooted in the relic of the normal vibrational modes of the ion. This causes the initial vibrational wavefunction of the product to differ from the wavefunction of its zero-th vibrational level, even in instances where the corresponding equilibrium separations force constants of the the ion and the product are virtually the same (as they commonly are). If the ion is bent, as for example in $OCOH^+$, an impulsive couple may act on one or more of the products and cause high rotational excitation (Bates 1993b).

3. Tidal termolecular ionic recombination

Experimental measurements by Mezyk *et al* (1989, 1991) have shown that the rate coefficient for the process

$$Xe_2^+ + Cl^- + Xe \longrightarrow XeCl^* + 2Xe \tag{2}$$
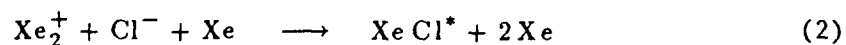
is enhanced relative to that given by the universal curve that describes termolecular recombination of structureless atomic ions. This is attributed to Cl^- exciting internal modes of Xe_2^+ during passage through the perihelion part of the orbit. We have simulated the electrostatic tidal effect by the Monte Carlo technique and have obtained excellent agreement with the experimental data. It is reasoned that the tidal action cannot enhance the rate of termolecular recombination of small valence-bound ions like O_2^+ and O_2^- appreciably. However, its influence is pervasive because complex ions are commonly present when the ambient gas density is enough for termolecular recombination to be of interest. For example, O_4^+ is the main positive ion if the ambient gas is pure oxygen. Enhanced mutual neutralization may obscure the experimental evidence, but may be disregarded in the processes

$$H_3O^+ (H_2O)_n + NO_3^- + \{He, Ar\} \longrightarrow neutrals. \tag{3}$$
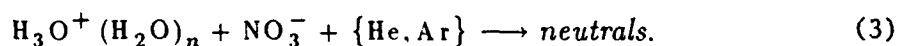
Experimental research by Lee and Johnsen (1989) has shown that the rates of these two processes are enhanced relative to the universal curve. The only possible explanation

for that enhancement seems to be tidal action. A paper describing our preliminary computations was published (Bates and Morgan, 1990), and a paper containing a more detailed discussion and the results of our extensive computations has been published (Morgan and Bates, 1992b).

4. Radiative and termolecular association

Earlier calculations on association in $CH_3^+ + H_2$ and $CD_3^+ + D_2$ collisions have been extended and refined (Bates, 1992b). It was concluded that there are serious discrepancies between, on the one hand, recent measurements made by Gerlich and Kaefer (1989) with an 80 K low-pressure ion-trap, and, on the other hand, theory and measurements made by Smith *et al* (1982) with a *SIFT* apparatus at 80 K, 0.4 torr and measurements made by Barlow *et al* (1984) using a 13 K ultra-low-pressure trap. No explanation could be offered.

5. Nightglow emissions from oxygen in the lower thermosphere

Several independent trains of reasoning have led to the conclusion that $O_2(c\,^1\Sigma_u^-)$ is the precursor for the emission of the green line of atomic oxygen (Bates, 1992c). We have shown that the measured altitude profile of the volume emission rate of the Hertzberg I system is reproduced by using the expected rate coefficients for the production of $O_2(A\,^3\Sigma_u^+)$ by termolecular association and rate coefficients for quenching by atomic and molecular oxygen that accord with laboratory evidence. Contrary to the common belief, we have inferred that termolecular association does not contribute directly to the Atmospheric system because the $O_2(b\,^1\Sigma_g^+)$ it generates is mainly in high vibrational levels and deactivation of these by interchange of electronic energy with normal oxygen molecules is not rapid enough to prevent deactivation to $O_2(a\,^1\Delta_g)$ or $O_2(X\,^3\Sigma_g^-)$ from occurring. We have shown that the prime source of the $O_2(b\,^1\Sigma_g^+\ v=0)$ is the excitation of the $O_2(X\,^3\Sigma_g^-\ v=0)$ collision partner involved

in $O_2(A\,^3\Sigma_u^+)$, $O_2(A'\,^3\Delta_u)$ and $O_2(c\,^1\Sigma_u^-)$ deactivation. This source can account for the measured altitude profile of the volume emission rate of the Atmospheric system.

6. Nightglow emissions from atomic oxygen in the ionosphere

The O_2^+ dissociative recombination quantum yields $f(^1S)$ and $f(^1D)$ that have been deduced by Sobral *et al* (1992) from the nocturnal rocket measurements on the volume emission rates $V(5577)$ and $V(6300)$ in the equatorial F-region have been analysed to see if they are consistent with the results of the *ab initio* computations of Guberman and Giusti-Suzor (1991) on dissociative recombination (Bates. 1992d). In the case of the 557.7 nm emission. the only serious problem we have found is that the rocket $f(^1S)$ values are much larger than would be expected from the *ab initio* computations in the region below about 220 km. The most interesting feature of the apparent $f(^1D)$ altitude profile that we have calculated is that it is markedly influenced by the transport of the suprathermal $O(^1D)$ atoms produced by the dissociative recombination.

7. Nightglow: the source of the green continuum

By analysing observations, Barbier *et al* (1951) established that there is a continuum in the green region of the nightglow spectrum. The accepted theory (Krassovsky 1951) is that it arises from the NO_2 air afterglow from the composite process

$$NO + O + M \longrightarrow NO_2 + M + h\nu \qquad (4)$$
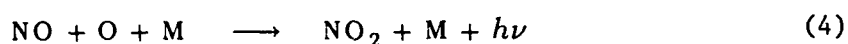
with the NO being regenerated by the fast reaction between NO_2 and O. However, by analysis of the observational evidence, we have shown that this standard theory is untenable. Furthermore, we have examined and eliminated all of the conceivable "stock" sources of the continuum emission. The observational evidence points unambiguously to a novel source of the continuum emission. namely, metastable

oxygen molecules colliding with ambient gas molecules and thereby forming complexes that dissociate by allowed radiative transitions.

Let $O_2^\dagger$ denote an oxygen molecule in one of the six metastable states ($a\,^1\Delta_g$, $b\,^1\Sigma_g^+$, $c\,^1\Sigma_u^-$, $A'\,^3\Delta_u$, $A\,^3\Sigma_u^+$ and $^5\Pi_g$) that are populated by termolecular association. We propose that a collision between $O_2^\dagger$ and another molecule or atom is intimate enough to form a complex that dissociates radiatively by an allowed transition. Inspection of the potential curves of diatomic molecules shows that conditions for an allowed transition are, in many instances, created when a metastable atom approaches a normal atom. This must also be true of molecules, with the vital difference that the duration of the intimate collision may be much longer because of the high energy density of the rovibrational levels of the complex. In general the radiative transition ensures the dissociation of the complex, so that the emission forms a continuum. If, for instance, the collision partner is a normal oxygen molecule, the proposed sequence is then

$$O_2^\dagger + O_2\,(X\,^3\Sigma_g^-) \quad \rightleftharpoons \quad O_4^\star \tag{5}$$

$$O_4^\star \quad \longrightarrow \quad O_2' + O_2'' + h\nu$$
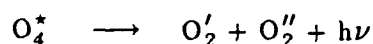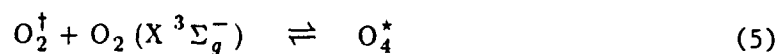
the primes being reminders that the products are not necessarily in the ground electronic state.

Using rocket data (Greer *et al* 1986) we find that if the collision partner is $O_2\,(X\,^3\Sigma_g^-)$ or $N_2\,(X\,^1\Sigma_g^+)$ the emission would peak near 96 km and that the thickness of the luminous layer (defined as the vertical distance between the levels where the intensity is half the maximum) would be 10 km. These values are in satisfactory agreement with the rocket measurements of McDade *et al* (1986).

To account for the observed nightglow intensity, the maximum volume emission must be around 1×10^3 cm^{3}s^{-1} in the visible region and 5×10^3 cm^{3}s^{-1} in the infrared region. We have estimated that such values can be attained by our proposed new mechanism, although laboratory measurements are needed to check the estimated rates that we have used.

This work has been published: see Bates (1993c).

8. The ionosphere

A history of some aspects of ionospheric research has been written (Bates, 1993e). Seriously mistaken beliefs, for example that negative ions are the ⸱⸱arriers of negative charge in the E-layer, have been widely held. Ionograms leᴅ ⸱erception on the diurnal variation of N, the number density of free electrons, that forced theorists to propose that electrons and molecular positive ions disappear by a process that is many orders of magnitude faster than had earlier been inferred for any other loss process envisaged. The proposal regarding recombination is correct. ⹁ wever, incoherent scatter radar studies have given that N in the E-layer has an asymmetry with respect to noon that is in the opposite sense to that deduced from ionograms. and this behaviour has been satisfactorily reproduced by numerical simulation. The harmony is not complete, good reason not having been given for neglecting the results of the ionogram research.

9. Heavy carbon dioxide enhancement in the stratosphere

The commonly accepted source of the heavy CO_2 enhancement in the stratosphere is transfer from the heavy O_3 enhancement. It is reasoned (Bates, 1991a) that another source is provided by the effect of the avoided crossing of the O_3 $(1\,^1B_2)$ state that is reached by absorption in the Hartley band, and we have shown that the sources are equal if the heavy O_3 enhancement is by about 20 per cent.

10. Heavy ozone in the stratosphere

Flips in which one of the end atoms in an energized complex like $^{16}O\,^{16}O\,^{18}O\,^*$ ceases to be effectively bound to the central atom and becomes effectively bound to the other end atom (so that ^{18}O is transformed into the central atom) have been treated. Using the Monte Carlo method to follow the motion of three oxygen atoms on the ground-state potential-energy surface of ozone, it has been shown that such flips do indeed

occur and that their frequency relative to the dissociation frequency is consistent with the available experimental results (Morgan and Bates 1992a).

11. Photoionization of atomic nitrogen

A study of the photoionization of atomic nitrogen was made (Bell et al 1992) by extending the work of Bell and Berrington (1991) to a consideration of photoionization of the six excited states $2s^2 2p^3\,^2D^o$, $2s^2 2p^3\,^2P^o$, $2s^2 2p^2(^3P)3s\,^4P$, $2s^2 2p^2(^3P)3s\,^2P$, $2s2p^4\,^4P$ and $2s^2 2p^2(^3P)3p\,^2S^o$. The R-matrix method was used and thirteen target states of N^+ have been included in the calculation: $2s^2 2p^2\,^3P$, ^1D, ^1S; $2s2p^3\,^5S^o$, $^3D^o$, $^3P^o$, $^1D^o$; $2s^2 2p3s\,^1P^o$, $^3P^o$; $2s2p^3\,^3S^o$; $2s^2 2p3p\,^1P$, ^3D; $2s2p^3\,^1P^o$. Each of these thirteen N^+ states was represented by configuration interaction wavefunctions.

The present results for the $2s^2 2p^3\,^2D^o$ and $2s^2 2p^3\,^2P^o$ states can be compared with the earlier less sophisticated work of Zeippen et al (1980). The close agreement between the two calculations is significant in that it demonstrates that the R-matrix calculations have converged and that the cross section is now known to an accuracy of better than a few per cent. The agreement is particularly satisfactory in the region of the $2s2p^4\,^2P$ resonance and the background cross section in general in both cases.

The cross sections for $2s^2 2p^2(^3P)3s\,^4P$ and $2s^2 2p^2(^3P)3s\,^2P$ are notable for an increase in the value of the cross section at the $3s\,^3P^o$ threshold — the increase corresponding to the ionization of the 2p electron into the continuum with the 3s electron behaving like a 'spectator' electron. A similar increase is found for the $2s2p^4\,^4P$ case. No experimental data exists for any of these cases.

For the $2s^2 2p^2(^3P)3p\,^2S^o$ state the 'kink' or shallow minimum in the cross section (associated with a Cooper minimum) is confirmed. However, considerable divergence of the present work for the asymmetry parameter for this state occurs in comparison with earlier calculations (Theodosiou 1988, Nahar and Mason 1989, and Mason 1988). Although the single experimental point (Pratt et al 1987) is insufficient to support

any theoretical result, we believe that the present calculation is the most accurate presently available.

12. Photoionization of atomic oxygen

The R-matrix method has been used to calculate the cross sections for photoionization of ground-state atomic oxygen, leading to the production of several possible final-ion states:

$$O\,(1s^2 2s^2 2p^4)^3P + h\nu \rightarrow \begin{cases} O^+\,(1s^2 2s^2 2p^3)^4S^o,\,^2D^o,\,^2P^o + e^- \\ O^+\,(1s^2 2s 2p^4)^4P,\,^2P + e^-. \end{cases} \tag{6}$$

Data on these processes are of fundamental importance in the quantitative understanding of the ionosphere.

Details of the R-matrix codes for photoionization calculations have been given by Berrington $et\ al$ (1987), with the associated theory described by Seaton (1987). The present calculation is done in LS-coupling and neglects relativistic effects. The states of O^+ included in the wavefunction expansions are: $2s^2 2p^3\,^4S^o$, $^2D^o$, $^2P^o$; $2s 2p^4\,^4P$, ^2D, ^2P; $2s^2 2p^2 3s\,^4P$, ^2P, ^2D, ^2S. Each of these ten final-ion states was represented by configuration-interaction type wavefunctions obtained by employing the 1s, 2s and 2p orbitals of Clementi and Roetti (1974) and the 3s, $\overline{3p}$ and $\overline{3d}$ orbitals of Bell $et\ al$ (1989). The R-matrix radius was taken to be 12.4 a_0, and 20 continuum orbitals were used for each of the required angular momenta $(0,\ldots,5)$. The set of correlation functions was comprised of all configurations arising from $2s 2p^3$, $2s^2 2p^2$ and $2p^4$ plus two electrons from the given set of bound orbitals. The cross sections were calculated in the length formulation, and, in the light of previous work (Bell $et\ al$ 1987), we believe that the our total photoionization cross sections should be accurate to a few percent. We thus claim that the present work on photoionization of ground-state atomic oxygen is the most reliable calculation yet performed. It has been published: see Bell and Stafford (1992).

Our results for photoionization in which a 2p electron is removed, producing $O^+(2s^2 2p^3\,^4S^o)$, $O^+(2s^2 2p^3\,^2D^o)$ or $O^+(2s^2 2p^3\,^2P^o)$, are not too disparate from other

calculations. Thus, for photoionization that yields $O^+(2s^2 2p^3\ ^4S^o)$ our results are in close agreement with those of Pradhan (1978) and Kirby et al (1979), except that for wavelengths below 360 Å our data decrease more rapidly than those of Kirby et al. Similarly, our results for photoionization that produces $O^+(2s^2 2p^3\ ^2D^o)$ agree closely with the data of Kirby et al (1979), although they are significantly above the values reported by Pradhan (1980). The agreement between our work and other work is not so good for photoionization that produces $O^+(2s^2 2p^3\ ^2P^o)$. Our results are below those of Kirby et al (1979) and of Pradhan (1980).

For photoionization in which a 2s electron is removed, producing $O^+(2s 2p^4\ ^4P)$ or $O^+(2s 2p^4\ ^2P)$, our results differ dramatically from previously reported data. The present results have led, for the first time, to a theoretical fit in agreement with the rocket data on the 834 Å airglow (Link et al 1993).

13. Electron–molecule collisions

Extensive calculations, using the R-matrix method, have been made on electron scattering by oxygen molecules. The R-matrix method, as applied to electron–molecule scattering, was first described by Burke et al (1977), with the essential techniques set out by Gillan et al (1987). Electron excitation of O_2 to the $a\,^1\Delta_g$ and $b\,^1\Sigma_g^+$ states has been studied by the R-matrix method by Noble and Burke (1986), but they considered only the three lowest electronic states of the the target.

In the first calculations of the present study (Noble and Burke 1992), the lowest nine states of O_2 were included within the R-matrix framework. Electronic excitation cross sections for transitions to the $a\,^1\Delta_g$, $b\,^1\Sigma_g^+$ and '6 eV' states were calculated for impact energies up to 15 eV. Important contributions from a $^2\Pi_u$ resonance, in addition to the well-known $^2\Pi_g$ resonance, were found to modify significantly previous theoretical predictions. Also, integral elastic cross sections were obtained for the first time for a complicated open-shell system using an ab initio method.

In the second phase of the study (Higgins et al 1994), the earlier work by Noble and Burke (1992) has been extended. The same nine states of O_2 have

been included, but the CI wavefunctions describing those states were improved by including additional configurations. Also, a broad range of values of R, the inter-nuclear separation, have been considered — the earlier work considered the equilibrium value only, $R = R_e \approx 2.3\,a_0$. The cross sections have been calculated for elastic scattering and for electronic excitation from the $X\,^3\Sigma_g^-$ ground state to the $a\,^1\Delta_g$, $b\,^1\Sigma_g^+$ and the '6 eV' states and compared with experimental data whenever possible. The positions and widths of the resonances in the $^2\Pi_g$ and $^2\Pi_u$ scattering symmetries have been calculated as functions of R for $1.85\,a_0 \leq R \leq 2.90\,a_0$, and their effect on the cross sections determined. The results show the importance of using a good target representation in order to obtain consistent results as functions of R. The value of R is also found to have a profound effect on the scattering cross sections, particularly in the resonant $^2\Pi_g$ and $^2\Pi_u$ symmetries.

The data produced by the R-matrix calculation of Noble and Burke (1992) has been used to study the change in polarization of transversely polarized electrons scattered by randomly-oriented oxygen molecules in their ground $X\,^3\Sigma_g^-$ state. The theory of how this information can be calculated from the T-matrix elements produced in the R-matrix calculation has been described by Bartschat and Madison (1988). Changes in polarization can be due to exchange interactions or spin-orbit interactions, the former being expected to be more significant for a light molecule such as O_2. Hence, our study should cast light on the important issue of the relative strength of the exchange interaction in low-energy electron-molecule collisions.

We have found that the polarization fraction for elastic collisions from $O_2\,(X\,^3\Sigma_g^-)$ is close to unity for all angles and energies between 1 eV to 15 eV. This confirms the experimental findings of Hegemann $et\ al$ (1990), and the results from the earlier, simpler calculation of da Paixão $et\ al$ (1992). The $^2\Pi_g$ resonance produces sharp structure for energies below 1 eV. Structure due to the $^2\Pi_u$ resonance at 8 eV can be seen at small and large scattering angles, but the effect is small and probably not measurable. For energies between 10 eV and 15 eV, our results may be sensitive to the $^4\Sigma_u^-$ resonance, and agreement with experiment in this energy-range may be improved by more extensive scattering calculations. Our results for the polarization change in

collisions that excite the oxygen molecule are the first to be reported. We have found a wide variation in the polarization fraction as a function of angle and as a function of energy, a manifestation of the strong influence of the $^2\Pi_u$ resonance. This work has been published: see Fullerton *et al* (1994).

14. Electron-impact ionization of metastable inert gases

Total and single differential cross sections for electron impact ionization of helium atoms have been calculated using the R-matrix method of Bartschat and Burke (1987). In addition to the ground state, ionization from the two metastable states has been investigated, and the possibility of producing an excited helium ion has been included:

$$e(k_0 l_0) + \left\{ \begin{array}{c} \mathrm{He}\,(1s^2)\,^1\mathrm{S} \\ \mathrm{He}\,(1s2s)\,^1\mathrm{S} \\ \mathrm{He}\,(1s2s)\,^3\mathrm{S} \end{array} \right\} \longrightarrow e(k_1 l_1) + \mathrm{He}^+(nl) + e(k_2 l_2) \qquad \cdot \quad (7)$$

where k_i and l_i denote the wave-numbers and angular momenta when the electrons are described by partial-wave expansions. Six final states of He^+ were included: 1s, 2s, 2p, 3s, 3p and 3d. The 2^λ-pole components, with $\lambda \leq 4$, of the $e_f + \mathrm{He}$ interaction were included, giving five possible He-continuum symmetries. Due to the inclusion of states of the final ion with $n = 3$ and to the initial state being excited, it was necessary to use a large value of the R-matrix boundary, necessitating a large number (25) of continuum orbitals. The calculated energies of the initial states of $\mathrm{He}(1\,^1\mathrm{S})$, $\mathrm{He}(2\,^1\mathrm{S})$ and $\mathrm{He}(2\,^3\mathrm{S})$ indicates that the bound states generated by the R-matrix method are reliable.

The results have been compared with experiments and other theoretical data. The discrepancy between our results and experiment for total cross sections suggests that there is a need to include the effects of exchange between the "fast" electron and the electrons of the target. The discrepancies between our results and those from other theoretical approaches, especially the close coupling results of Rudge (1988), demonstrate the sensitivity of the calculated cross sections to the wavefunctions of

the initial bound state and the final continuum states, and perhaps also to the use of distorted waves rather than plane waves for the "fast" electron. We take this as vindicating our use of the R-matrix formulation, even though the excitation-autoionization process, for which the R-matrix formulation is particularly adept, is not significant in the present study. The close coupling in the final continuum states is crucial for excitation of final-ion states, such as $He^+(2p)$, that cannot be produced by simple removal of one electron.

This work on helium has been published: see Raeker *et al* (1994). It has provided a valuable test of the method for excited targets, enabling us to proceed to consider ionization of metastable Ne and Ar.

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Final Remark

Sir David Bates died suddenly on January 5, 1994. The news of his death was received with great sadness and sense of loss by his colleagues at The Queen's University of Belfast and by his many friends and collaborators throughout the international science community. This report has been completed by Sir David's colleagues at Belfast, who feel sure that he would have wanted them to express his gratitude to the Air Force Office of Scientific Research for their support, which has extended over many years. This support enabled Sir David to pursue his research with undiminished enthusiasm and vigour to within days of his death.