The solar corona has been known since ancient times. It is seen around the limb of the sun during total solar eclipses. The spectrum of the corona was first obtained at the eclipse of 1869, when the green coronal line at wavelength 5303 Å was discovered. The spectrum has been observed at many eclipses since that time, and more recently it has been observed without an eclipse by means of coronographs. A number of coronal lines are now known in the visible spectrum. With the advent of rocket spectroscopy observations of the coronal ultraviolet spectrum became possible, and a large number of additional lines were discovered.

The identification of the coronal lines in the visible spectrum was a difficult problem and was not solved until 1941. Edlén (the most accessible account of his work is Edlén 1945) showed that the lines were forbidden transitions in highly ionized atoms of iron and nickel. A few representative examples are listed in Table 7-1; a more extensive list may be found in Billings (1966, pp. 304-05). The high degree of ionization found for the coronal ions established that the corona is at a temperature of $10^{6.8}$ K. (There is much independent evidence which confirms this interpretation.)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Wavelength (Å)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe XIV</td>
<td>5303</td>
<td>$3s^23p^6,^2P_3 \rightarrow ^2P_1$</td>
</tr>
<tr>
<td>Fe X</td>
<td>6374</td>
<td>$3s^23p^6,^2P_3 \rightarrow ^2P_1$</td>
</tr>
<tr>
<td>Ca XV</td>
<td>5694</td>
<td>$2p^6,^3P_1 \rightarrow ^3P_0$</td>
</tr>
<tr>
<td>Fe XV</td>
<td>7059</td>
<td>$3s^23p^6,^2P_3 \rightarrow ^2P_1$</td>
</tr>
<tr>
<td>Fe XIII</td>
<td>10747</td>
<td>$3p^6,^3P_1 \rightarrow ^3P_0$</td>
</tr>
<tr>
<td>Fe XIII</td>
<td>10798</td>
<td>$3p^6,^3P_2 \rightarrow ^3P_1$</td>
</tr>
<tr>
<td>Fe XIII</td>
<td>3388</td>
<td>$3p^6,^1D_2 \rightarrow ^3P_2$</td>
</tr>
<tr>
<td>Fe XV</td>
<td>2842</td>
<td>$3s^23p,^1P_1 \rightarrow 3s^2,^1S_0$</td>
</tr>
<tr>
<td>Fe XV</td>
<td>417</td>
<td>$3s^23p,^1P_1 \rightarrow 3s^2,^1S_0$</td>
</tr>
<tr>
<td>Fe XVII</td>
<td>16.77</td>
<td>$2p^6,^1S_1 \rightarrow 2p^6,^1S_0$</td>
</tr>
<tr>
<td>Fe XXV</td>
<td>1.87</td>
<td>$1s2p,^1P_1 \rightarrow 1s^2,^1S_0$</td>
</tr>
</tbody>
</table>

Table 7-1. Some coronal lines
The coronal gas is highly ionized so that there are many free electrons. The electron density decreases sharply outward from the solar limb; a typical value in the solar inner corona (where the coronal emission lines are most easily seen) is about $10^8$ electrons per cm$^3$. It was soon realized that these electrons (with energies of the order of 100 eV) were responsible for exciting the coronal lines. In Fe XIV, which has a lowest electron configuration $3s^2 3p$ and term $^2P$, the ions are excited from the $^2P_1$ to $^2P_1$ levels by electron excitation, and then the ions spontaneously emit the 5303 Å line, returning to the ground state (Fig. 7-1). Calculations show that excitation by absorption of solar radiation and deexcitation by collisions are negligible.

In this work it was tacitly assumed that higher energy levels play no part in the excitation of the 5303 Å line. After ultraviolet rocket observations had shown the existence of many strong ultraviolet coronal emission lines, all permitted transitions from high energy states, it was realized that these transitions may contribute to the population of the upper state of the 5303 Å line and hence to the intensity of the line. The problem was worked out by Pecker and Thomas (1962). They included in their calculations excitations and deexcitations for all levels in the $3s^2 3p$ and $3s3p^2$ configurations (Fig. 7-1) in Fe XIV. As expected, their results showed that the

---

**Fig. 7-1.** Energy levels in Fe XIV, not to scale. All the levels of the $3s^2 3p$, $3s3p^2$, and $3s^2 3d$ configurations are shown. The visible coronal line 5303 Å is indicated as well as lines identified in the ultraviolet spectrum. The energies (in electron volts) are indicated on the left.
ratio of the population of the $3s^2 3p^2 2P_3/2$ state to that of the $3s^2 3p^2 2P_1/2$ state is increased when allowance is made for the $3s3p^2$ configuration, by factors ranging from 2% at an electron density of $10^7$ cm$^{-3}$ to a factor of nearly 2 at an electron density of $10^{10}$ cm$^{-3}$. Pecker and Thomas also performed calculations on Fe X allowing for the excited configurations $3s3p^6$ and $3s^2 3p^4 3d$ and obtained a result similar to that for Fe XIV.

In calculations of atomic parameters of the types needed in work on coronal-line intensities care must be taken to allow for configuration interaction where this is significant. Garstang (1962) studied Si X, Fe X, and Fe XIV. In the case of Fe XIV he found configuration interaction between the terms $3s^2 3d^2 2D$ and $3s3p^2 2P_d$ to be very large. The $3s^2 3d^2 2D$ term was unknown in the laboratory; its position had to be predicted by extrapolation. Transition probabilities were computed for all the allowed and forbidden transitions within and between the $3s^2 3p$, $3s^2 3d$, and $3s3p^2$ configurations. It was of course necessary to work in intermediate coupling because spin-orbit effects are large. Many individual lines were found to have line strengths which differed substantially from those calculated without the inclusion of configuration interaction. The importance of the interaction of the $3s^2 3d$ and $3s3p^2$ configurations is a good example of the importance of the concept of a complex for highly ionized atoms. (A complex is a set of electron configurations in an atom with a defined parity and a prescribed set of principal quantum numbers, in this case three electrons with $n = 3$ and any allowable azimuthal quantum numbers.)

The next development was the realization that proton collisional excitation may make a significant contribution. Seaton (1964) calculated proton collisional excitation of the $3s^2 3p^2 2P_3/2$ level of Fe XIV. In the solar corona the mean energy of the protons is far greater than the excitation energy (2.3 eV) of the $2P_3/2$ level, and, because for a given energy the protons have lower velocities than the electrons, the circumstances are closer to the maximum of the proton impact cross section than to the maximum of the electron impact cross section. One expects the proton reaction rate to be about 40 times that of the electrons. (This is the square root of the mass ratio, the reaction rate is $\langle v\sigma\rangle$, and $\sigma \propto v^{-2}$ for high energies.) This factor is reduced by the Coulomb field of the Fe XIV ion, which increases the electron cross section and reduces the proton cross section. Detailed calculations are needed to clarify the precise relative importance of proton and electron collisions. Seaton obtained the excitation rate for Fe XIV $3s^2 3p^2 2P_3/2 \rightarrow 2P_1/2$. For a temperature of $10^{6.9}$ K and $2 \times 10^{6.9}$ K, he found the excitation rates, $\langle v\sigma\rangle$, in Table 7-2. The importance of including cascades from higher levels and (at least for $T = 2 \times 10^{6.9}$ K) proton excitation is clearly demonstrated by these results.
Table 7-2. Excitation rates $\langle \sigma v \rangle$ for Fe XIV, from Seaton (1964)

<table>
<thead>
<tr>
<th></th>
<th>$T = 1 \times 10^6$K</th>
<th>$T = 2 \times 10^6$K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron direct excitation</td>
<td>$1.0 \times 10^{-9}$</td>
<td>$0.7 \times 10^{-9}$</td>
</tr>
<tr>
<td>Electron excitation via cascades</td>
<td>$2.5 \times 10^{-9}$</td>
<td>$3.2 \times 10^{-9}$</td>
</tr>
<tr>
<td>Proton direct excitation</td>
<td>$0.3 \times 10^{-9}$</td>
<td>$1.2 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

The importance of dielectronic recombination at high temperatures was realized by Burgess (1964). In ordinary recombination we get a process such as

$$\text{Fe}^{+15}(3s) + e \rightarrow \text{Fe}^{+14}(3s, n\ell) + h\nu$$

In dielectronic recombination the corresponding process would be

$$\text{Fe}^{+15}(3s) + e \rightarrow \text{Fe}^{+14}(n^{l1}, n\ell)$$

and

$$\text{Fe}^{+14}(n^{l1}, n\ell) \rightarrow \text{Fe}^{+14}(3s, n\ell) + h\nu$$

Here $(n^{l1}, n\ell)$ denotes a doubly excited state of Fe$^{+14}$ lying in the single ionization continuum corresponding to Fe$^{+15}(3s) + e$. The $(n^{l1})$ makes a downward transition to any lower state, the ground state $3s$ being the important one in practice. Burgess showed that one could consider a total recombination rate to include all processes and that this rate might be 20 times the ordinary recombination rate. There is a corresponding increase in ionization rates by autoionization following an inner-shell excitation. This inverse to dielectronic recombination was studied by Bely (1967).

The importance of intermediate coupling in making radiative transitions possible between states of different total spin is well known. It was not realized until 1967 that this could be a large effect in collision cross sections. For a transition such as Fe XIII $3p^2 \ 3P_2 \rightarrow 1D_2$, there is a contribution arising from electron exchange. This type of contribution generally dominates processes of this kind in the low stages of ionization of an atom. For highly ionized atoms, spin-orbit interaction becomes very important and mixes states of the same total angular momentum $J$. In Fe XIII $3p^2$ the $1D_2$ and $3P_2$ states are mixed. This allows part of the collision strength of the $3P_2-3P_2$ transition (not observable—a level to itself—but having large matrix elements) to be transferred to the $3P_2-1D_2$ transition. Bely, Bely, and Vo Ky Lan (1966) obtained the collision strengths in Fe XIII as shown in Table 7-3. Exchange effects (not included in these results) are estimated to contribute about 0.03 to the collision strengths.
Table 7-3. Collision strengths in Fe XIII, from Bely, Bely, and Vo Ky Lan (1966)

<table>
<thead>
<tr>
<th></th>
<th>L-S coupling</th>
<th>Intermediate coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^3)P(_2) - (^1)D(_2)</td>
<td>0.00</td>
<td>0.32</td>
</tr>
<tr>
<td>(^3)P(_0) - (^3)P(_2)</td>
<td>0.14</td>
<td>0.16</td>
</tr>
</tbody>
</table>

In many cases the collision cross section for the excitation of an allowed transition is proportional to the optical oscillator strength of the transition. One might expect that forbidden transitions would have small cross sections. This is by no means true in the general case. Bely and Bely (1967) computed the cross sections for the excitation of Fe XVII ions from the ground configuration \(2p^6\) to the excited configurations \(2p^53s\), \(2p^53p\), and \(2p^53d\) and to some higher states. The cross section of the transition \(2p^6\,^1S_0 - 2p^53p\,^1S_0\) is large, and that of the transitions \(2p^6\,^1S_0 - 2p^53s\,^3P_1\) and \(^1P_1\) is smaller. The cross sections of the permitted transitions need not be the largest, at least in cases where there is a change of principal quantum number in the transition. Bely and Bely showed that when their new cross sections were used the agreement between the calculated and observed intensities of ultraviolet coronal lines was improved. We illustrate a few of the transitions of Fe XVII in Figure 7-2. There are in effect two cycles of excitation processes,

\[
2p^6 \rightarrow 2p^53d \rightarrow 2p^6 \quad \text{and} \quad 2p^6 \rightarrow 2p^53p \rightarrow 2p^53s \rightarrow 2p^6
\]

(There are many additional energy levels of Fe XVII not shown in Figure 7-2, but they do not alter this rough picture.)

Fig. 7-2. Energy levels in Fe XVII, not to scale. Only a few levels of the \(2p^53s\), \(2p^53p\), and \(2p^53d\) configurations are shown. The collision strengths are indicated for upward transitions and transition probabilities for downward transitions.
Another ion which has been studied in some detail is Fe XV. It is of note because, among other reasons, it is the only case for which an identified coronal line (7059 Å, in Table 7-1) arises from a transition within a configuration which is not the ground configuration. The ultraviolet resonance lines of Fe XV have been observed at 417 Å and 284 Å, these lines being surprisingly strong. Bely and Blaha (1968) showed that it is necessary to include the 3s3d configuration in calculations of the Fe XV line intensities. In considering the $3s^2 \ ^1S \rightarrow 3s3p \ ^3P$ cross sections both exchange effects and intermediate coupling effects were included. The values of the collision strength are shown in Table 7-4. A further correction for resonances (mentioned below) was introduced by Bely and Blaha.

Table 7-4. Collision strength values for Fe XV, from Bely and Blaha (1968)

<table>
<thead>
<tr>
<th>Transition</th>
<th>Exchange</th>
<th>Intermediate Coupling</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1S_o \rightarrow 3P_2$</td>
<td>0.004</td>
<td>—</td>
<td>0.004</td>
</tr>
<tr>
<td>$1S_o \rightarrow 3P_1$</td>
<td>0.011</td>
<td>0.034</td>
<td>0.045</td>
</tr>
<tr>
<td>$1S_o \rightarrow 3P_2$</td>
<td>0.018</td>
<td>—</td>
<td>0.018</td>
</tr>
</tbody>
</table>

An important improvement in the theory of collision cross sections has arisen through the recognition of the importance of autoionizing states and resonances in electron-ion collisions. An example of this was discussed by Bely and Petrini (1966). If an electron hits a positive ion it can be captured into a doubly excited state of a once-less ionized atom, and this unstable autbonizing state can break up leaving the ion in the original stage of ionization but in an excited state. The apparent rate of excitation of this state is greater than one would expect on the basis of direct collisional excitation alone. Bely and Petrini showed that for Ca II the collision strength for $4s \rightarrow 3d$ is roughly doubled by this process in the incident energy range between the 3d and 4p levels. This phenomenon occurs (Bely and Blaha, 1968) in Fe XV for energies between the 3s3p $^3P$ and $^1P$ terms.

Another example which has been discussed in work (as yet unpublished) by Prof. M. J. Seaton's group in London is O III, where the state $2s2p^33s^2D$ of O II lies just above the $2s^22p^2 \ ^1D$ state of O III, and the cross section for $2s^22p^2 \ ^3P \rightarrow \ ^1D$ in O III shows a resonance just above the threshold. There is clearly room for further investigations along these lines.

Gabriel and Jordan (1969) reported that in the solar spectrum a line at 22.09 Å is observed close to the O VII $1s^2-1s2p \ ^1P_1$ resonance line at 21.55 Å, and similar lines have also been observed near the resonance lines of C V, Ne IX, Na X, and Mg XI. The intensity is in all cases nearly as
high as the resonance line. Gabriel and Jordan suggested that the lines are the \(1s^2 \, ^1S_0-1s2s \, ^3S_1\) transition. This transition was subsequently shown by Griem (1969) to be a magnetic dipole transition made possible in a relativistic approximation. (In nonrelativistic theory a zero magnetic dipole line strength is obtained for a transition involving a change of principal quantum number.) For O VII he estimated the transition probability of the line to be 33 sec\(^{-1}\). The \(1s2s \, ^3S_1 \rightarrow 1s^2 \, ^1S_0\) transition can also take place by a two-photon decay, but this is of lower probability: Drake, Victor, and Dalgarno (1969) obtained for this process in O VII the transition probability 0.25 sec\(^{-1}\).

The most recent development in the area of solar coronal deexcitation processes is work by Garstang (1969) on magnetic quadrupole radiation. He showed that transitions of the form \(s^2 \, ^1S_0-sp \, ^3P_2\) are allowed for magnetic quadrupole radiation (but for no lower order radiation). Transitions of this type occur in several ions of interest in the solar corona, and other types of magnetic quadrupole transition are

\[
p^6 \, ^1S_0-p^5s \, ^3P_2 \quad \text{and} \quad p^6 \, ^1S_0-p^5d \, ^3P_2, \, ^1D_2, \, ^3D_2, \, ^3F_2.
\]

Garstang showed that in Fe IX the \(3p^5d \, ^3P_2 \rightarrow 3p^6 \, ^1S_0\) transition is an important deexcitation mechanism, and in Fe XVII the transition \(2p^53s \, ^3P_2 \rightarrow 2p^6 \, ^1S_0\) is important. The transitions \(2s2p \, ^3P_2 \rightarrow 2s^2 \, ^1S_0\) in Fe XXIII and \(3s3p \, ^3P_2 \rightarrow 3s^2 \, ^1S_0\) in Fe XV are unimportant. Lastly, in Fe XXV we have the remarkable situation that the magnetic quadrupole transition

\[
1s2p \, ^3P_2 \rightarrow 1s^2 \, ^1S_0 \quad (A = 6.5 \times 10^9 \text{ sec}^{-1})
\]

has a higher probability than the fully allowed electric dipole transition

\[
1s2p \, ^3P_2 \rightarrow 1s2s \, ^3S_1 \quad (A = 5.1 \times 10^8 \text{ sec}^{-1})
\]

This magnetic quadrupole transition may well become observable in the solar spectrum in the near future: the resolving power of rocket spectrographs has now reached the point where resolution from \(1s2s \, ^3P_1 \rightarrow 1s^2 \, ^1S_0\) is possible. When this and other observations have been made it will be possible to make further checks on the theory of the solar corona and perhaps discover other mechanisms which contribute to the physical processes in the corona.

Acknowledgment

The writer's own work on magnetic quadrupole transitions was supported in part by National Aeronautics and Space Administration contract NGR-06-003-057 and by National Science Foundation Grant GP-11948.
REFERENCES

2. NEGATIVE IONS

Negative ions of atoms and molecules were first discovered in mass spectrograph analyses. Those found included $\text{O}^-$, $\text{O}_2^-$, $\text{NO}^-$, $\text{NO}_2^-$, $\text{OH}^-$, $\text{H}^-$, $\text{C}^-$, $\text{CH}^-$ and $\text{Li}^-$. Much work has been directed to understanding why negative ions exist. If $E_0$ is the energy of the ground state of the neutral atom and $E_-$ is the energy of the (ground state of the) negative ion, the quantity $E_0 - E_-$ is called the electron affinity of the atom, and this is the energy needed to detach the extra electron from the negative ion. The negative ion is stable if $E_0 > E_-$. In addition Pauli's principle must be fulfilled, so that, for example, we would not expect helium, with a $1s^2$ closed shell, to form a negative ion with electron configuration $1s^3$. Thus we expect some limitation on the atoms which can form negative ions. In this lecture we shall review a few aspects of the study of negative ions. For a survey of the older literature, reference may be made to the book by Massey (1950), and for more recent work to the review articles by Branscomb (1957, 1962, 1964), Moiseiwitsch (1965), Ferguson (1967, 1968), Smith (1968), and Bardsley and Mandl (1968).

I should make it clear at the outset that in this chapter I shall be able to deal with only a few aspects of the subject. I have chosen to discuss primarily several lines of work in which some of my colleagues in Boulder have been engaged, and space does not permit discussion, or even mention, of many important contributions by other workers.

Electron Affinities

Efforts to determine reliable electron affinities of negative ions date back to Hylleraas' calculation on $\text{H}^-$ in 1930. This work was refined by many later workers. Electron affinities of atoms have been determined by extrapolations along isoelectronic sequences and by photodetachment experiments. There have also been some calculations by Hartree—Fock methods with the calculations including correlation effects. Electron affinities have been determined for some molecules from lattice energies, electron impact, surface ionization, and photodetachment. An illustrative selection of results which have been obtained is given in Table 7-5. No doubly charged atomic negative ions are thought to exist. A few excited
Table 7-5. Electron affinities of selected\(^a\) atoms and molecules

<table>
<thead>
<tr>
<th>Atom</th>
<th>Electron Affinity (eV)</th>
<th>Molecule</th>
<th>Electron Affinity (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.754</td>
<td>H(_2)</td>
<td>0.9</td>
</tr>
<tr>
<td>He (see text)</td>
<td>0.08</td>
<td>OH</td>
<td>1.83</td>
</tr>
<tr>
<td>C ((^4)S)</td>
<td>1.25</td>
<td>O(_2)</td>
<td>0.15</td>
</tr>
<tr>
<td>((^2)D)</td>
<td></td>
<td>O(_3)</td>
<td>2.9</td>
</tr>
<tr>
<td>N</td>
<td>not stable</td>
<td>C(_2^+)</td>
<td>3.1</td>
</tr>
<tr>
<td>O</td>
<td>1.478</td>
<td>SH</td>
<td>2.32</td>
</tr>
<tr>
<td>F</td>
<td>3.45</td>
<td>CN</td>
<td>3.6</td>
</tr>
<tr>
<td>Si ((^4)S)</td>
<td>1.39</td>
<td>NO</td>
<td>0.9</td>
</tr>
<tr>
<td>((^2)D)</td>
<td>0.88 (?)</td>
<td>NO(_2)</td>
<td>4.0</td>
</tr>
<tr>
<td>S</td>
<td>2.07</td>
<td>NO(_3)</td>
<td>3.9</td>
</tr>
<tr>
<td>I</td>
<td>3.076</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Selected from the compilation of Moiseiwitsch (1963), where data are given for many other atoms and molecules and references are given to the original papers, and supplemented by more recent data for He (Brehm, Gusinow and Hall, Phys. Rev. Letters 19:737, 1967), O (Berry, Mackie, Taylor and Lynch, J. Chem. Phys. 43:3067, 1965), OH (Branscomb, Phys. Rev. 148: 11, 1966), and SH (Steiner, J. Chem. Phys. 49:5097, 1968).

The value for H\(_2\) is the vertical detachment energy, not the electron affinity (~3.6 eV).

States may exist, the most interesting being C\(^-\) (\(^2\)D) and Si\(^-\) (\(^2\)D). Perhaps the most interesting experimental work in this area is that of Berry, Mackie, Taylor, and Lynch (1965). They studied the emission spectrum produced by the recombination reaction O + e \to O\(^-\) + hv in the threshold region \(\lambda\)7800 to \(\lambda\)8800 in shock-heated vapors of potassium peroxide and rubidium oxide in neon and argon carrier gas. They saw the individual thresholds \(O(3\,P_2) \to O^-(2\,P_3)\) at \(\lambda\)8592, \(O(3\,P_2) \to O^-(2\,P_2)\) at \(\lambda\)8386, and \(O(3\,P_1) \to O^-(2\,P_1)\) at \(\lambda\)8276 and deduced an electron affinity of O\(^-\) of \(1.478(\pm 0.002)\) eV and a doublet splitting of the O\(^-\)\(^2\)P state of \(285(\pm 15)\) cm\(^{-1}\). This was the first and, so far, the only measurement of a term splitting in a negative ion.

An outstanding experiment performed by B. Brehm, M. A. Gusinow, and J. L. Hall (1967) at the Joint Institute for Laboratory Astrophysics of the National Bureau of Standards and University of Colorado in Boulder is the direct measurement of the electron affinity of the \(1s2s\,^3S\) state of helium (to form He\(^-\) \(1s2s2p\,^4P_3\)). The existence of a metastable state of this kind had been predicted theoretically by a quantum mechanical variational calculation, but a reliable electron affinity is hard to determine because it involves the difference of two large energies.
In the experiment, positive ions of helium and deuterium are extracted from a hot-cathode arc discharge source (Fig. 7-3). The ion beam is passed through an oven containing potassium vapor at low pressure. Here some positive ions double-charge exchange to produce He\(^-\), H\(^-\), and D\(^-\) ions. The negative ions are separated from the positive ions by electrostatic deflection, and the negative ion beam is mass analyzed. The beam of He\(^-\) ions passes through an interaction chamber where it is crossed with an argon ion laser operating at 4880 Å or 5145 Å. The electrons produced by photodetachment pass through a hemispherical electron analyzer and are collected. The ion current is also collected. It is thus possible to measure the kinetic energy spectrum of the photodetached electrons. An important correction is to allow for the velocity of the negative ion: The electrons must be emitted in a slightly backward direction in the center-of-mass system if they are to be measured perpendicular to the beam in the laboratory frame. Measurements on H\(^-\) and D\(^-\) ions enabled the apparatus to be calibrated. The final result was 80 ± 2 millielectron volts for the electron affinity of He 1s2s \(^3\)S, forming He\(^-\) 1s2s2p \(^4\)P\(_2\).

**Laser Two-Photon Photodetachment**

Another experiment illustrating the power of lasers for negative ion experiments done at the Joint Institute for Laboratory Astrophysics by J. L. Hall, E. J. Robinson, and L. M. Branscomb (1965) was on iodine. They observed and measured the photodetachment of I\(^-\) by 1.785 eV photons (6943 Å). Because I\(^-\) has only one bound state (electron affinity 3.06 eV), two photons must be involved in the photodetachment. Measurements were made of the laser photon flux and the electrons detached, and the probability of the two-photon process was determined to be \(2.7 \times 10^{-49}\).
$F^2 \text{sec}^{-1}$, where $F$ is the flux density in photons cm$^{-2}$ sec$^{-1}$. In the laser used, $F$ was about $10^{27}$ photons cm$^{-2}$ sec$^{-1}$. This result was later confirmed by theoretical calculations by Robinson and Geltman (1967), who obtained a probability $2.1 \times 10^{-49} F^2 \text{sec}^{-1}$ by using one-electron continuum states in an assumed central field adjusted to reproduce the observed binding energies of the negative ions.

**Drift Tube Experiments**

We mention two experiments selected from many which have been performed with drift tubes. Chanin, Phelps, and Biondi (1962) studied the attachment of low energy ($<1$ eV) electrons to oxygen molecules by the reaction $e + 2O_2 \rightarrow O^- + O_2$. The principle of the experiment is simple (Fig. 7-4); for details the original paper should be consulted. An ultraviolet light pulse strikes the photocathode and releases electrons, which drift down the tube under an applied field, and some of them attach to the $O_2$ molecules in the gas. The $O^-_2$ ions start to drift down the tube (much more slowly than the electrons) and their arrival at the anode is measured as a function of time (with the aid of the control grid used as a shutter). If the attachment rate is $K$ and the electron drift velocity is $w_e$, we have

$$\frac{dn_e}{dt} = \frac{\partial n_e}{\partial t} + w_e \frac{\partial n_e}{\partial z} = -K[O_2]^2 n_e$$

and for a moderately long pulse $\partial n_e/\partial t \approx 0$, so that $n_e = n_e(0) \exp(-\alpha z)$ where $\alpha = K[O_2]^2/w_e$. The initial distribution of $O^-_2$ ions will have this same $e^{-\alpha z}$ factor. The $O^-_2$ ions drift down the tube with velocity $w_i$, and their rate of arrival at the anode must satisfy

$$\frac{\partial [O^-_2]}{\partial t} + w_i \frac{\partial [O^-_2]}{\partial z} = 0$$

which leads to $[O^-_2] \propto \exp(\alpha w_i t)$. Measurement of the time dependences leads to values of $w_i$, $\alpha$, and $w_e$, and hence of $K$. The final value obtained
was \( K = 2.8 \times 10^{-30} \text{cm}^6 \text{sec}^{-1} \) at 300°K. Other processes (such as \( e + O_2 \rightarrow O + O^- + h\nu \)) are possible, but in the ionosphere of the Earth, where these processes are of interest, the three-body process dominates at all altitudes of interest.

One other example of a drift-tube experiment is that by Woo, Branscomb, and Beatty (1969) on photodetachment of electrons from \( O_2^- \). Ions from a discharge are thermalized; they then enter the reaction region of a drift tube where they are irradiated with light of the desired spectral distribution. (In this experiment light approximating sunlight was used.) The detached electrons are collected and measured, and the ion current can also be measured, separated from the electron current by time resolution (the ion-drift velocity being much slower than the electron-drift velocity). The final result is a detachment rate for \( O_2^- \) in sunlight of 0.3 sec\(^{-1}\).

**Geometrical Hindrance in Molecular Ion Formation**

One new factor which has recently come to light is the effect of geometrical factors. When electrons are mixed with \( N_2O \) or with \( CO_2 \) molecules we do not seem to get \( N_2O^- \) or \( CO_2^- \) ions. The reason seems to be connected with the fact that \( N_2O \) and \( CO_2 \) are linear molecules, whereas \( N_2O^- \) and \( CO_2^- \) are predicted to be bent (angle about 135°) from comparisons with isoelectronic molecules. The electron affinity for attachment to a linear molecule may be negative even if the electron affinity for attachment to a bent molecule is positive. This topic was discussed by Ferguson, Fehsenfeld, and Schmeltekopf (1967). It is clear that further developments can be expected in this area of molecular ion studies.

**Negative Ion-Molecule Reactions**

We now turn to another area of negative ion studies. Although processes involving electrons and molecules had been studied for many years, it was not until about 1967 that it became possible to measure the rates of reactions between negative ions and molecules. An outstanding series of contributions in this area has been made by a group under Dr. Eldon Ferguson at the Environmental Science Services Administration laboratories in Boulder, Colorado, U.S.A. This work included both positive and negative ion reactions with molecules (and occasionally with atoms). Excellent review articles have been written by Ferguson (1967, 1968). After some general remarks we shall discuss briefly that part of his work which deals with negative ions.
If $\sigma$ is the cross section for one incident particle hitting one target particle and there are $n$ incident particles and $N$ target particles per unit volume with a relative velocity $v$ between the incident and target particles, the number of collisions per second is $N n v \sigma$. In practice there is a range of velocities (usually a Maxwell distribution), and the cross section is a function of the incident energy. We therefore write the number of collisions per second as $k N n$, where $k = \langle v \sigma \rangle$. This is the reaction rate for an ion-molecule reaction if every collision produces a reaction; otherwise the rate will be reduced by the probability of getting a reaction being less than 1 per collision, and this factor is included in $\sigma$ when $\sigma$ is calculated by quantum mechanical methods.

When an ion approaches a neutral atom or molecule they interact because of the polarization of the neutral particle by the ion. This interaction is an attraction, and to a good first approximation it may be derived from a polarization potential $-\alpha e^2/2r^4$, where $\alpha$ is the polarizability of the neutral particle as usually defined in quantum mechanics. It is instructive to consider the classical trajectories under such a potential. Suppose an incident charged particle has mass $M$ and velocity $v_0$ at a large distance from a fixed-target neutral particle and the impact parameter is $b$. We write down the equations of motion in polar coordinates $(r, \theta)$ under the potential $-\alpha e^2/2r^4$ and obtain expressions for $\dot{r}$ and $\ddot{r}$. Examination of these expressions shows that there is a critical value, $b_0$, of the impact parameter. If $b > b_0$ the incident particle at first approaches the target, then it reaches a point where $\dot{r} = 0$ and $\ddot{r} > 0$, and finally it recedes from the target to infinity. This is elastic scattering. If $b < b_0$, then $\dot{r}$ starts negative, maintains a constant sign and a finite value which never approach zero and which behaves as $r^{-2}$ for $r$ tending to zero. The incident particle falls into the target. The value of $b_0$ is given by requiring that $\dot{r} \to 0$ and $\ddot{r} \to 0$ simultaneously at a finite distance $R$ from the target. The classical cross section is $\pi b_0^2$. Particles striking within this area fall into the target, those outside this area are elastically scattered. Carrying out the elementary classical calculation we find that $R = b_0/\sqrt{2}$ and that

$$\sigma = \frac{2\pi \left(\frac{e^2 \alpha}{M}\right)^{1/2}}{v_0}$$

Typical values of $\alpha$ are about $10^{-24}$ cm$^3$ and of $M$ about $2 \times 10^{-23}$ gm (reduced mass of two particles such as O and O$_2$). This gives a rate coefficient $k \approx 10^{-9}$ cm$^3$ sec$^{-1}$ and an impact parameter $b_0 \approx 20$ Bohr radii. Quantum mechanical effects will of course modify $k$ somewhat, but in any event we predict cross sections of order 400 $\pi a_0^2$, which is very large, and $k$ is therefore very large.
Many reaction rates for ion-molecule reactions have now been measured. We have space to describe only the work of Ferguson's group: Detailed references to the original papers of his group and to the work of other authors may be found in the review articles listed at the end of this chapter. The apparatus used by Ferguson is sketched in Figure 7-5. A carrier gas (usually helium) is introduced at one end, and in some experiments another gas is introduced at the side entrance 1. The gas passes through a microwave discharge which produces ions. The ionized gas enters the reaction tube, 100 cm long and 8 cm diameter, and is pumped

down the tube with a flow velocity about $10^4$ cm per sec, the pressure being 0.3 Torr. Other reactant gases are introduced at one or both of the entrances 2 and 3 at measured flow rates small compared to that of the carrier gas. A mass spectrometer at the end of the tube samples both primary and product ions. The distance from the point of entrance of reactant to the mass spectrometer divided by the flow velocity gives the reaction time, and the flow rate of reactant gas gives the density of reactant gas molecules. The velocity in the tube was determined by following the progress of a pulse of plasma down the tube. Under typical conditions electron and ion densities of $5 \times 10^{10}$ cm$^{-3}$ are obtained in the tube.

We illustrate the reduction of the experimental data by considering a simple positive ion experiment. Helium is the carrier gas, and O$_2$ is introduced at entrance 2. The microwave discharge in the helium produces He$^+$ ions and He ($2^1S$) and He ($2^3S$) metastable atoms. We consider the reaction

$$\text{He}^+ + \text{O}_2 \rightarrow \text{He} + \text{O} + \text{O}^+$$  \hspace{1cm} (7-1)$$

In a steady flow the He$^+$ concentration (denoted by [ ]$^+$) satisfies the differential equation

$$v \frac{\partial}{\partial z} [\text{He}^+] = -A[\text{He}^+] - k[\text{He}^+][\text{O}_2]$$

where $v$ is the flow velocity, $z$ the distance along the tube, and $A$ is a constant which allows for diffusive loss of He$^+$ to the walls. If we introduce
O₂ so that [O₂] ≫ [He⁺] we may treat [O₂] as constant along the flow tube, and then the solution of the above equation is

\[ \log \left( \frac{[\text{He}^+][\text{O}_2]}{[\text{He}^+]_0} \right) = (A + k[\text{O}_2]) \tau \]

where the reaction time \( \tau = l/v \) for a distance \( l \) from entrance 2 to the mass spectrometer, and the subscripts 0 and \( \tau \) denote the initial and final He⁺ concentrations. We measure [He⁺], recorded by the mass spectrometer, as a function of [O₂], determined by the O₂ gas flow. A plot of \( \log [\text{He}^+] \) against [O₂] gives \( k \). For the He⁺ + O₂ reaction, Ferguson's group found \( k = 1.5 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1} \).

There are many additional complications in this work, and much further discussion and experimental details may be found in Fehsenfeld et al. (1966) and in Golden et al. (1966). The most important general conclusion which emerges from this work is the large size of \( k \) which is obtained for many reactions. In terms of the elementary classical concepts discussed above every collision within the cross section \( \pi b_0^2 \) must have a probability of order 1 of giving a reaction. This is contrary to what might be expected on the basis of the Massey adiabatic hypothesis (McDaniel 1964, p. 240), that when two atomic systems approach with a velocity low compared with typical electron orbital velocities the electrons in the atoms will adiabatically adjust to the perturbation and the probability of a reaction (electronic transition) will be small. This hypothesis is obeyed for atomic nonresonant charge transfer processes (such as \( \text{He}^+ + \text{Ar} \rightarrow \text{He} + \text{Ar}^+ \)), for which the cross sections are small at low energies. The reasons for the large cross sections found in the ion-molecule work are not fully understood, but the presence of large numbers of vibrational and rotational energy levels in a molecule may increase the probability of near resonances, and in some cases the formation of intermediate complexes may be responsible for the large rate.

Before leaving the general discussion of Ferguson's work we mention that in the discharge there is also produced a significant concentration of metastable He(2^3S). If we introduce O₂ at entrance 2 we get a reaction of the Penning type

\[ \text{He}(2^3S) + \text{O}_2 \rightarrow \text{He} + \text{O}_2^+ + e \]

We can then work with the O₂⁺ ions and introduce another reactant at entrance 3. Another possibility is to introduce argon in entrance 1 and O₂ at entrance 2, when we get \( \text{Ar}^+ + \text{O}_2 \rightarrow \text{Ar} + \text{O}_2^+ \). This method has the advantage of producing O₂⁺ ions without contaminating O⁺ ions (which cannot be produced for energy reasons in this reaction, but which would be produced by Reaction 7-1 if helium was used without argon). One other
possible extension is to pass a reactant gas through a subsidiary microwave discharge before entering at entrance 2. In this way it is possible to introduce atomic O and N after dissociation from O\textsubscript{2} and N\textsubscript{2} in the subsidiary discharge.

We now mention the applications of this method to negative ion reactions. The only modifications are in the production of the ions. If O\textsubscript{2} is added through entrance 1, the resulting plasma contains O\textsuperscript{-} ions produced by the dissociative attachment reaction

\[ e + O\textsubscript{2} \rightarrow O\textsuperscript{-} + O \]

If N\textsubscript{2}O is introduced through entrance 1, we get NO\textsuperscript{-} ions. Then introducing O\textsubscript{2} through entrance 2 gives O\textsubscript{2}\textsuperscript{-} ions by the reaction

\[ NO\textsuperscript{-} + O\textsubscript{2} \rightarrow O\textsubscript{2}\textsuperscript{-} + NO \]

The introduction of H\textsubscript{2}O through entrance 1 gives OH\textsuperscript{-} ions. In an experiment on H\textsuperscript{-}, H\textsubscript{2} was introduced through entrance 1, the discharge producing H atoms, and the H\textsuperscript{-} ions were produced by the reaction

\[ NH\textsubscript{3} + e \rightarrow H\textsuperscript{-} + NH\textsubscript{2} \]

using electrons from a hot filament.

Some negative ion reaction rates are given in Table 7-6. So far experiment in this area has far outpaced theory. Ferguson (1968) discusses some attempts to improve on the simple classical model, but so far there do not seem to have been any attempts to explain negative ion-molecule reaction rates by detailed mechanisms or models.

**Negative Ions in the Ionosphere**

The Earth's upper atmosphere contains many positive ions and some negative ions. Above 100 km, positive ions predominate (species include O\textsuperscript{+}, N\textsuperscript{+}, NO\textsuperscript{+}, O\textsubscript{2}\textsuperscript{+}, and N\textsubscript{2}\textsuperscript{+} with H\textsuperscript{+} and He\textsuperscript{+} above 500 km). Below 100 km, down to about 60 km, the ionospheric D region is believed to contain many negative ions. The densities at 75 km (particles per cm\textsuperscript{3}) are roughly (rounded to nearest power of 10) total 10\textsuperscript{15} (these are mostly O\textsubscript{2} and N\textsubscript{2} in a ratio 1:4) and lesser constituents: O, 10\textsuperscript{11}; CO\textsubscript{2}, 10\textsuperscript{11}; O\textsubscript{3}, 10\textsuperscript{9}; H\textsubscript{2}, 10\textsuperscript{5}; H\textsubscript{2}O, 10\textsuperscript{5}; NO, 10\textsuperscript{4}; H, 10\textsuperscript{7}; NO\textsuperscript{+}, 10\textsuperscript{3}; electrons, 10\textsuperscript{3}; O\textsubscript{2}\textsuperscript{+}, 10\textsuperscript{2}; O\textsuperscript{-}, 10; O\textsubscript{2}\textsuperscript{-}, 1; O\textsubscript{3}, 10\textsuperscript{-2}. The negative ions are thought to be far more important for ionospheric physics (radio propagation and absorption) than their low densities might suggest. The study of these negative ions is only just beginning. Up to 1967 there were very few reaction rates known and no direct measurements by rocket techniques of the D-region negative-ion composition.
### Table 7-6. Negative ion reaction rates*

<table>
<thead>
<tr>
<th>Type</th>
<th>Reaction</th>
<th>Rate(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge transfer</td>
<td>(\text{O}^- + \text{O}_3 \rightarrow \text{O}_3^- + \text{O})</td>
<td>(5.0 \times 10^{-10})</td>
</tr>
<tr>
<td></td>
<td>(\text{O}_3^- + \text{O}_3 \rightarrow \text{O}_3 + \text{O}_2)</td>
<td>(3.0 \times 10^{-10})</td>
</tr>
<tr>
<td></td>
<td>(\text{O}^- + \text{NO}_2 \rightarrow \text{NO}_2^- + \text{O})</td>
<td>(1.2 \times 10^{-9})</td>
</tr>
<tr>
<td></td>
<td>(\text{O}_3^- + \text{NO}_2 \rightarrow \text{NO}_2 + \text{O}_2)</td>
<td>(8.0 \times 10^{-10})</td>
</tr>
<tr>
<td>Associative Detachment</td>
<td>(\text{O}^- + \text{O} \rightarrow \text{O}_2 + \text{e})</td>
<td>(2.0 \times 10^{-10})</td>
</tr>
<tr>
<td></td>
<td>(\text{O}^- + \text{NO} \rightarrow \text{NO}_2 + \text{e})</td>
<td>(1.8 \times 10^{-10})</td>
</tr>
<tr>
<td></td>
<td>(\text{O}_3^- + \text{O} \rightarrow \text{O}_3 + \text{e})</td>
<td>(3.0 \times 10^{-10})</td>
</tr>
<tr>
<td></td>
<td>(\text{H}^- + \text{H} \rightarrow \text{H}_2 + \text{e})</td>
<td>(1.3 \times 10^{-9})</td>
</tr>
<tr>
<td>Ion-Atom Interchange</td>
<td>(\text{O}_3^- + \text{NO} \rightarrow \text{NO}_3^- + \text{O})</td>
<td>(1.0 \times 10^{-11})</td>
</tr>
<tr>
<td></td>
<td>(\text{O}_3^- + \text{CO}_2 \rightarrow \text{CO}_3^- + \text{O}_2)</td>
<td>(4.0 \times 10^{-10})</td>
</tr>
<tr>
<td></td>
<td>(\text{CO}_2^- + \text{O} \rightarrow \text{O}_2^- + \text{CO}_2)</td>
<td>(8.0 \times 10^{-11})</td>
</tr>
<tr>
<td></td>
<td>(\text{CO}_2^- + \text{NO} \rightarrow \text{NO}_2^- + \text{CO}_2)</td>
<td>(9.0 \times 10^{-12})</td>
</tr>
<tr>
<td>Three-Body</td>
<td>(\text{O}^- + 2\text{O}_3 \rightarrow \text{O}_3^- + \text{O}_2)</td>
<td>(4 \times 10^{-31} \text{cm}^6 \text{sec}^{-1})</td>
</tr>
<tr>
<td>Attachment</td>
<td>(\text{e} + 2\text{O}_3 \rightarrow \text{O}_2^- + \text{O}_2)</td>
<td>(1.4 \times 10^{-30} \text{cm}^6 \text{sec}^{-1})</td>
</tr>
<tr>
<td></td>
<td>(\text{e} + \text{O}_3 \rightarrow \text{O}^- + \text{O}_2)</td>
<td>(4.0 \times 10^{-11})</td>
</tr>
<tr>
<td>Photodetachment</td>
<td>(h\nu + \text{O}^- \rightarrow \text{O} + \text{e})</td>
<td>(1.4 \text{ sec}^{-1})</td>
</tr>
<tr>
<td>(sunlight)</td>
<td>(h\nu + \text{O}_3^- \rightarrow \text{O}_2 + \text{e})</td>
<td>(0.4 \text{ sec}^{-1})</td>
</tr>
</tbody>
</table>

*a Selected from Ferguson (1967), where five additional negative ion reaction rates are given. Results for many other reactions are given in Ferguson (1968), Fehsenfeld et al. (1967), and LeLevier and Branscomb (1968).

*b In cm\(^3\) sec\(^{-1}\) unless otherwise indicated.

The main D-region negative-ion production mechanism is believed to be

\[\text{e} + 2\text{O}_2 \rightarrow \text{O}_2^- + \text{O}_2\]

which we discussed earlier. The rate of this reaction depends on the square of the \(\text{O}_2\) density, which explains why it is important only at lower altitudes. There are some other reactions which may be important in the D region, and a selection of these are listed in Table 7-6. The process

\[\text{e} + \text{O}_3 \rightarrow \text{O}^- + \text{O}_2\]

may be a significant source of \(\text{O}^-\) ions.

A theory of the negative-ion chemistry requires us to identify the loss mechanism for \(\text{O}_2^-\) and \(\text{O}^-\) ions. Two likely mechanisms are

\[\text{O}_2^- + \text{O} \rightarrow \text{O}_3 + \text{e} \quad \text{and} \quad \text{O}^- + \text{O} \rightarrow \text{O}_2 + \text{e}\]

A development of much interest is the possibility of producing other
negative ions by reactions such as

\[ O^- + O_3 \rightarrow O_3^- + O \]
\[ O^- + NO_2 \rightarrow NO_2^- + O \]
\[ O^- + NO \rightarrow NO_3^- + O \]
\[ O_3^- + CO_2 \rightarrow CO_3^- + O_2 \]

and there are others. A suggested scheme interlinking the ions is shown in Figure 7-6. This was discussed in Ferguson (1967) and in LeLevier and Branscomb (1968). The loss processes for the NO_2^-, NO_3^-, and CO_3^- are not yet known, but these ions are comparatively stable, and they may exist in substantial abundance in the D region. The greatest need in this area is some rocket measurements of negative-ion abundances in the D region. There are many associated problems, such as variability of the composition of the D region with the solar cycle, diurnal variations, and latitude effects. The large abundance of neutral particles in the D region also increases the difficulty of measuring negative ion concentrations.

**Negative Ions in Astrophysics**

It has been known for many years that photodetachment from the H^- ion is an important contributor to the opacity of the cooler stellar atmospheres. One problem of interest is how the H^-:H ratio is maintained. Pagel suggested that the reaction

\[ H^- + H \rightarrow H_2 + e \]

is important. The rate of this reaction has been measured (Schmeltekopf, Fehtenfeld, and Ferguson 1967) and found to be \( k = 1.3 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1} \). This is a very fast rate. There are other collisional processes involving H^-, for example H^- + e \rightarrow H + 2e, but these are believed to be unimportant in stellar atmospheres. The cross section for H^- + e \rightarrow H + 2e was measured by Tisone and Branscomb (1968) in a crossed beam experiment.
They found a maximum cross section of $50\pi a_0^2$ at 20 eV energy. The cross section is probably several orders of magnitude smaller at thermal energies. The $\text{H}^- + \text{H}$ reaction is rapid compared with photoionization processes ($\text{H}^- + hv \rightarrow \text{H} + e$), and the concentration of $\text{H}^-$ appears to be collisionally controlled and hence in local thermodynamical equilibrium.

Other molecular ions (OH$^-$, Cl$^-$, for example) are predicted to occur in late-type stellar atmospheres, on the basis of equilibrium calculations, but they do not yet appear to have been directly observed.

Acknowledgment

The many years of work of my colleagues in the various laboratories in Boulder has been made possible by generous support from many sources, including the Advanced Research Projects Agency, the Defense Atomic Support Agency, the National Bureau of Standards, the Environmental Science Services Administration, and the National Bureau of Standards. My own work in preparing this lecture was supported in part by National Science Foundation Grant GP-11948.

SELECTED REFERENCES—BOOKS AND REVIEWS


SELECTED REFERENCES—INDIVIDUAL ARTICLES

*Multiplet Splitting*

Laser Photodetachment

Two-Photon Photodetachment

Drift-Tube Experiments

Geometrical Hindrance

Ion-Molecule Reactions

Electron Impact Detachment

Ionospheric Negative Ions
3. FORBIDDEN ATOMIC TRANSITIONS

Many years ago atomic spectral transitions were discovered which violated the usual selection rules, and such transitions became known as forbidden transitions. The first transitions to be recognized as such were the $^2\text{D} - ^2\text{S}$ transitions in the alkali metal spectra, the

$$6^3\text{P}_2 - 6^1\text{S}_0 \quad \text{and} \quad 6^3\text{P}_0 - 6^1\text{S}_0$$

transitions in HgI and the auroral line $^1\text{S}_0 - ^1\text{D}_2$ in O I. The discovery by Bowen in 1928 that many of the strongest lines in gaseous nebulae (lines of ions such as O II, O III, N II, S II, and Ne III, to name but a few) are forbidden transitions gave a great impetus to the subject. Other forbidden transitions were found in peculiar stars. In 1942 Edén identified the previously unidentified emission lines in the visible spectrum of the solar corona as being caused by forbidden transitions in highly ionized atoms (such as Fe X, Fe XI, Fe XIV, and Ni XII).

Calculations of Transition Probabilities

Many of the important forbidden transitions mentioned above are due to magnetic dipole radiation, and others are due to electric quadrupole radiation. These types of radiation have been studied in detail: reviews by Garstang (1962, 1969) may be consulted for the original references. [For more recent work see also the next chapter in this book.] Transition probabilities have been calculated for most of the astrophysically interesting lines and for most lines which can be produced in the laboratory. It is very difficult to assess the accuracy of forbidden-transition probabilities. The evidence from the experimental work discussed below is encouraging. There is room for further studies of the effects of configuration interaction and of electron correlation on forbidden line strengths. An elaborate study of some cases has just been carried out with the theory of electron correlation by Sinanoğlu. For these and additional considerations, the reader is referred also to the next chapter.

The Fe II Problem

There has been considerable debate as to the correct amount that measures the abundance of iron in the solar atmosphere. Determinations
from the study of ordinary Fe I lines in the solar photosphere seem to indicate an abundance of iron about seven times lower than the abundance given by ultraviolet lines from the solar corona. One possible check is to use the faint forbidden lines of Fe II which are observable in the solar photosphere. A great deal of effort has been devoted to observing these lines, and their identification seems beyond question. There are uncertainties in the model atmospheres used in the interpretation of the lines, but it is hard to see how these could lead to such a large error. It is equally hard to see how the transition probabilities of the [Fe II] lines could be in error by an order of magnitude. Thackeray made some extensive observations of the emission line star $\eta$ Carinae, which shows a rich spectrum of Fe II, [Fe II], and other ions. He compared his intensities of [Fe II] and [Ni II] lines with the theoretical transition probabilities. The agreement is very good, and on the basis of the theoretically predicted intensities many new identifications could be made. The excellent agreement between theory and observation leads us to think that there are no gross errors in the relative intensities of lines within the various multiplets. One can conclude little from the comparison about the absolute intensities, except to say that there seem to be no major discrepancies. However, the magnetic dipole line strengths do not depend on the radial wavefunctions but are largely determined by spin-orbit interaction, and this seems reasonably well known in Fe II from energy level calculations. Thus we do not think that there can be gross errors in the magnetic dipole transition probabilities. The electric quadrupole transition probabilities depend on the radial quadrupole integrals (departures from L-S coupling are usually minor in many of the transitions in which electric quadrupole radiation predominates), and some uncertainty exists in these integrals but hardly enough to explain more than a factor 2 at worst, and probably much less. The evidence presently available suggests that something is wrong with the low value for the iron abundance obtained from the solar photosphere, but this remains an unsolved problem.

Experimental Intensity Measurements

There have been several laboratory investigations which lead to a comparison of theoretical and experimental intensities. When both magnetic dipole and electric quadrupole radiation are present in a particular spectrum line the corresponding intensities of the Zeeman components are not additive (for observations in a particular direction), but are modified by interference effects which vary with the direction of observation. Hults in 1966 made a careful study of the $^1D_2-^3P_1$ line in
[Pb I] and the $^2P_3 - ^2P_1$ line in [Pb II]. From observations of the intensities of Zeeman components it was possible to determine the percentage contribution to each of the whole lines made by electric quadrupole radiation. Hults obtained 4% and 3% for the two lines, compared with 3.2% and 5.0%, respectively, from theory. This indicates that there is no major discrepancy between theory and experiment and is a general confirmation of the theory.

In another experiment, Husain and Wiesenfeld (1967) studied the flash photolysis of trifluoroiodomethane, which produces a large concentration of iodine atoms in the upper $^2P_1$ level of the ground doublet term. This decays to the lower $^2P_3$ level by a magnetic dipole transition at 1.315 microns wavelength. After correction had been made for collisional deactivation effects and diffusion effects there was found a measurable residual decay rate, which was attributed to the spontaneous radiative decay rate of the $^2P_1$ level. The result was $22 (± 6) \text{sec}^{-1}$ for the spontaneous transition probability, which may be compared with the theoretical value of $8 \text{sec}^{-1}$. This discrepancy should not be regarded as serious in view of the difficulties and pioneering nature of the experiment. There is clearly room for more work of this type.

Several investigations have checked the relative intensities of pairs of lines arising in emission from a common upper level. In the [O I] spectrum the lines $\lambda 5577 ({}^1S_0 - {}^3D_2)$ and $\lambda 2972 ({}^1S_0 - {}^3P_1)$ originate from the same upper $^1S_0$ level, so that their transition probabilities are in the same ratio as their photon emission rates. The corresponding pair of lines in the [S I] spectrum has been measured. In [O I] the ratio of the intensities of the lines $\lambda 6300 ({}^1D_2 - {}^3P_1)$ and $\lambda 6363 ({}^1D_2 - {}^3P_2)$ from the common upper level $^1D_2$ has also been measured. In all these cases the agreement between theory and experiment is excellent.

**Magnetic Quadrupole Radiation**

In 1964 Mizushima drew attention to the possible occurrence of magnetic quadrupole (and higher magnetic multipole) radiation for $\Delta S = ± 1$, which is forbidden for electric multipole radiation and for magnetic dipole radiation in L-S coupling, but which is allowed for magnetic quadrupole radiation provided that there is in addition a parity change and that $\Delta J = 0, ± 1, ± 2 (0 \leftrightarrow 0, 0 \leftrightarrow 0, ± 1, ± 2 \leftrightarrow ± 2)$, and $\Delta L = 0, ± 1 (0 \leftrightarrow 0)$. In many cases where magnetic quadrupole radiation occurs electric dipole radiation made possible by spin-orbit interaction also occurs and is stronger, effectively preventing the observation of the magnetic quadrupole radiation. This does not happen for $\Delta J = ± 2$, and of the transitions satisfying this the transition $s^2 {}^1S_0 - sp {}^3P_2$ is perhaps
the best case for a search for magnetic quadrupole radiation. A competition with nuclear-spin-induced radiation is possible in this case, and it is necessary to calculate both to determine which is dominant. It turns out that for Mg I (3s \(^2\) \(^1\)S_0–3s3p \(^3\)P_2) and for Zn I (4s \(^2\) \(^1\)S_0–4s4p \(^3\)P_2) magnetic quadrupole radiation predominates. For similar transitions in Cd I and Hg I nuclear-spin-induced radiation is dominant. The Zn I line has been observed in the laboratory, the only recorded observation of a predominantly magnetic quadrupole line. The Mg I line has been identified in the planetary nebula NGC 7027. Magnetic quadrupole radiation may be important for some highly ionized atoms, and this possibility is mentioned in this volume in my chapter on excitation processes in the solar corona.

In conclusion mention should be made of two other types of forbidden transition. One involves two-quantum processes. The transition 2s \(^2\)S \(\rightarrow\) 1s \(^2\)S \(_1\) in hydrogen and hydrogen-like ions and the transition 2 \(^1\)S \(_0\) \(\rightarrow\) 1 \(^1\)S \(_0\) in He I and helium-like ions both occur by the spontaneous emission of two photons. The other type involves magnetic dipole radiation in a relativistic approximation. This transition, 2 \(^3\)S \(_1\)–1 \(^1\)S \(_0\) in helium and helium-like ions, has been observed in the solar corona in the ion O VII, and is mentioned in my solar corona chapter in this volume. Two photon processes can in principle compete with the relativistic magnetic dipole process but are found on investigation to be extremely weak, and quite negligible for O VII.

REFERENCES

These are review articles and contain extensive bibliographies of original papers.

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