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Experimental studies on electron scattering from atoms and molecules: the state of the art

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Electron–atom/molecule scattering has been the subject of intense research activity, both experimentally and theoretically, for nearly a century, yet particularly for electron–molecule scattering our understanding of the dynamics of such processes remains limited. Due to their importance in many industrial, astrophysical, atmospheric and biological processes, absolute electron-scattering cross-sections are required for most atomic and molecular systems, however, the current database is limited to a few easily prepared systems. Only recently have experimental studies been extended to unstable reactive and free-radical species, while new experimental techniques incorporating advances in atom trapping and laser spectroscopy are being adapted to provide new insight into electron collision dynamics.

In this paper we survey the current status of the field and discuss the new experimental techniques that are providing fresh insights into the electron-scattering problem while providing invaluable data for the applied-science community.

Keywords: electron scattering; spectroscopy; electric–molecule resonances;
polyatomic molecules; radicals; atmospheric gases

1. Introduction

The interaction of electrons with atoms and molecules plays an important role in many natural and industrial processes. For instance, our understanding of ionospheric processes, the design and operation of lasers and related gas discharges and the development of plasma-etching processes used in the semiconductor industry all rely upon an intricate understanding of the collision dynamics of electrons with atomic, molecular and ionic systems. Electron collisions with atoms and molecules have therefore been studied experimentally for almost a century since the pioneering work of Franck & Hertz (1914) and Ramsauer (1921). Franck & Hertz provided a validation of the Bohr theory on the discrete nature of atomic energy levels, while Ramsauer provided the first evidence of the polarization of the target charge cloud by an incident charged particle, hence demonstrating the need for a quantum-mechanical representation of the scattering of discrete particles. The first quantum-mechanical calculations of Massey & Mohr (1931) established the now traditional interactive development of theoretical and experimental techniques in this research field. A good example of such experimental/theoretical interactive development was the experimental discovery of short-lived negative ion 'resonances' by Schulz (1963) that led to the development of time-dependent calculations incorporating nuclear motion. The intricacy of theoret-

ical calculations also led to the development of coincidence experiments to test the theoretical treatments of electron–atom excitation processes.

The field of electron–atom/molecule scattering is therefore well established and we have a good understanding of the major mechanisms and dynamics involved in collisional processes. However, the demand for accurate scattering cross-sections and knowledge of the final quantum-mechanical states of the collisional 'reactants' has grown rapidly in the last decade. Models of planetary atmospheres and molecular clouds in interstellar space require data on electron interactions with over one hundred atomic, molecular and ionic systems (Rees 1989), while models of fusion reactors such as JET require detailed data on over 200 electron processes (Joachain & Post 1982). The design and operating parameters within industrial plants to fabricate the next generation of fast silicon chips crucially depend upon the ability to model accurately the electron-induced processes involved in plasma etching (National Research Council Report 1996). Electron-induced processes in biological systems are being increasingly recognized as of prime importance to our understanding of the mammalian nervous system and consciousness (Glass & Varma 1991), while the role of high-energy electrons in biological degradation has been recognized as a key process in radiation interaction with tissue and cellular structure.

Therefore there remains a crucial need to provide extensive data on electron–atom, electron–molecule and electron–ion collision cross-sections, however, after 80 years of experimental study we have 'complete' information on only a few target systems (the rare gases), while several targets (e.g. radioactive atoms and free-radical molecules) have yet to be studied. Even if it were feasible to collect all the data presently required by the applied-science community, it would require the attention of the whole of the world's atomic and molecular research teams for over 50 years! Hence, in the past 20 years, great emphasis has been placed upon the development of reliable theoretical techniques that, once validated experimentally, will be able to produce the data required to an acceptable level of accuracy. Great advances have been made by the theoretical community, e.g. the development of the R-matrix method by Burke and co-workers (see Tennyson & Morgan, this issue) and the adoption of parallel computational techniques, but theory alone is not yet capable of producing the volume and accuracy required for the many systems of interest. Therefore experimentalists are continuously developing techniques to provide stringent tests of the developing theoretical treatments of electron-collision processes. In this article we will review the current state of experimental progress and suggest how the field may develop in the next decade. The article will not discuss electron–ion collision processes, where great advances have been made recently (see, for example, Müller, this issue; Williams & Newell, this issue), but will concentrate upon electron collisions with neutral atoms and molecules.

2. Electron–atom collisions

The first detailed experimental study of electron–atom scattering was reported by Franck & Hertz (1914) and demonstrated that electron scattering may be used to study the *spectroscopy* of a target. Measurement of the energy of an electron scattered from the target atom provides a direct measure of the energy transferred to the target. Below the ionization energy, such energy transfer must excite a discrete state, hence measurement of the electron energy-loss (EEL) spectrum provides a con-

venient method for determining excitation probabilities of specific quantum states. Such excitation cross-sections are of critical importance to the industrial community since they determine the amount of fluorescence emitted from the decaying atomic system, vital in lighting and gas discharge design. Should the excited state be *metastable* in nature then the excitation probability may have an important role in the local chemistry (e.g. the excitation of helium in the helium–neon laser). The cross-sections for excitation of many simple atomic systems are now well established experimentally and are in good agreement with recent theoretical treatments; for example, the excitation cross-section for lowest excited states of helium measured by Allan (1995) are in excellent agreement with the refined calculations of Sawey *et al.* (1990).

Dynamical information on the scattering event is provided by measurement of differential cross-section (DCS) to show the angular distribution of the scattered electrons. Measurement of the DCS for any scattering process provides detailed information on the local interaction between the incident electron and the target and thence the shape of the atomic charge cloud both prior to and after the collision event. Therefore, DCS measurements have traditionally provided a more stringent test of the theoretically derived interaction potentials. However, experimental methodology has long been limited by the inability of apparatus to measure DCS at backward angles since finite space is required for the apparatus needed to produce a well-collimated high-resolution (low-energy-spread) electron beam incident upon a gaseous target. Although special apparatus has been developed to measure scattering at 0 and 180° (see, for example, Asmis & Allan 1997), DCS between 120 and 180° were seldom accessible, yet it is just in this angular scattering region that theory predicts interesting structures arising from polarization of the target or exchange between an incident electron and an electron in the charge cloud. Recently, a novel experimental technique has been developed (Read & Channing 1996) that will allow DCS to be measured over all scattering angles. Figure 1 shows the DCS for electrons scattered from helium in exciting the $2\,^3$S state. Incorporation of this device in existing electron spectrometers will therefore provide a major advantage in our study of electron–atom interactions and may be equally well applied to molecular targets.

Low-energy electron scattering is often dominated by the appearance of 'resonance' structures. Electron–atom/molecule resonances are formed by the temporary attachment of the incident electron to the target, i.e.

$$\mathrm{e}^- + \mathrm{A} \to \mathrm{A}^-$$

followed by autodetachment of the electron, leaving the atom in either the ground state or an excited state A^*:

$$\mathrm{A}^- \to \mathrm{A}(^*) + \mathrm{e}^-.$$
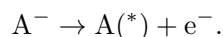
If the target is left in the ground state, then the resonance will be clearly observed in the elastic scattering channel and the ejected electron will have approximately the same kinetic energy as the incident electron, while if the target is left in an excited state the resonance will be observed both in the EEL spectrum and in the fluorescence or metastable yield of the atom. Resonances may lead to order of magnitude changes in the cross-section often over only a small incident energy region (less than 100 meV) and, in a few cases, the role of the resonance dominates the cross-section. Figure 2 shows the excitation cross-section, close to threshold of the He $(2\,^3$S) metastable
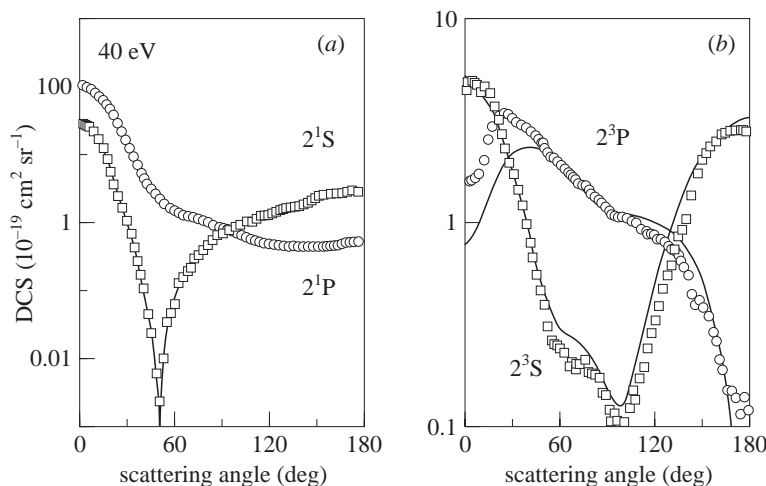
Figure 1. DCS for electron–helium scattering between 0 and 180° using the new magnetic angle-changing technique (Cubric *et al.* 1999).

state, important in many discharge and laser systems. A broad resonance dominates the first 2 eV with sharper narrower resonances prevalent at higher energies. The nature of these resonances and their magnitude have been the testbed for electron–atom scattering theory over the past 30 years, since they require careful treatment of both polarization and exchange effects as well as the coupling of many target states. The most recent 29-state calculation using the R-matrix method has reproduced the experimental data to within a few per cent and correctly predicts the width of the observed resonances, which in turn determine the lifetime of the temporary negative ion states (Sawey *et al.* 1990).

Electron-impact ionization is the dominant process in most plasma systems from those developed for the commercial implementation of fusion to those used to manufacture silicon chips. Very accurate electron–atom ionization cross-sections can be measured since the resultant ion may be detected with near-unity quantum efficiency (in contrast to the few per cent for fluorescence or metastable yields in electron-impact excitation) and therefore the electron-impact ionization cross-sections are well established for all the stable atomic targets. However, once an atom is ionized the scattered electron and the ejected electron may interact in a *post-collisional* process that dominates the DCS of the scattering electron. Such *correlation phenomena* are particularly important close to threshold where both the scattered and ejected electrons are moving relatively slowly with respect to each other in the coulombic field of the atomic ion. Such a system provides a powerful tool for the study of fundamental coulombic interactions that remain so difficult to treat theoretically due to the long-range nature of the Coulomb force.

The most refined electron–atom scattering experiments measure the scattered electron in coincidence with the ejected electron or emitted photon. Such $(e, e + h\nu)$ and $(e, 2e)$ experiments have been able to map out the shape of the excited atom charge cloud (Anderson & Bartschat 1996; Cvejanovic & Crowe 1998) and describe, in intricate detail, post-collisional dynamics; they have therefore provided the most definitive tests of electron–atom scattering theories. The recent close-coupling meth-
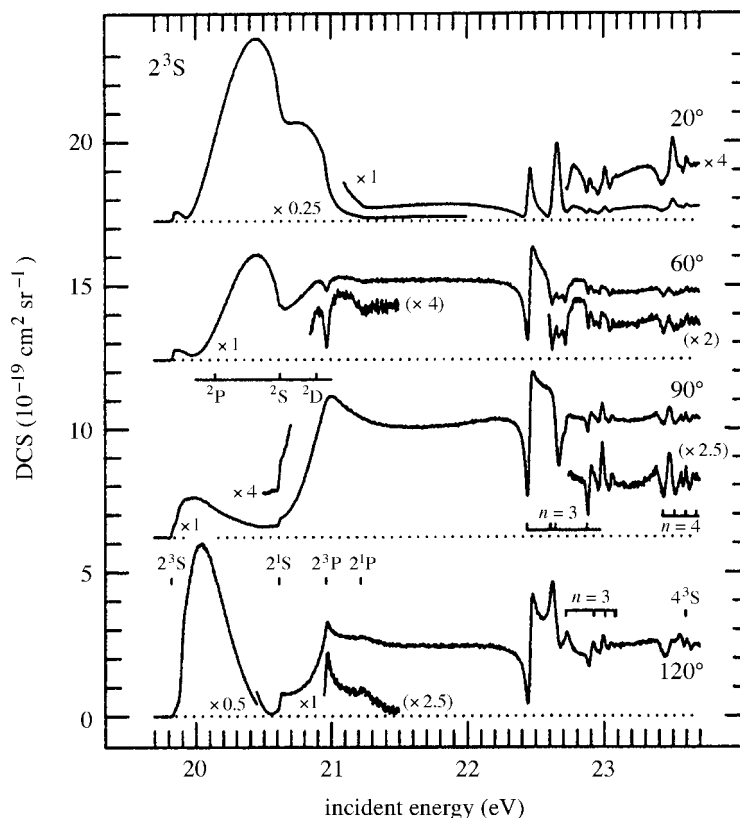
Figure 2. Excitation cross-section for He $(2\,^3S)$ revealing rich resonance structure (Allan 1995).

ods developed by Bray and co-workers (see, for example, Bray & Fursa 1996) and the R-matrix method (Andersen & Bartschat 1997) are proving to be astonishingly accurate in their ability to reproduce the experimental observations (figure 3), and therefore suggest that we may now be close to a full understanding of the electron–atom scattering problem.

3. Electron–molecule scattering

Molecular systems dominate the structure, dynamics and transfer processes in both inanimate and living bodies. Understanding electron–molecule collision processes is therefore of fundamental importance. However, electron scattering from molecular systems is much more complex than electron–atom scattering. The increased degrees of freedom in the target molecule introduce new excitation mechanisms. In electron–molecule scattering rotational and vibrational excitation compete with and complement the simple electronic excitation found in atomic systems, while molecular dissociation competes with ionization as a new fragmentation channel. The formation of anions (AB^-) and their dissociation mechanisms are also important in low-energy electron–molecule scattering and provide a new decay mode for electron–molecule scattering resonances that was not available in electron–atom scattering. New inter-
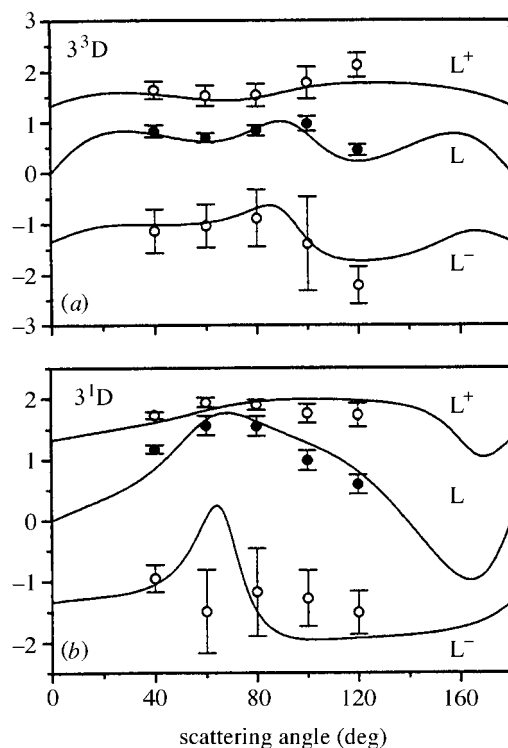
Figure 3. Electron-impact excitation of the three-dimensional states of helium.
Comparison between theory (——) and experiment (● and ○) (Fursa *et al.* 1997).

action potentials between the incident electron and the target also arise from the
ability of the molecular target to have a permanent dipole moment.

Perhaps one of the greatest limitations in experimental electron–molecule scatter-
ing is the finite resolution of the incident electron beam. While the best gas-phase
electron spectrometers may allow atomic transitions to be well resolved, they have
not been able to observe rotational structures in EEL spectra (except for H_2 and
its isotopes) and often vibrational spectra in the ground and excited states cannot
be resolved. These are serious limitations since rotational modes of most molecules
are thermally excited at room temperature but cannot be observed in current EEL
experiments.

Furthermore, vibrational levels may also be populated by thermal processes; the
population of an upper level of a molecule being given by the well-known Boltzmann
distribution

$$N_R = \frac{g_R \mathrm{e}^{-E_R/kT}}{\sum g_R \mathrm{e}^{-E_R/kT}},$$

where N_R is the percentage population, g_R are the statistical weights, E_R is the
energy relative to the ground state, k is Boltzmann's constant and T is the ambient
temperature of the surrounding environment.

For simple diatomic molecules E_R is high (greater than 100 meV) and hence at
room temperature ($T = 298$ K) only a small percentage of the molecules will be in
excited vibrational states. However, for even the simplest polyatomic molecules (e.g.

CO_2) vibronic spacings are much less and hence the lowest vibrational states will be populated even at room temperature. In gas discharges and plasmas, temperatures in excess of 600 K are not uncommon, whereupon the ground-state population of the molecular target may fall to below 50%, while if the molecular species are produced in chemical reactions, then many electronic and vibrational modes may be excited and most of the molecules are energy 'rich'. Clearly then, we need to understand electron scattering from rotationally and vibrationally excited molecules. However, present theoretical treatments assume a fixed nuclei approximation (frozen vibrational motion) and experiments have not been able to select the initial molecular rovibrational target state but have been performed with a composite target incorporating molecules in a wide variety of rovibrational states.

For these reasons our knowledge of electron–molecule scattering is not as advanced as that for electron–atom scattering. Nevertheless, recent developments in both experimental technique and computer technology are producing significant advances in both our knowledge and understanding of the dynamics of electron–molecule scattering.

(*a*) *Ultra-low-energy and high-resolution electron scattering*

To probe rotational and vibrational excitation of the ground state of molecules it is necessary to produce electron beams with both low energy (less than 1 eV) and high resolution (less than 10 meV). At such low energies electron beams are ultrasensitive to stray electric and magnetic fields within the electron spectrometer. Intense electron beams (μA) at low energies will expand due to electron–electron coulombic interactions producing a divergent electron beam with a greater energy spread (lower resolution). Therefore, most electron spectrometers operate at energies in excess of 2 or 3 eV. Experimental studies of rotational excitation and the formation of many stable (and temporary) anions at low (zero) energies is therefore limited. However, in the last decade several experimental groups have designed apparatus to study such 'ultra-low-energy' collisions.

Märk and co-workers (see, for example, Matejcik *et al.* 1997) in Innsbruck have modified a conventional trochoidal electron monochromator using a thermionic emission electron source to operate with high resolution (less than 10 meV) at incident energies between zero and 10 eV. Field and co-workers have developed a unique photoelectron source that uses synchrotron radiation to produce photoelectrons by photoionization of argon (figure 4), giving electron beams of 3 meV resolution over the energy range 10 meV to 10 eV (Field *et al.* 1991). Hotop and co-workers in Kaiserslautern used a laser source to produce photoelectrons with a resolution of much less than 1 meV and were able to measure cross-sections at energies as low as 20 μeV (Schramm *et al.* 1998). A novel, but comparable, technique was developed by Dunning and co-workers (see Poppel *et al.* (1995) for a concise review) where atoms in high Rydberg states were collided with atomic and molecular targets. The outermost electron in the Rydberg orbital is so weakly attached to the target that in any Rydberg–atom/molecule collision it is essentially a free electron and thus the scattering of μV to meV electrons may be measured by studying Rydberg–atom/molecule interactions.

The ability to study such low-energy electron collisions allows the experimentalist to study threshold phenomena and probe basic electron–molecule interactions,
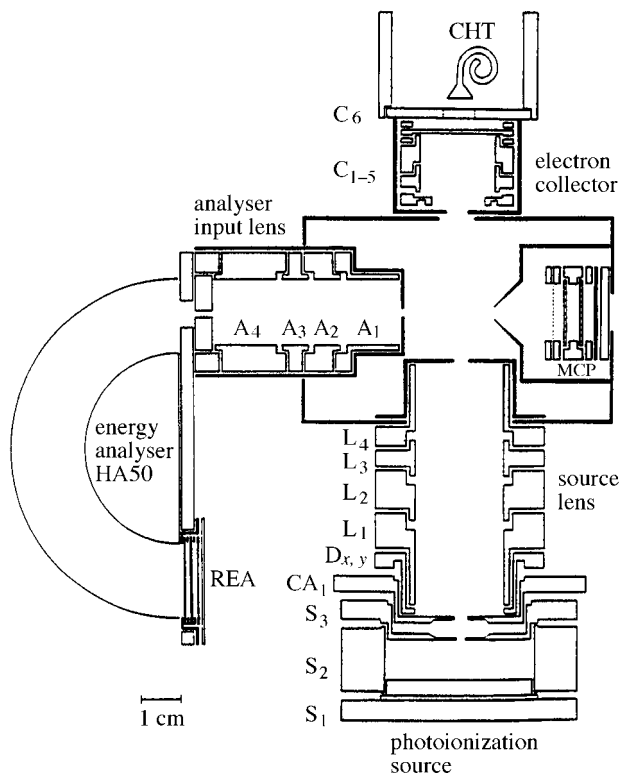
Figure 4. Synchrotron radiation photoelectron source (Field *et al.* 1991).

because at low energies the incident electron spends a long time in the vicinity of the target and is therefore sensitive to its internal structure. The experiments performed to date have revealed that, at low energies, electron scattering may be adequately represented by scattering of only a few partial waves, the s-wave in many instances dominating the scattering cross-section. The scattering cross-sections (elastic or inelastic) show interesting features at the onset of vibrational modes; either step-like functions (Hotop *et al*. 1995) (figure 5) or, in the case of molecular chlorine, a complex resonance structure (Gulley *et al*. 1998*a*) (figure 6).

It is now interesting to consider the role and magnitude of rotational excitation in electron–molecule collisions. Hitherto, due to the inability of the experimentalist to study rotational excitation, models incorporating rotational excitation (e.g. plasma discharges) have relied upon the Born approximation to calculate the magnitude of rotational excitation cross-sections. Recent low-energy experiments (Gulley *et al*. 1998*b*) on the interesting triatomic systems ozone and OClO (both having strong dipole moments) indicate that such calculations overestimate the rotational cross-section by a factor of two or more at low energies (figure 7).

With the development of even higher-resolution electron spectrometers (photoelectron spectrometers of 1–2 meV (Martensson *et al*. 1994) and surface science instruments of less than 1 meV (Ibach 1993) we can soon expect to be able to measure discrete rotational cross-sections and hence test the development of those electron–molecule calculations that are no longer reliant upon the fixed nuclei approximation.
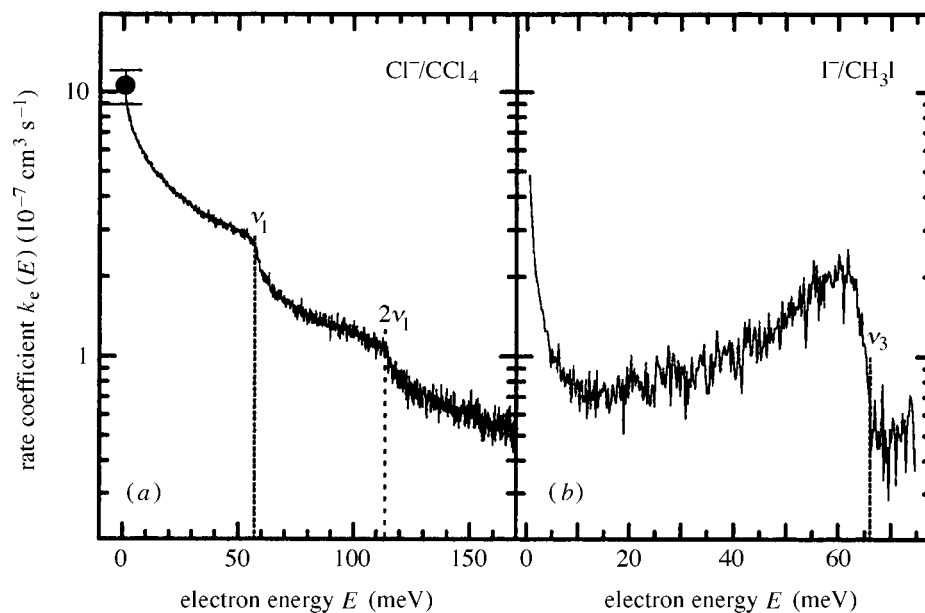
Figure 5. Step structure observed at the vibrational-onset low-energy electron scattering from CCl_4 and CH_3I (Hotop *et al.* 1995).
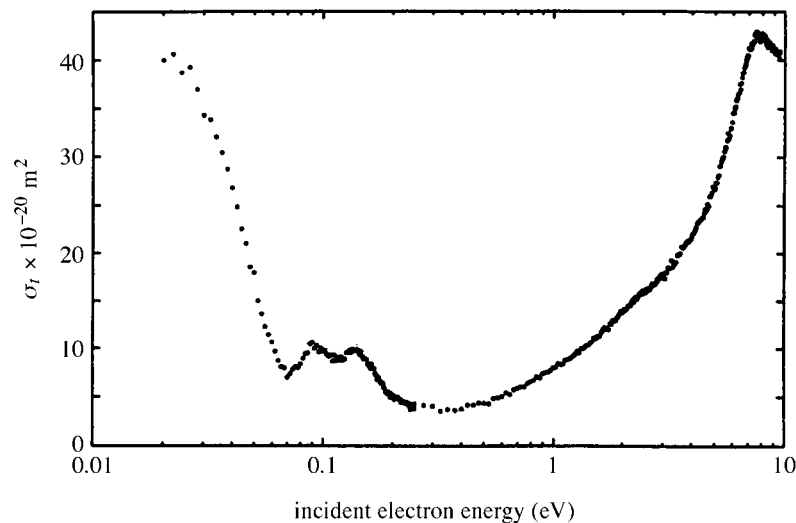

Figure 6. Resonance structure observed at the onset of vibrational excitation in the total electron-scattering cross-section of Cl_2 (Gulley *et al.* 1998*a*).

(*b*) *Resonance formation in electron–molecular scattering*

The colliding electron may be captured by the target molecule in the same way as it can by an atom. The temporary anion may then decay either by autodetachment leaving the molecule in its ground or excited state, or it may decay by dissociation resulting in anionic fragments.
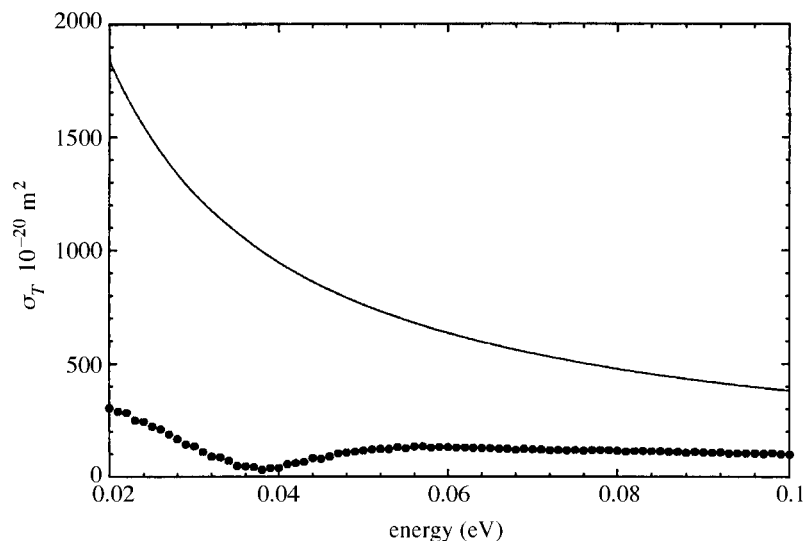
Figure 7. Total cross-section in OClO showing breakdown of Born approximation for rotational scattering: •, experiment; ——, Born theory (Gulley *et al.* 1998*b*).

Vibrational excitation by electron impact is dominated by the formation of resonances. Typically, the vibrational excitation cross-section is an order of magnitude larger when a resonance occurs compared to direct electron impact. In many discharge and atmospheric systems the production of such vibrationally excited molecules is of key importance to the local chemistry; for example, the vibronic excitation of ozone by low-energy electrons is dominated by two shape resonances, one lying at 4 eV and the other at 6 eV (figure 8). Furthermore, one resonance seems to selectively excite bending modes while the other excites stretch modes of vibration (Allan *et al.* 1996*a*).

The resonant formation of anions by electron attachment (EA) is known to play a major role in many industrial plasmas. Figure 9 shows the formation cross-section of Cl^- from CCl_4; a single resonant-like feature is observed at electron energies close to zero. In such dissociative EA processes the product anion or neutral fragment(s) may be formed with significant amounts of kinetic energy and may be internally excited influencing the local chemistry. Indeed the kinetic and internal energy of chlorine and fluorine containing fragments produced by DEA are believed to play a key role in the fabrication of semiconductors.

DEA may also be important in the interstellar medium (ISM). In some regions of the ISM there are molecular clouds of which the origin remains the subject of some debate. Spectroscopic analysis reveals not only simple diatomics (H_2 and CO) but also the presence of larger polyatomics such as ethanol and acetic acid (vinegar!). The mechanisms by which such molecules may be formed is still unclear, but it is believed to involve some form of heterogeneous chemistry on dust grains comprising primarily carbon and/or silicon. Polycyclic aromatic hydrocarbons (PAHs) are also thought to play an important role in the ISM since they are photolytically stable under background UV radiation. However, to date no laboratory experiment on such compounds has been able to accurately reproduce the IR emissions observed, and it has been postulated that the PAHs exist in either cationic or anionic states.
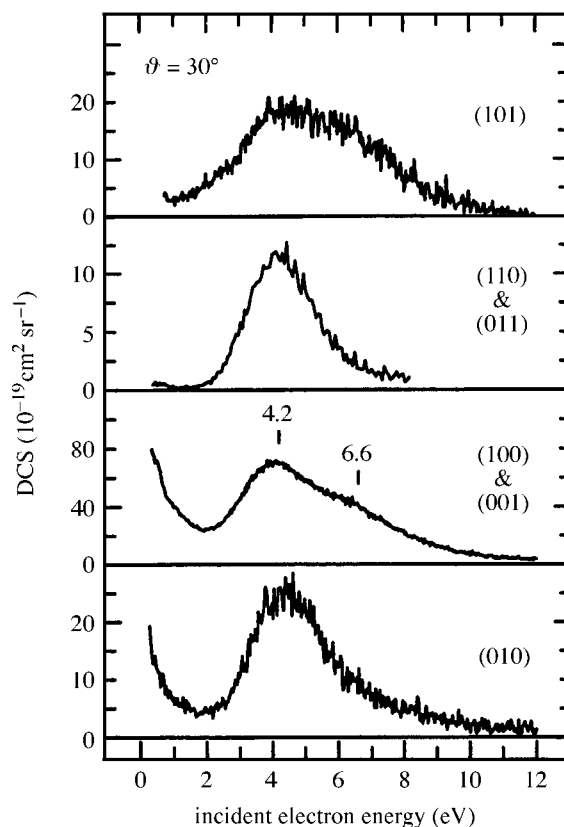
Figure 8. Resonant excitation of the bend and stretch modes in ozone (Allan *et al.* 1996*a*).

The recent discovery of C_{60} showed that in large caged structures it is possible to delocalize electronic charge across the surface, and hence C_{60} acts as an 'electron sponge', which at low energies may readily capture electrons (Matejcik *et al.* 1995). Similar processes may occur with the larger PAHs such that, within the ISM, local (an)ion–molecule chemistry may be important in the formation of larger molecular systems. Adoption of the low-energy high-resolution techniques described above, in combination with new molecular beam sources of PAHs, should therefore shortly allow DEA and EA of the PAHs to be studied. Such research may then be expanded to prototype biological systems (e.g. simple amides, the building blocks of proteins). Indeed the first electron-impact studies of DNA have already been reported (Huels *et al.* 1998).

4. Electron scattering from reactive targets

In many applications the molecular systems interacting with free electrons are not stable molecular systems but highly reactive compounds or free radicals. Hitherto there has been little experimental study of molecular targets that are not readily available in 'gas bottles'. Only recently have the methodologies of chemical synthesis been coupled with the technique of EEL spectroscopy to study such reactive and free radical targets.
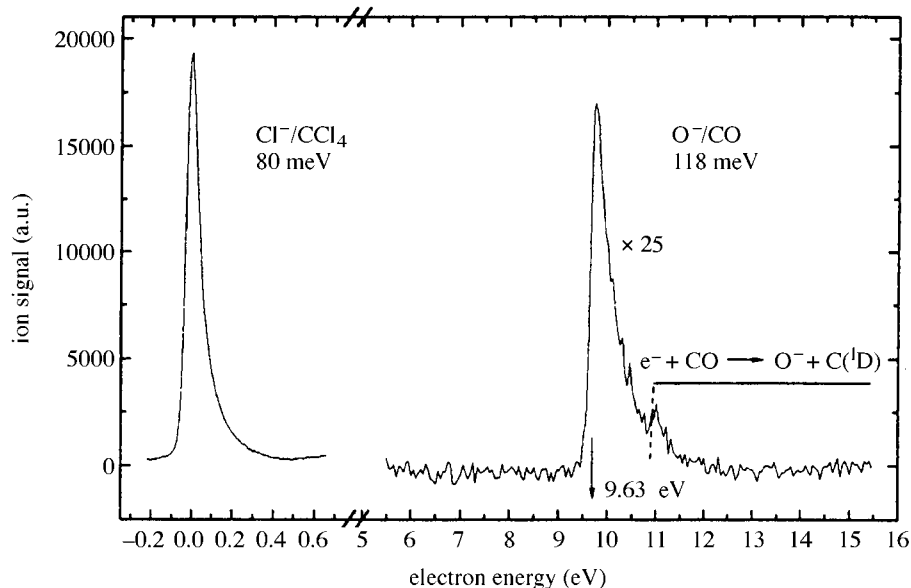
Figure 9. The formation of Cl^- from CCl_4 and O^- from CO studied by high-resolution electron beams.

(a) *Electron scattering as a spectroscopic tool*

EEL spectroscopy is an excellent tool for studying molecular spectroscopy, being able to probe both optically allowed and forbidden states. If the incident electron energy T is sufficiently large ($T > 100$ eV) and the scattering angle small ($\theta \approx 0°$), the electric field induced at the site of the molecule by a passing electron is very similar to that which would be caused by an incident photon pulse (Celotta & Heubner 1979). The electric field acts most strongly with the transition dipole of the molecule such that electric dipole (or optically allowed) transitions are predominantly excited, and hence the inelastic electron-scattering process simulates the photoabsorption process. An additional advantage of using EELS to measure optical absorption spectra is that a wide wavelength range may be recorded simultaneously without the need to change filters and detectors. It is possible to relate the energy-loss spectrum obtained at $\theta \approx 0°$ and high incident energy ($T \gg E_L$, the EEL) to the differential oscillator strength and thence the optical absorption cross-section. Since EELS does not suffer from the effect of 'line saturation', such derived cross-sections may provide a more accurate value of the absorption strength of particular electronic states than simple single-photon absorption experiments. EELS may therefore be used to probe the spectroscopy of reactive molecular systems

Figure 10a shows an energy-loss spectrum in ozone collected under scattering conditions favouring optically allowed transitions (Johnstone *et al.* 1992). The broad energy-loss band between 4 and 6 eV is the well-known 'Hartley band' of ozone, which is responsible for filtering out harmful solar UV radiation as it passes through the Earth's atmosphere. Comparison of cross-sections with optical data is shown in figure 10b; excellent agreement is found between the two sets of data.

At low impact angles and large scattering angles ($\theta > 90°$), i.e. the conditions of large momentum transfer within the collision event, structure observed in the
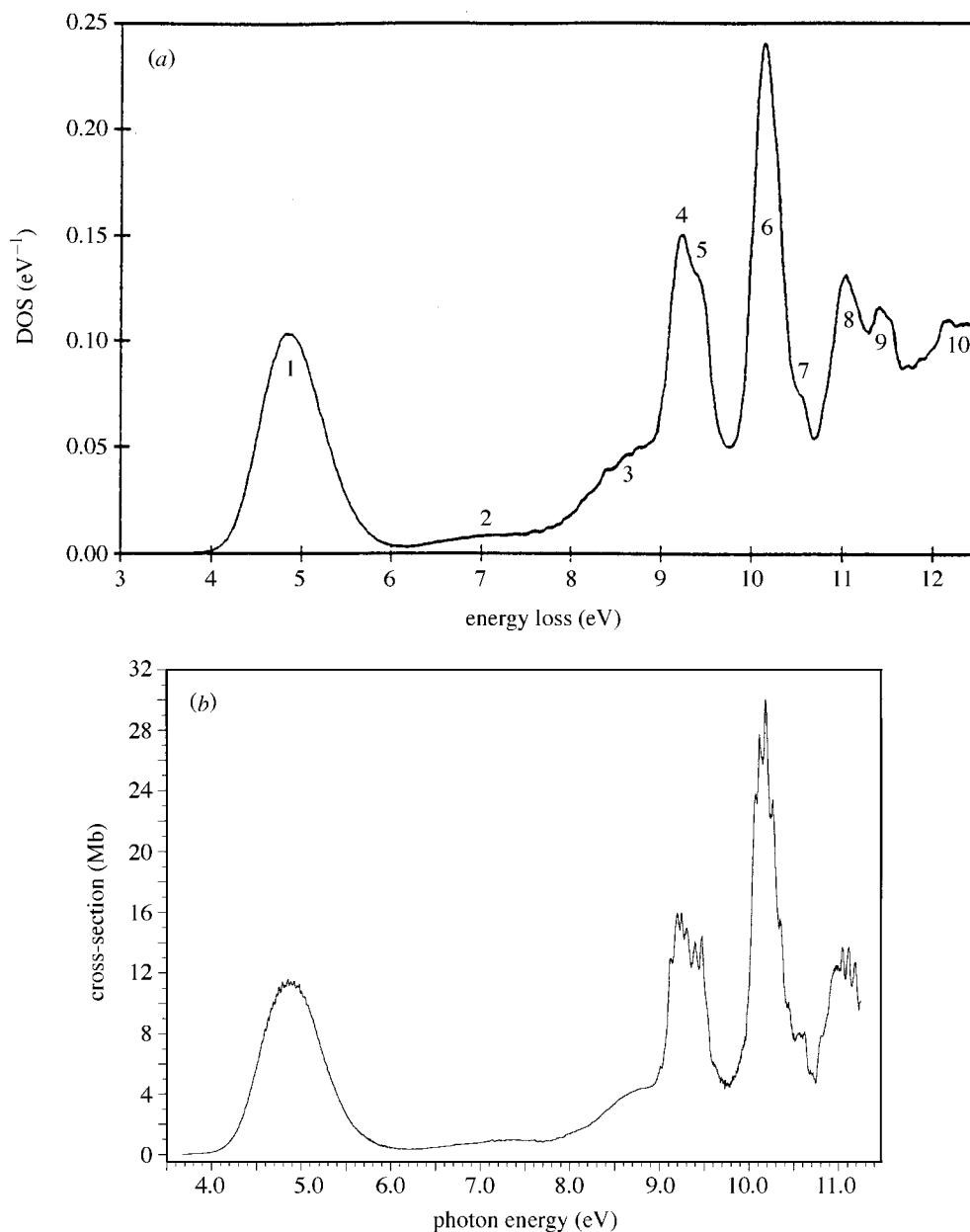
Figure 10. (*a*) Energy-loss spectrum in ozone (Johnstone *et al.* 1992); (*b*) optical absorption cross-section in ozone (Mason *et al.* 1996).

energy-loss spectra will be due to forbidden transitions. Hence, by selective adjustment of scattering parameters towards large momentum transfer, it is possible to probe those electronic states that are not able to be observed in one-photon absorption experiments, but which may be excited in the Earth's atmosphere. Figure 11 shows the energy-loss spectrum in ozone under conditions favouring excitation of forbidden states (Allan *et al.* 1996*b*). A new band is observed between 1 and 3 eV
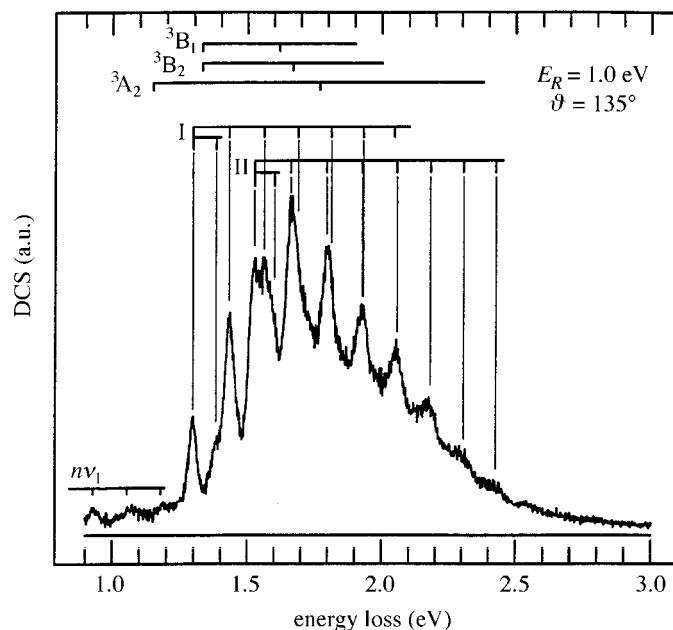
Figure 11. Energy-loss spectrum in ozone revealing bound nature of some of the forbidden states of ozone (Allan *et al.* 1996*b*).

with superimposed vibronic structure. This band comprises the lowest triplet excited states of the ozone molecule, all of which are forbidden electric dipole transitions. The observation of vibronic structure was the first direct evidence for these states being bound, albeit only able to support two or three modes of vibration. Most theoretical calculations on the electronic structure and excitation of ozone suggested that these states were purely repulsive and could not support vibronic excitation and therefore emphasizes the usefulness of EELS as a probe of molecular spectroscopy.

(*b*) *Electron scattering from free radicals*

Free radicals are a class of highly reactive molecular species that are frequently produced in plasmas. To date, experimental studies of such species are extremely limited but, with the development of theoretical calculations, are likely to become a major area of future study. Electron-impact ionization cross-sections have been reported with an accuracy of 20% for SiF_x and CF_x ($x = 1$–3), NF_2, NF and SO, while Sugai *et al.* (1995) have measured absolute and relative dissociation cross-sections for various molecules relevant to plasma technology (SiH_4, CF_4 and CH) using threshold mass spectrometry. However, to date, no elastic, vibrational or electronic excitation cross-sections have been reported and no DCS recorded for such compounds, despite their vital importance in the modelling of plasma-processing systems. This may be ascribed to the difficulty in preparing molecular beams of the relevant free radicals.

In the last few years major advances have been made in the study of electron scattering from atmospheric radical species, in particular ozone and the chlorine oxides (OClO and Cl_2O). A review of electron scattering from ozone has been recently published (Mason & Pathak 1997). The low-energy spacing between the lowest unoccu-
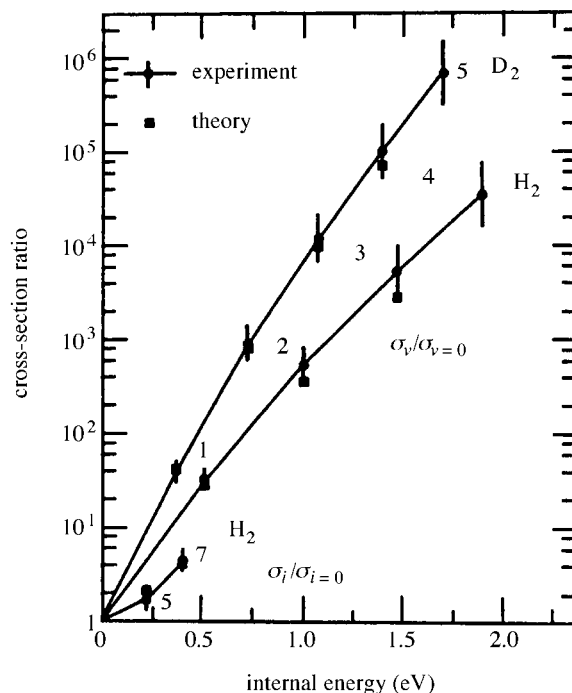
Figure 12. Dissociative electron attachment in molecular hydrogen and deuterium showing strong vibronic dependence. The cross-section for a vibronic state ν as a ration of the cross-section for DEA to the ground state (Hall *et al*. 1988).

pied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) in the ozone biradical leads to some interesting spectroscopy and collisional dynamics. The presence of no fewer than five low-lying excited states (less than 5 eV) provides several possible parents for resonance formation that may subsequently decay by dissociative electron attachment. In one DEA channel the O_2^- subsequently autodetaches producing electrons of well-defined energy from which the spectroscopy of the O_2^- anion may be deduced (Allan *et al*. 1996*c*). Similar processes may exist for other radical species such as SO^- produced from SO_2 and CS^- from CS_2.

Elastic and inelastic DCS cross-sections for electron scattering from ozone have also been reported by two independent experimental groups (Allan *et al*. 1996*a*; Shyn & Sweeney 1996). It is therefore possible to predict that further DCS for radical species will become available in the next few years. Indeed EEL spectra and dissociative electron attachment from the OClO radical have recently been reported (Davies *et al*. 1995; Marston *et al*. 1998).

Of all the radical species perhaps the most important to study both experimentally and theoretically is OH. The hydroxyl radical plays a key role in the terrestrial atmosphere and in all plasma deposition systems, yet no experimental electron scattering data exist for this molecule. Recently the R-matrix method has been used to calculate cross-sections for the OH molecule (Chen & Morgan 1997). These theoretical predictions should now be experimentally verified using the OH beam sources developed for reactive beam experiments.
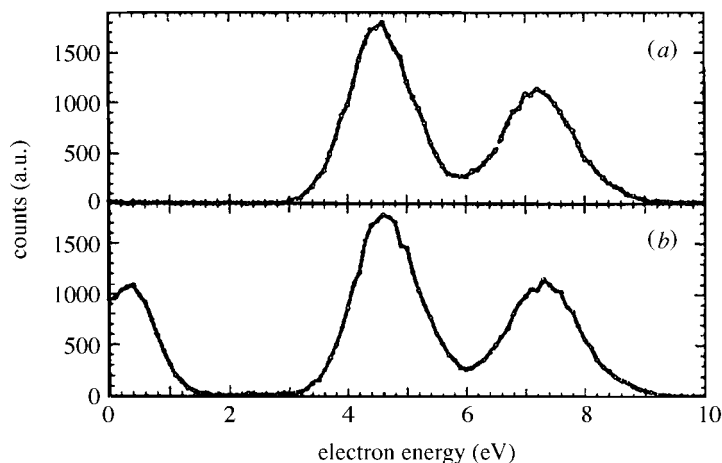
Figure 13. DEA in SO_2. O^- formation from: (*a*) the ground state;
(*b*) a laser-excited state (Krishnakumar *et al.* 1996).

5. Electron scattering from excited states

As has already been mentioned, no molecular system is without internal energy,
usually rotational modes and the lowest vibrational modes are excited. However, in
many technological applications (e.g. gas discharges, lasers, pulsed power switches
and MHD) electronically excited states also play an important role. The limited
knowledge on electron-excited molecule interactions clearly shows that the cross-
section for certain electron–molecule collision processes can be considerably differ-
ent from those involving ground-state molecules. For example, dissociative electron
attachment cross-sections in molecular hydrogen change by orders of magnitude for
different initial vibrational modes (figure 12) (Hall *et al.* 1988) while DEA from
optically pumped SO_2 shows that new dissociation channels (Krishnakumar *et al.*
1996) may be opened when the molecular target is in an electronically excited state
(figure 13).

Little is known about slow-electron scattering from vibrationally/rotationally ex-
cited molecules, either elastic, inelastic or superelastic (if the target is in an excited
state the incident electron may gain energy from the target in the collision). Ferch
et al. (1989) and Buckman *et al.* (1987) reported total cross-sections for electron
scattering from thermally heated CO_2. Thermal population of the vibrational states
produced a significant proportion of the target beam in the bent vibrational mode.
Scattering from such a target (with its larger dipole moment) led to larger scattering
cross-sections at all incident energies and the $CO_2^-(^2\Pi_u)$ resonance was observed to
appear at a lower energy (approximately equal to the vibrational energy). The first
DCS for electron scattering from vibrationally 'hot' targets was reported by John-
stone *et al.* (1993, 1995) (figure 14) and suggested that cross-sections for scattering
from vibrationally excited states may be 15% higher than from the ground state.
Similarly, Mason (1994) found evidence for an increase in the dissociation cross-
section of N_2O and CO_2 into metastable fragments with increased kinetic energy of
the fragments. However, since there was no state selection in the target beam such
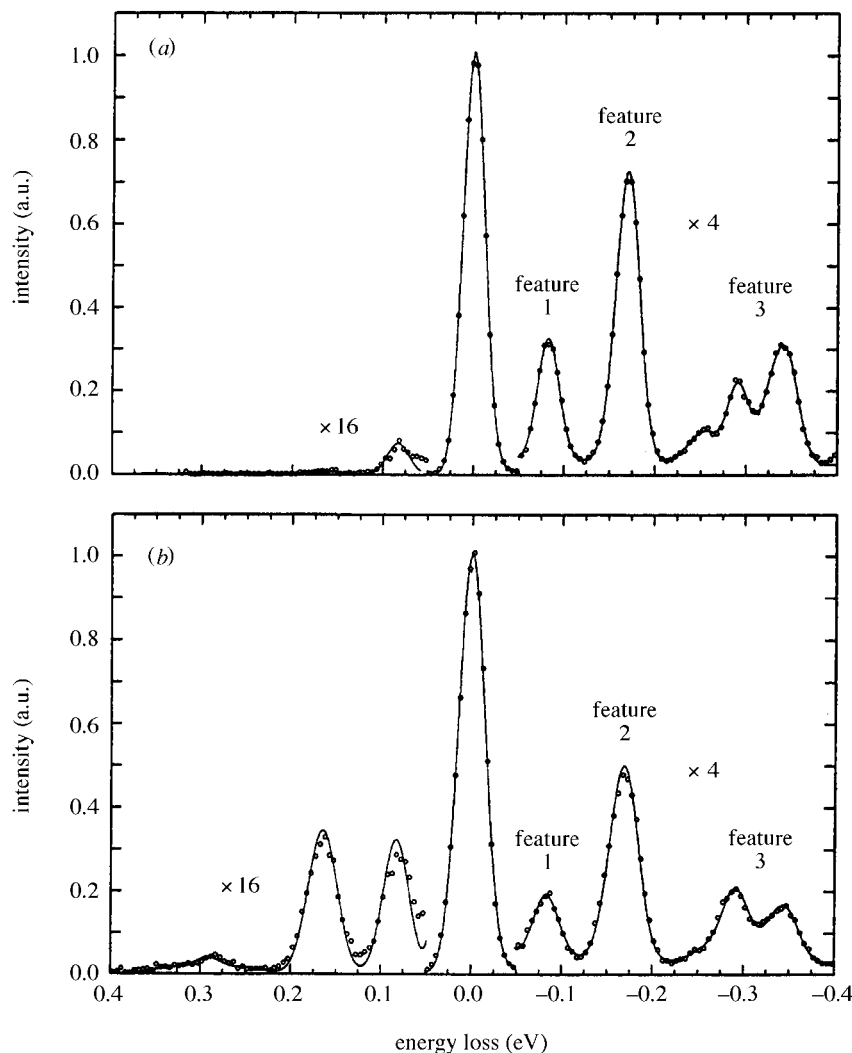experiments can only provide limited information on such processes.

Figure 14. Electron scattering from an excited CO_2 molecule (Johnstone *et al.* 1993).

The use of modern diode laser systems coupled with supersonic gas sources provide the opportunity for the preparation of molecular systems in specific rovibrational states. When coupled with laser-analysis techniques (e.g. REMPI and LIF) it should now be possible to produce state-to-state electron scattering cross-sections. The first experimental apparatus to measure state-to-state cross-sections are currently under development (Harries *et al.* 1998; Kaminski *et al.* 1998), with the first experimental results being expected shortly.

6. Electron-impact dissociation

An important but neglected electron–molecule scattering process is that of electron-impact dissociation. The production of chemically reactive atomic, molecular or
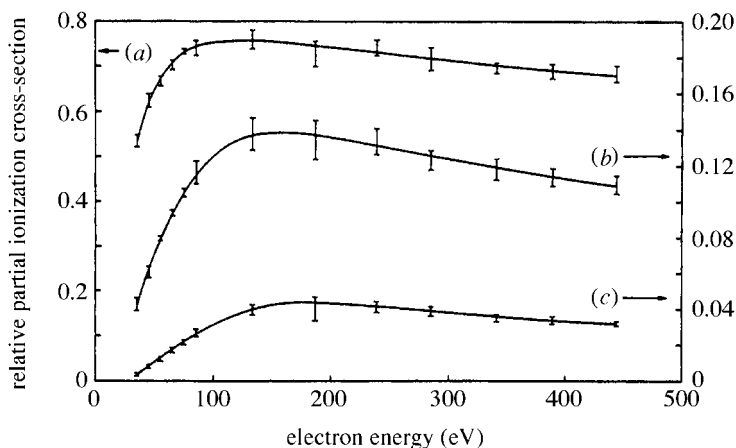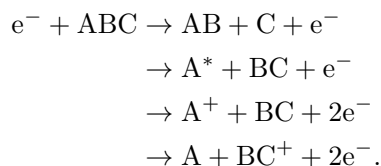
Figure 15. Partial ionization cross-sections for forming: (*a*) NO^+, (*b*) O^+ and (*c*) N^+ by electron impact on N_2O_5 (O'Connor *et al.* 1997).

cationic fragments in such dissociation processes plays a crucial role in the local chemistry of the media:

$$e^- + ABC \rightarrow AB + C + e^-$$
$$\rightarrow A^* + BC + e^-$$
$$\rightarrow A^+ + BC + 2e^-$$
$$\rightarrow A + BC^+ + 2e^-.$$

The adoption of mass-spectrometric techniques allows the production rates and branching ratios of cationic fragments to be quantified, while time-of-flight spectroscopy allows the kinetic energies of such fragments to be measured. Such techniques have been widely adopted for both stable and unstable (reactive) targets. Figure 15 shows the partial cross-sections of N_2O_5 (O'Connor *et al.* 1997), an unstable atmospheric compound important in the ozone depletion problem.

Less information is available when one or more of the dissociative fragments are neutral species. If the fragment fluoresces, the quantum yield of the emitted radiation may be measured and relative cross-sections estimated. Similarly, if the fragment is produced in a metastable or high Rydberg state, solid surface detectors may be used to detect the product and, when coupled with time-of-flight spectroscopy, the translational energy may be ascertained. From such data it is often possible to gain information on the nature of the dissociative state from which the fragments arose (i.e. from repulsive or bound potential-energy curves). Figure 16 shows two possible channels resulting in $O(^5S)$ from molecular oxygen. The channel producing fragments with low (zero) kinetic energies arises from a bound potential curve of the parent molecule, while those with finite kinetic energy arise from a purely repulsive curve. Such experiments can therefore provide valuable detail on the nature of highly excited molecular (ionic) states. However, far more information can be obtained if the scattered electron is detected in coincidence with the fragment. Scattered electrons have been detected in coincidence with the product ion (see, for example, Price & Eland 1990) providing accurate potential-energy surfaces of the parent molecule. Currently
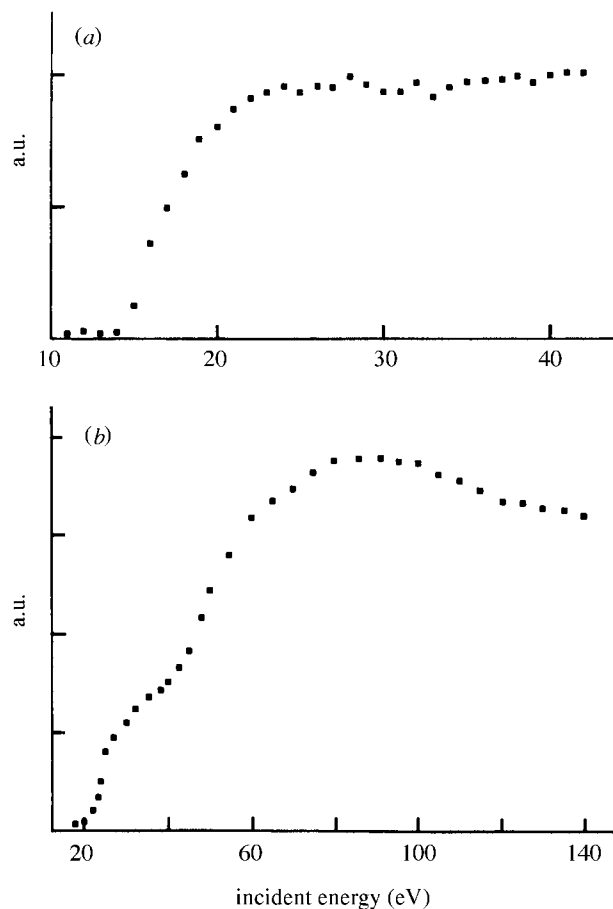
Figure 16. Production of O(^{5}S) by electron-impact dissociation of molecular oxygen: (*a*) those atoms arising from a bound state; (*b*) those atoms arising from repulsive states (Mason & Newell 1990).

this technique is being developed to measure the scattered electron in coincidence with product metastable species (Jones *et al*. 1998).

Photochemists have been studying photodissociation processes for over 20 years, using one laser to dissociate the molecule while a second laser probes the products (using LIF or REMPI). Collision physicists are now adopting these techniques to probe the final state of the electron-impact collision (Kaminski *et al*. 1998) with the advantage that, unlike laser beams, an electron beam is continuously tuneable with all states (allowed and forbidden) accessible. Electron-dissociation experiments performed in conjunction with laser detection should therefore provide a detailed analysis of the dissociation pathways of molecular systems pertinent to many applied areas of science and technology.

7. Collisions with trapped atoms

The development of magneto-optical traps (MOT) and the ability to trap cold atoms and ions has proved to be one of the major advances of atomic physics in the second
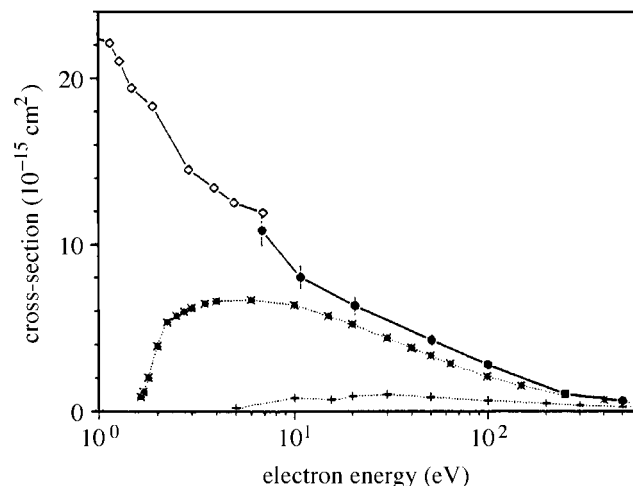
Figure 17. Total electron-scattering cross-section from rubidium derived from scattering of electrons from trapped Rb vapour: •, data points from trap experiment; ✻, optical cross-section for 5S–5P transition; ◇, data from beam experiment; +, ionization cross-section (Schappe *et al.* 1995).

half of the 20th century, with the ultimate achievement of Bose–Einstein condensation being a defining moment for quantum mechanics (see Butcher *et al.*, this issue). The ability to prepare a target of quasi-stationary well-contained atoms has been recognized by collision physicists as providing a method for measuring benchmark total cross-sections with accuracies of 1–2%.

In measuring an absolute scattering cross-section one can either monitor the scattering of the incident particle or the target. Monitoring the scattering of the incident beam requires making an absolute measurement of the target density, which is a non-trivial problem. Monitoring the scattering of the target has the advantage that absolute measurements of the target density are not required to obtain an absolute cross-section, but one must still make an absolute measurement of the incident particle flux. When any atomic or molecular target is involved in a collision, momentum is transferred from the projectile to the target. Measurement of the atomic recoil has been used for over 30 years to measure absolute total scattering cross-sections (Bederson & Kieffer 1971), but in crossed-beam experiments it is very difficult to distinguish small-angle forward scattering from the incident atomic beam. If atoms trapped in an MOT are in collision with a particle beam, the momentum transferred might be sufficient to cause the scattering atoms to escape from the trap. Hence, monitoring the atom flux in the MOT before and after the electron collision provides a simple method for determining the total number of atoms that have undergone impact. If the incident electron density is known, then total scattering cross-sections can be readily calculated with an accuracy of 1–2% (e.g. for Rb vapour (Schappe *et al.* 1995) (figure 17)).

If the MOT trapping fields are pulsed on and off, it is possible to determine the rate of atom loss from the trap and hence estimate the momentum transfer cross-section and perhaps even the differential cross-sections. If the trapping fields are such as to contain all the scattered atoms after the collision, only those atoms that have

been ionized will escape from the trap and hence total ionization cross-sections may be measured.

The use of an MOT for scattering experiments should therefore prove to be a powerful tool for reliable measurements of scattering cross-sections. Since it is possible, in theory, to trap any atoms or ions in an MOT, scattering from those targets that are less amenable to the formation of atomic beams is then possible. Indeed, electron scattering from trapped ions has been successfully performed by several groups, in instruments called electron-beam ion traps (EBITs) (Donnets 1998). Another advantage of MOTs is the ability to produce substantial quantities of excited-state atoms, and hence it should now be possible to measure accurate electron-scattering cross-sections from excited states of many atomic systems including those metastable states so important in laser-gas design (e.g. He ($2\,^3$S) in He–Ne lasers and Ar (^{3}P$_{0,2}$) in excimer lasers).

The recent success of Weinstein *et al.* (1998) in trapping calcium monohydride molecules (CaH) suggests that similar scattering experiments with molecular systems may soon become possible.

8. Electron scattering from surfaces

Electron scattering from atoms and molecules is obviously dependent upon their local environment. In the gas phase every target may be considered to be independent of the others, but within a liquid or upon a surface the concentration of the target atoms/molecules may be such that each target interacts with its nearest neighbours such that collective phenomena may be observed. The condensed-matter community has studied surface absorbates for many years, but only recently have discrete electron collisions been studied in detail (Sanche 1990, 1995). Electron scattering from well-controlled layers of rare gases on a metallic substrate shows a gradual transition away from effective gaseous conditions to those in which the electron–surface interaction is dominant with the role of 'image potentials' being dominant in the electron-scattering dynamics (figure 18). The role of the surface substrate is most dramatically demonstrated by the observation of resonance phenomena (Palmer & Rous 1992). When the electron interacts with atoms/molecules on the surfaces of a thick film, the position and lifetime of the resonance is essentially that determined in the free gas. However, as the surface coating is thinned the influence of the image potential is such that the position of the resonance shifts to lower energy and the lifetime is reduced until in some films the resonance cannot form at all. Thus it is unwise to use gas-phase data for modelling electron scattering from surface layers; such surface data are needed in the plasma-etching industry.

Currently two major experimental groups (those of Sanche in Sherbrook, Canada, and Palmer in Birmingham, UK) are transferring gas-phase electron-spectroscopy techniques to study electron scattering from absorbed molecules. Such experiments are providing test data for the development of gas-phase scattering codes to scattering from condensed-matter targets (see Burke *et al.*, this issue).

Electron scattering from liquid surfaces remains in its infancy, not withstanding its importance in biological systems. This is partly due to the difficulty in preparing well-controlled liquid surfaces. However, recently the first electron scattering from the surfaces of non-volatile liquids has been reported (Eschen *et al.* 1996). Initial results suggest that the energy-loss spectrum for electron scattering from such a surface is
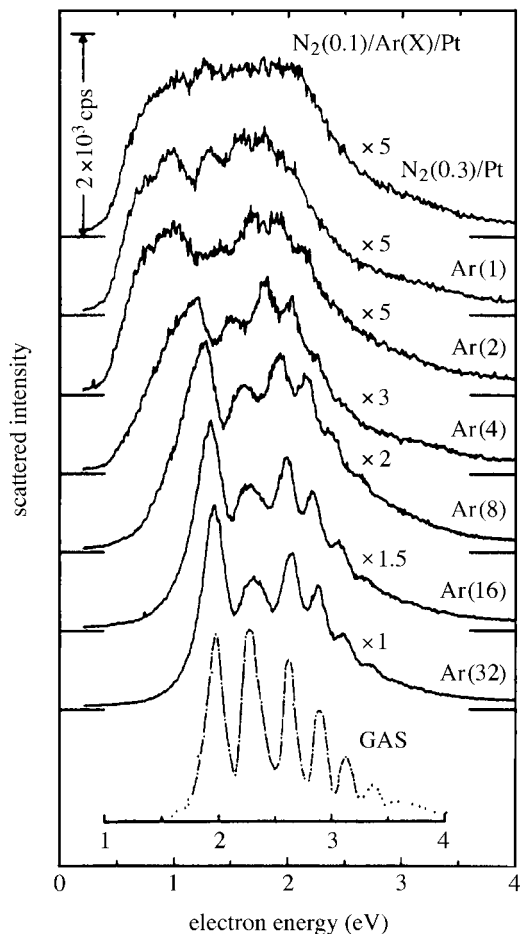
Figure 18. The nitrogen resonance observed for differing molecular layers of N_2 upon Pt surfaces (Sanche 1995).

remarkably similar to that observed in the gaseous phase (Gingell & Mason 1998) (figure 19). However, the role of resonance excitation has yet to be ascertained, as have the effects of surfactants when placed upon the liquid surface.

Interfacial chemistry and physics are of key importance to the life sciences and the catalysis industry, and therefore a greater understanding of electron transfer at such surfaces will be required in the future. These pioneering experiments are therefore likely to provide a new avenue for electron-collision studies in the next millennium.

9. Conclusions

Electron–atom/molecule scattering has been the subject of intense research activity, both experimentally and theoretically, for nearly a century, yet, particularly for electron–molecule scattering, our understanding of the dynamics of such processes remains limited. Due to their importance in a myriad of industrial, astrophysical, atmospheric and biological processes, absolute electron-scattering cross-sections are
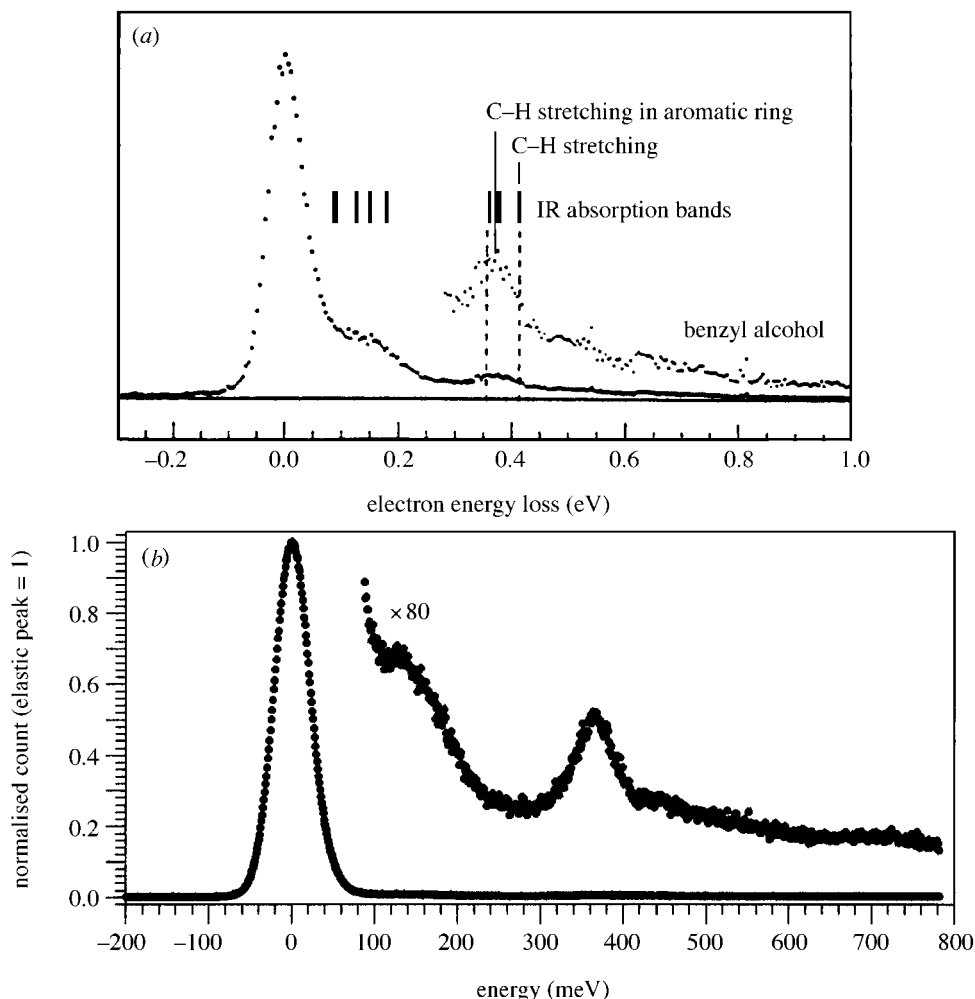
Figure 19. (*a*) EEL spectrum from a surface of liquid benzyl alcohol (Eschen *et al.* 1996) compared with (*b*) the gas-phase EEL spectra (Gingell & Mason 1998).

required for most atomic and molecular systems, yet the current database is limited to a few easily prepared systems. Only recently have experimental studies been extended to unstable reactive and free-radical species, while new experimental techniques incorporating advances in atom trapping and laser spectroscopy are being adapted to provide new insight into electron-collision dynamics. The combination of traditional gas-phase electron spectroscopy with condensed-matter techniques is allowing collective effects to be probed, while electron-scattering studies from clusters provide a useful intermediate between free atom/molecules in the gas phase and collective effects in the condensed phases. Experimental electron scattering is therefore undergoing something of a renaissance, and as we enter the next millennium (and the centenary of the first electron-scattering experiments approaches) we may at last be able to understand most of the basic physical electronic-scattering interactions.

It is with the greatest pleasure that we dedicate this article to Professor P. G. Burke on the

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