# EXPERIMENTAL STUDIES OF TRANSIENT MOLECULES BY ELECTRON IMPACT

## N.J.Mason, N.C.Jones, L.Kaminski, P.Tegeder, P.Kendall

Department of Physics and Astronomy, University College London,
Gower Street, London WCIE 6BT, United Kingdom

Transient molecules play a key role in the chemistry of many diverse processes including aeronomy. industrial plasmas and biological systems. However since transient species are hard to prepare and preserve in the experimental laboratory there have been relatively few experiments on the interaction of electrons with such compounds. In this brief report we will review recent progress in the production of such compounds and describe some recent experiments to study their spectroscopy and interaction with electrons.

## 1. Introduction

A transient molecule may be described as a molecule that exists for only a short time. Thus a molecule may be described as transient if it is; (i) in an excited state with a short lifetime, (ii) highly reactive and therefore rapidly removed from the system by chemical reactions or (iii) inherently 'unstable' and dissociates into two or more stable products. Examples of the first type include all electronic states of molecules excited in photon or electron collisions. Examples of reactive species include aeronomic species such as ozone, astrophysical molecules such as $C_2O_3$ and $CH_2$ and those compounds described by chemists as 'radicals' e.g. CH, CF, SO and NO. 'Unstable' molecules include the stratospherically important dinitrogen pentoxide $N_2O_5$ and the halogen nitrates ($XONO_2$ where $X$ = Cl or Br) which are thermally unstable at room temperature. In all cases the presence of transient molecules may effect the local physics and chemistry such that the role of transient species is important in many natural and industrial processes. For example stratospheric ozone depletion is dominated by the solar ultraviolet photodissociation of $N_2O_5$ to yield NO and $NO_3$ [1]. The etching rate of silicon wafers in the industrial fabrication of integrated circuits is determined by the appearance of $CF_x$ radicals (where x = I to 3) produced within a cold plasma by electron bombardment [2]. In astrophysics CH, produced by photo-dissociation of simple hydrocarbons, is an active molecule in the synthesis of organic compounds in the InterStellar Medium (ISM). Transient species also play a key role in radiation chemistry with free radicals causing much of the damage within biological tissue after exposure to x-ray or y-ray irradiation [3].

However the very nature of such molecules has limited their study in the experimental laboratory since, even if they can be prepared with sufficient number densities, they may decay prior to the completion of any experiment to measure their spectroscopic properties or their interaction with photons and electrons. However recently new preparation techniques and faster data analysis procedures have allowed experimentahsts to begin to study such species. In this brief review a guide to recent advances in this freld and the prospects for future research will be given together with some selected examples.

## 2. Preparation of transient species

Transient molecules may be prepared either in situ or remote from the experiment. In the latter case preparation techniques are in general chemical in nature the product molecules being stored in a reservoir prior to transport to the experimental apparatus. Typical transient molecules prepared in this way are the stratospheric compounds such as

ozone, the halogen nitrates and dinitrogen pentoxide, all reactive compounds but molecules that may be stored for a period of days. Typical compounds that must be prepared in situ include all excited states of molecules and radical species such as $CF_x$, $CH_x$, SO and CS.

### 2.1: Chemical production of stratospheric compounds

Figure 1 shows a typical facility for the production and storage of high purity samples of ozone. Ozone itself is a stable molecule once formed but is highly reactive and therefore decays upon contact with most surfaces also, due to its low lying excited states (all of which are dissociative in nature) it is also unstable at high temperatures. High purity concentrations of ozone (>90%) may be readily prepared using a atmospheric gas discharge of molecular oxygen. In such discharges molecular oxygen is reduced to atomic oxygen which subsequently forms ozone via the three body reaction;

$$O + O_2 + M \rightarrow O_3 + M$$

where M is a third body ($O_2$) required to stabilise the product ozone. Typically only 1–2% of the effluent gas from the discharge is ozone, not enough to conduct electron coUision experiments. However ozone may be collected on a cooled sihca gel surface ($T < 250$ K) while molecular oxygen does not 'stick' to the same surface. Running the gas discharge for an hour produces typically a gram of ozone on the sihca gel. After turning off the discharge and pumping off the excess oxygen warming the sihca gel to room temperature allows the ozone to be desorbed from the sihca gel and stored in a glass bulb (at pressures of typically 200 mTorr). Ozone samples stored in the dark (to prevent decay by solar radiation) may be maintained for a period of several days or even weeks with a typical sample decay rate of 1% per day. Using this apparatus the authors have been able to perform a series of experiments to study the spectroscopy and coUision dynamics of ozone [4].
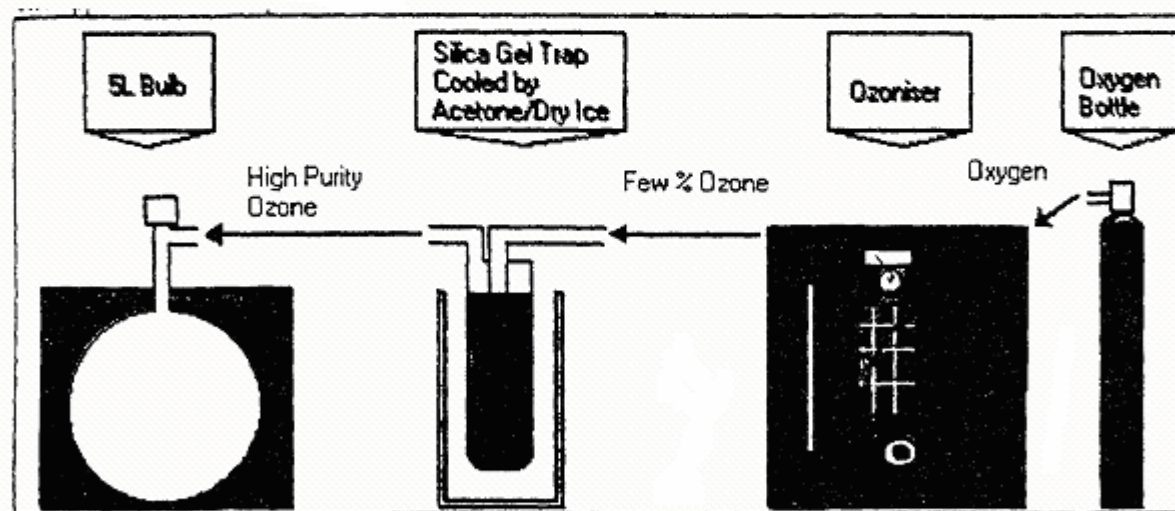


Fig. 1. Typical apparatus used for producing high purity sample of ozone for gaseous experiments.

Samples of the chlorine oxides (the so called reservoir species in which atmospheric chlorine liberated by photo-dissociation of the CFCs is stored in the atmosphere) may also be easily prepared by simple chemical reactions.

Flowing a pure stream of molecular chlorine over sodium chlorite ($NaOCl_2$) allows pure samples of OClO to be produced while the flow of chlorine over mercuric oxide (HgO) allows $Cl_2O$ samples to be prepared.
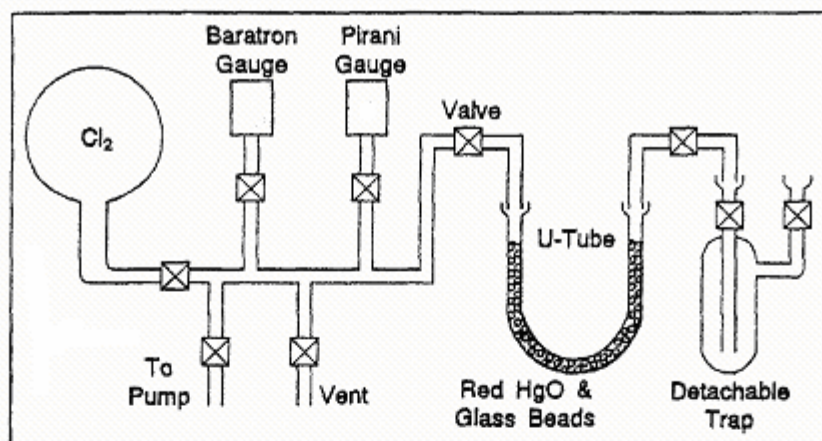
Fig. 2. Typical apparatus used for producing samples of OCIO and $Cl_2O$ for electron impact and spectroscopic experiments.

Having made these precursor molecules it is then possible to produce samples of other important stratospheric compounds, for example the reaction of ozone with $NO_2$ yields the higher nitrogen oxide $N_2O_5$ [1]. Reaction of OCIO with $N_2O_5$ produces another important stratospheric reservoir compound chlorine nitrate ($ClONO_2$) [5]. Samples of OClO, $Cl_2O$ and $ClONO_2$ may be stored in liquid nitrogen cold traps prior to transport to experimental systems.

## 2.2: Production of transient species by molecular fragmentation

Many transient molecules can only be produced in situ during the experiment. Compounds may be produced by microwave and RF discharges or (more recently) by laser photolysis. Microwave/RF discharges have been used to prepare sources of transient species for more than thirty years and were commonly used to measure the photoelectron spectra of such species. Number densities in excess of $10^{12}$ molecules/cm$^3$ are achievable however such sources are not state specific and it is possible to produce many different transients in one discharge also, since such discharges must be operated at relatively high pressures, it is often necessary to introduce one or more stages of differential pumping between the production region and the experimental chamber (Fig. 3). Nevertheless despite these complications microwave sources remain the standard method for producing most transient and radical sources and commercial microwave sources may be purchased that produce good yields of the atomic species of H, O, N and Cl. Microwave sources also provide a source of CS (from $CS_2$) and SO radical (from $SO_2$).
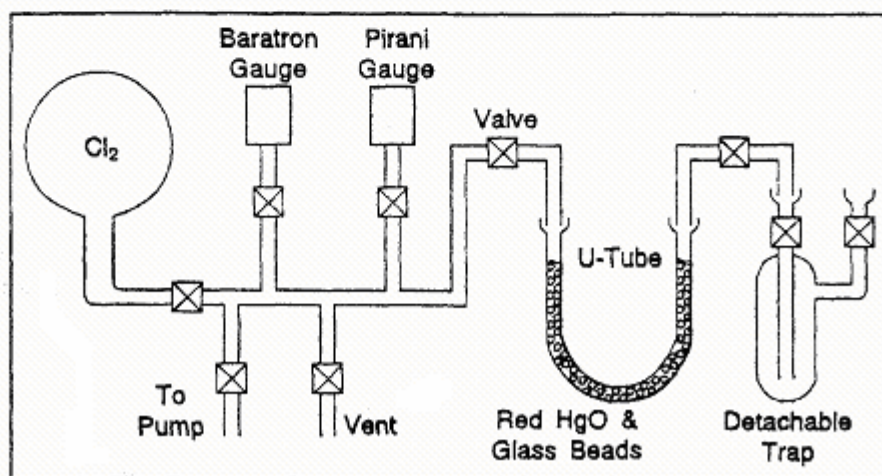
Fig. 3. Construction of a microwave source used to prepare transient molecules for electron scattering experiments. Microwave cavity (m); aperture (B); Ion removal plates ($S_1$) Teflon tube (T) Copper tube (C); O-rings ($O_x$) and PTFE bush (P).

The industrially important etching radicals $CF_x$ ($x$ = 1 to 3) may be produced by RF/microwave discharge of fluorocarbon compounds. Discharges of $CF_3I$ produce relatively pure yields of $CF_3$ radicals while discharges of $C_2F_4$ produce high yields of $CF_2$. Currently there is considerable interest in such discharges since these gases have been proposed for use in the next generation of industrial plasma reactors, since both have a lower global warming potential than the currently used $CF_4$ and $C_2F_6$ .

The second method for producing transient species is laser photolysis. Laser photolysis while more expensive than microwave/RF discharges is capable of providing state selectivity in the production of transient species for example tuneable dye lasers may be used to produce SiF from $SiF_4$ [6]. Laser pumping of molecules also allows excited molecular states to be prepared, the recent method known as STIRAP [7] being particularly effective in preparing molecules in specific vibrational states. However in general laser photolysis produces lower number densities of transient species such that it is not possible to use such sources for crossed electron/target beam experiments.

A third method for the production of beams of transient species has been developed by Becker and co-workers [8] and Helm and Crosby [9]. A commercial Coultron ion source is used to produce positive ions of the required transient species by dissociative ionization of a parent molecule. The positive ions are then passed through a gas cell where charge transfer yields neutral molecules. This methodology has been used to produce targets of CF, $CF_2$, NF, $NF_2$ and SiF for electron impact ionization experiments (see below).

### 3. Electron scattering from transient molecules

#### 3.1. Photoelectron experiments

The earliest experiments on transient species involved study of their spectroscopy. Photoelectron spectra recorded using HeI hght sources have recently been supplemented by new experiments performed on synchrotron light sources [10], coupled with VUV absorption measurements such experiments are providing important details on the electronic (Rydberg) states of many transient species playing a key role in global ozone Fig. 4 shows the PES spectra for $Cl_2O$.
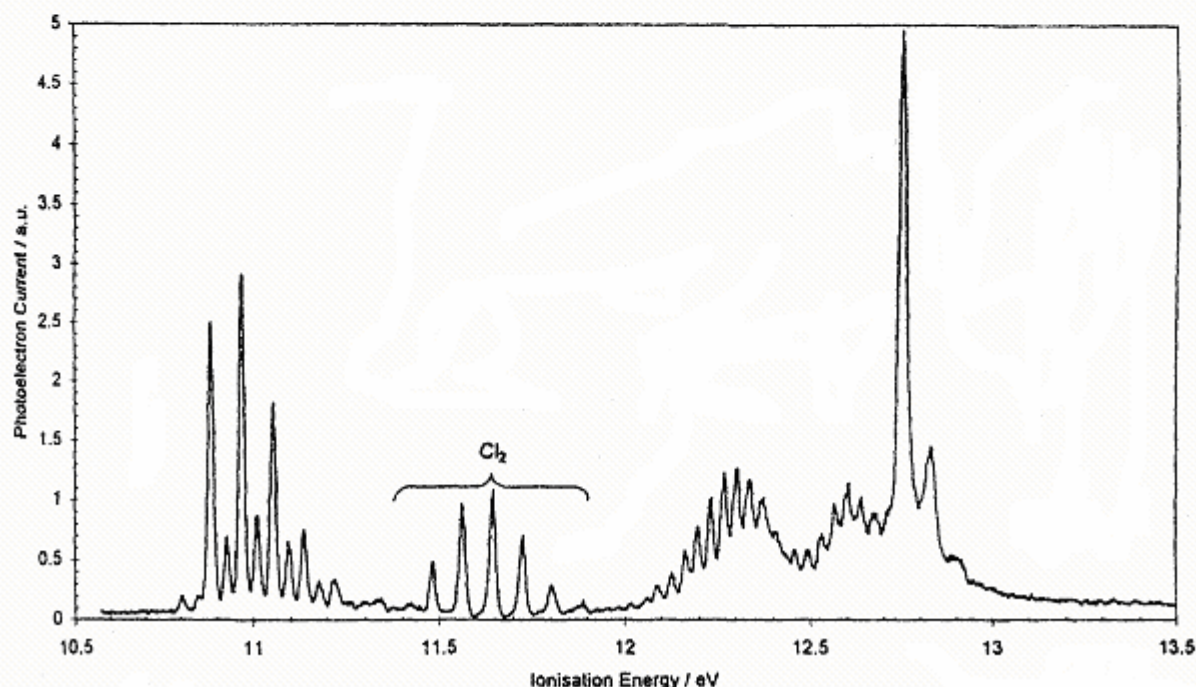


Fig. 4. Photoelectron spectra recorded for the stratospheric compound $Cl_2O$

The first direct electron scattering experiments performed on transient molecules measured their ionization cross sections, the product ions being detected using conventional mass spectrometry. Detailed electron impact fragmentation patterns have been measured for several stratospheric compounds $O_3$, $OClO$, $Cl_2O$, $N_2O_5$ and $HNO_3$ [11, 12]. Absolute electron impact ionization cross sections for ionization of $CF_x$, $CH_x$, $SiF_x$, and $NF_x$ have also been reported [13, 14].

In contrast to spectroscopic studies low energy electron scattering from transient molecules have only just begun [1,4,5,15]. Such studies are interesting because they will provide detailed information on the interaction between electrons and the molecular charge clouds. At very low energies (<100 meV) the incident electron interacts strongly with the molecular field. Many transient species have permanent dipole moments or unpaired electrons such that there is an additional long range Coulombic interaction between the incoming electron and the target molecule. This may lead to an enhancement in the scattering cross section at low incident energies or, contrary to initial expectation, may lead to a fall in cross section over a narrow energy range such that it appears that the molecule is 'transparent' to the incident electron.
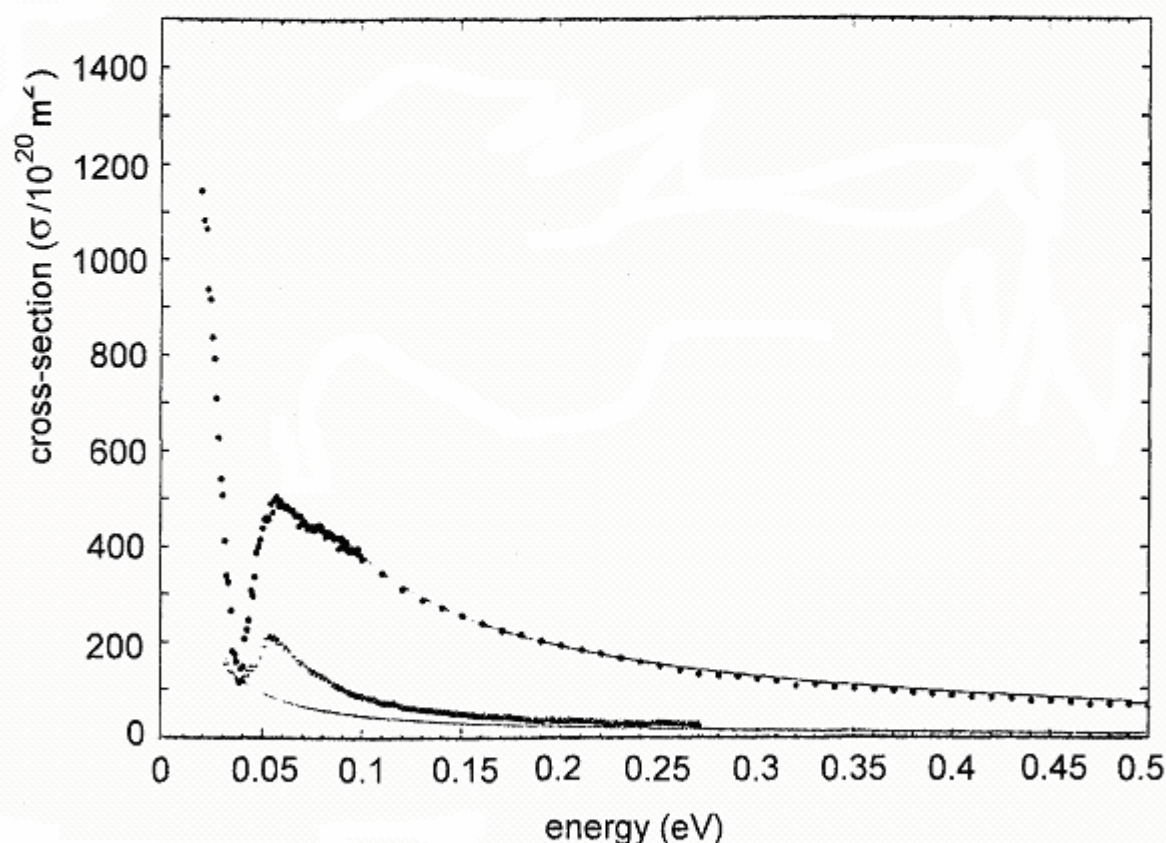


Fig. 5: Integral scattering cross-section for low energy electrons from OClO. Upper graph total scattering cross sections, lower graph backward scattering. Solid lines cross sections estimated with a Born approximation.

Figure 5 shows the total scattering cross section for low energy electrons from OClO, a sharp minimum is observed in the cross section around 70meV, such phenomena are also observed in $Cl_2O$ but not in $O_3$. The reason for such 'scattering windows' remains unclear but may arise from an interference between possible scattering processes. At

scattering energies below the onset of vibrational (and electronic) excitation pure elastic scattering and rotational excitation processes dominate the scattering cross section, interference between these two channels may explain the observed minima.

However another possible inelastic process accessible at low energies is dissociative electron attachment (DEA), i.e.

$$e^- + ABC \rightarrow AB^- + C \ ,$$
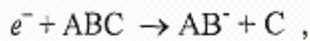
producing anionic fragments AB' or C' of the parent molecule ABC. DEA is particularly prevalent in those compounds containing halogen species. Studies of DEA from several transient compounds are now being performed in several laboratories with the resultant anions being detected by mass spectrometry. Measurement of the kinetic energy of the product anions provides information on the structure and dissociation dynamics of the parent anion ABC'. At higher incident energies such anions may decay by electron detachment leaving the molecule in a vibrationally excited state. Indeed the cross section for electron induced vibrational excitation of molecules is usually dominated by such processes described as 'resonance's' (since they cause an enhancement in the measured cross sections).
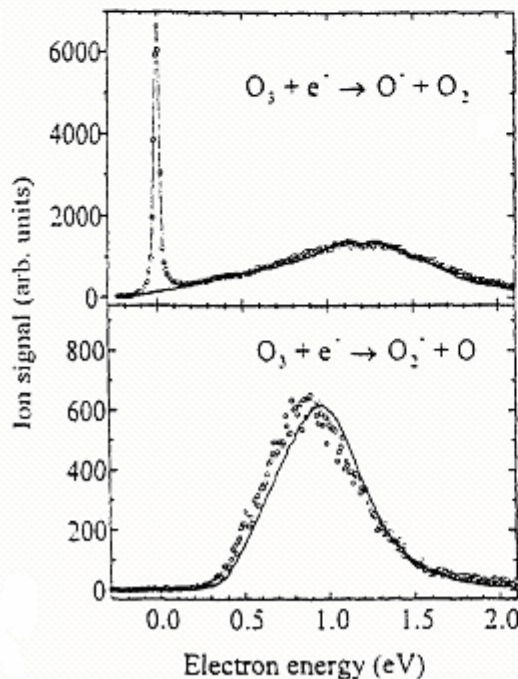


Fig. 6. Dissociative electron attachment cross section in ozone.

DEA attachment and resonant formation may therefore play a key role in the local chemistry. For example recent experiments have shown that the ozone molecule is efficiently destroyed by low energy electron bombardment since the DEA cross-section for O' formation is large (see Figure 6). This has important consequences not only for the formation of ozone in gaseous discharges (the low energy electrons in the discharge destroying the ozone as it is produced) but may provide a link between global ozone loss and ionospheric turbulence driven by the solar wind [16].

## 4. The Future

Due to their importance in many diverse areas of physics, chemistry, biology and technology an understanding of the interaction of electrons with complex molecular targets is urgently required. However experimental studies of electron scattering from transient molecular species is only just beginning. The first results suggest that the less symmetrical molecular structure of such targets leads to more complex scattering phenomena with low energy 'scattering windows', larger DEA cross sections and strong angular scattering correlations. The challenge for both the experimentalist and theorist in the next decade will be to both understand and be able to model the interaction of electrons with such targets such that we may be able to determine how they influence local chemistry in industrial plasmas, aeronomy, astrochemistry and even within biological media.

## References

1. B.A.Osboume, G.Marston, L.Kaminski, N.C.Jones, J.M.Gingell, N.J.Mason, I.C.Walker, J.Delwiche, M.J.Hubin-Franskin, *J. Quant. Spec. and Radiat. Transfer* (2000) 64 67
2. *Plasma Deposition of Amorphous Silicon Based Materials* (Ed. by G.Bruno, P.Capezzuto and A.Madan), Academic press, San Diego (1995)

3. *Physical and Chemical Mechanisms in Molecular Radiation Biology* (Ed. by W.A.Glass and M N Varma), Plenum Press, New York (1991)

4. N.J.Mason, *Comments in Atomic and Molecular Physics* (2000) (in press)

5. N.J.Mason, N.C.Jones, L.Kaminski, B.A.Osborne, G.Marston, M.A.Fernandez, I.C.Walker, E.A.Seddon, D.Newham, J.Ballard, *Int. J. Mass. Spec. and Ion.* (2000) (in press)

6. J.M.Jasinski, R.Beccerra, R.Walsh, *Chem. Rev.* **95**, 1203

7. M.Keil, J.T.Kolling, K.Bergmann and W.Meyer, *Europhys. D*, **7**, 55 (1999)

8. V.Tarnovsky, P.Kurunczi, D.Rogozhnikov and K.Becker, *Int. J. Mass Spectrom.* **128**, 181 (1993)

9. V.Tarnovsky, H.Deutsch and K.Becker, *J. Phys. B* **32**, L573 (1999)

10. J.D.Barr, L.Beeching, A.De Fanis, J.M.Dyke, S.D.Gamblin, N.Hooper, A.Morris, S.Stranges, J.B.West, A.E.Wright, T.G.Wright, *J. Elect. Spec. and Rel. Phenom.* **108** 47 (2000)

11. K.A.Newson, S.M.Luc, S.D.Price and N.J.Mason, *Int. J. Mass. Spec.* **148**, 203 (1995).

12. C.S.S.O'Connor, N.C.Jones and S.D.Price, *Chem. Phys.* **214**, 131 (1997)

13. H.Sugai, H.Toyoda, T.Hakano and M.Gioto, *Contrib. Plasma Physics* **35**, 415 (1995)

14. V.Tarnovsky and K.Becker. *J. Chem Phys.* **98**, 7868 (1993)

15. J.A.Davis, N.J.Mason, G.Marston and R.P.Wayne, *J. Phys. B.* **28** 4179 (1995)

16. G.Senn, J.D.Skalny, A.Stamatovic, N.J.Mason, A.Scheier, T.D.Maerk, *Phys. Rev. Lett.* **82**, 5028 (1999)

# ЕКСПЕРИМЕНТАЛЬНІ ДОСЛІДЖЕННЯ ПЕРЕХІДНИХ МОЛЕКУЛ ЕЛЕКТРОННИМ УДАРОМ

Н.Дж.Мейсон, Н.К.Джонс, Л.Камінський, П.Теджедер, П.Кендалл

Факультет фізики й астрономії, Лондонський університетський коледж, Лондон, Великобританія

Перехідні молекули відіграють ключову роль у хімії різноманітних процесів, зокрема, в аерономії, промисловому отриманні плазми та біологічних системах. Однак, оскільки перехідні сполуки важко отримати і зберігати в експериментальних лабораторних умовах, відомо досить мало експериментів з взаємодії електронів з такими сполуками. Тут подано короткий огляд останніх досягнень в одержанні таких сполук і описано деякі останні експерименти з їх спектроскопії та вивчення їх взаємодії з електронами.