

Studies of Autoionising States by Photon and Electron Impact*

John Comer

Physics Department, University of Manchester,
Manchester, M13 9PL, U.K.

Abstract

A variety of techniques can be used to probe the excitation and decay of autoionising states. Photoelectrons produced by monochromatic synchrotron radiation can be recorded as a function of both photon energy and electron emission energy to identify autoionising state energies and final states. Electron impact measurements are a complementary technique particularly for states excited by optically forbidden transitions.

1. Introduction

Resonance processes in photoionisation and electron scattering are important because they often dominate the cross section, particularly within the first few electron volts of the threshold for ionisation or excitation. In particular, the presence of such resonances can significantly modify the distribution of final states. In the case where neutral autoionising states are investigated using photons there is the possibility of employing photoabsorption (e.g. Madden and Codling 1965) or photoionisation (Berkowitz and Eland 1977). Photoelectron spectra give more detail because of the information they provide on decay routes. In particular it is possible to measure constant ionic state photoelectron spectra by scanning both the photon energy and detected electron energy in synchronism. This gives the photon energy dependence of the yield of electrons resulting in ionisation into a specific ion state. These spectra will contain contributions from both direct ionisation and the indirect process involving autoionisation. If such studies are carried out for a variety of vibrational and electronic final states, then this technique can be used to distinguish specific intermediate states.

An extension of this work involves measuring a photoelectron spectrum at a photon energy which is coincident with a resonance. Such measurements can give access to a range of final states which are not populated by direct ionisation. For example, this can lead to the excitation of vibrational levels outside the Franck–Condon region of the initial state (Reddish *et al.* 1988a).

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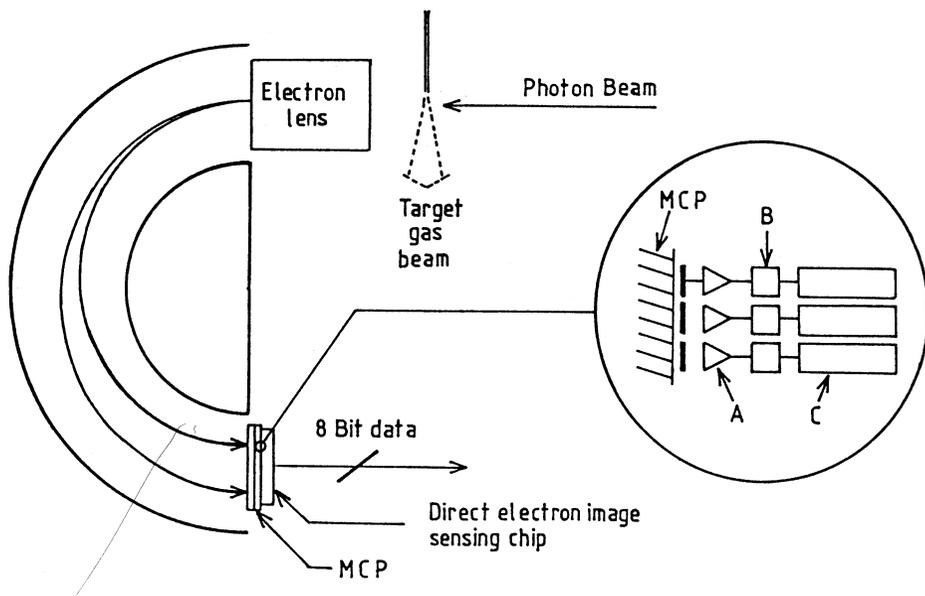


Fig. 1. Schematic diagram of a photoelectron spectrometer incorporating an integrated position-sensitive detector, where A is an amplifier, B a comparator and C an 8 bit counter.

2. Instrumental

Electrons emitted during autoionisation can be studied using a system typically with an electrostatic analyser. An example of such an instrument is shown in Fig. 1 (Haworth *et al.* 1985). Target gas from a hypodermic needle is crossed with a VUV photon beam from the Daresbury Synchrotron Radiation Source. Alternative discharge lamp line sources in the VUV have been commonly used but lack the tunability needed for studies of autoionising states where it is desirable to scan the wavelength over an extended range. In order to produce a monochromatic beam from the broad band synchrotron radiation, a vacuum UV monochromator must be used. In the work described below two different systems have been employed. A McPherson 5 m normal incidence monochromator provides energy selection in the range of about 10 to 30 eV with resolution down to 0.1 Å. At higher energies, up to 100 eV, a toroidal grating monochromator is used with resolution down to 0.02 eV. It is often not possible to operate these systems at the technical limit of resolution because of limitations in signal strength. An alternative approach for investigating autoionising states uses electron rather than photon impact. In the work described here an electron monochromator is employed with hemispherical deflectors to select the electron energy. This is capable of operating at an energy resolution as low as 0.005 eV (Reddish *et al.* 1988*b*). Often experiments using photons give superior resolution at low excitation energies, while electron impact systems with fixed energy resolution are superior at high energies (Shaw *et al.* 1982).

In the experiment described here the emitted electrons are energy analysed using a hemispherical deflector analyser and the energy-dispersed electron image is incident on a position-sensitive detector. The use of multidetectors to improve the sensitivity of spectrometers is becoming common. Devices which have been

employed, for example, are the resistive anode encoder (Moak *et al.* 1973), the backgammon detector (Martin *et al.* 1981), the discrete anode detector (Timothy and Bybee 1975) and detectors which involve optical conversion followed by a charge coupled device or photodiode array (Hicks *et al.* 1980). Although such detectors can in principle give a large improvement in efficiency because of their ability to measure a range of energies simultaneously, they do have drawbacks. Examples of these are the limited count rate that they can detect whilst maintaining intensity linearity and also problems with cross-talk between channels. These limitations are largely overcome in a new integrated multidetector (Hatfield *et al.* 1989, 1992) which is illustrated in Fig. 1. It is based on the discrete anode system but all the necessary circuitry together with the detector electrodes are integrated on a single chip. The face of the integrated circuit is fitted with microchannel plates so that single electrons arriving at the exit to the electron analyser are multiplied. The resulting charge pulses are picked up on the electrodes which are connected directly to amplifier/comparators so that the initial electrons can be recorded by the corresponding on-chip eight-bit counter. The device is capable of operating at very high count rates with good intensity linearity, particularly because the counters act as a data buffer on the device itself.

3. Results

In molecules the decay of autoionising states into different vibrational levels of the final ion state can be highly selective and this can provide important information about the intermediate states. This selectivity is illustrated in Fig. 2 (Cafolla *et al.* 1990), which shows the incident photon energy dependence of the yield of photoelectrons resulting from ionisation into a range of vibrational levels of the $b^4 \Sigma_g^-$ state of O_2^+ . There is very intense structure corresponding to Rydberg states converging on the $B^2 \Sigma_g^-$ state of O_2^+ with a $np\sigma_u$ electron. This region of the spectrum is almost completely dominated by four vibrational levels of the Rydberg series. These spectra show clearly how different vibrational levels of the Rydberg series populate vibrational levels of the positive ion state. The $n = 4$ levels have anomalously large widths, which is an indication of their non-Rydberg nature. This effect has been discussed by Morin *et al.* (1982). The higher levels correspond to a Rydberg series converging on the $c^4 \Sigma_u^-$ ion state at 24.56 eV (Madden and Codling 1965).

Fig. 2 illustrates that the intensity distribution of vibrational and electronic ion states observed in photoelectron spectra will have a very strong dependence on photon energy. A more complete investigation requires photoelectron spectra to be taken as a function of both photon energy and electron kinetic energy. This technique was employed by Cafolla *et al.* (1988) to investigate the photon energy dependence of ionisation into vibrational levels of the ground state of HCl^+ . A more recent investigation of higher states of this ion is shown in Fig. 3 (Wills *et al.* 1991a). This is a photoelectron surface in which the measured electron intensity increases as the grey scale becomes darker. This spectrum shows diagonal lines where the electron energy increases with photon energy and these are due to molecular photoionisation:



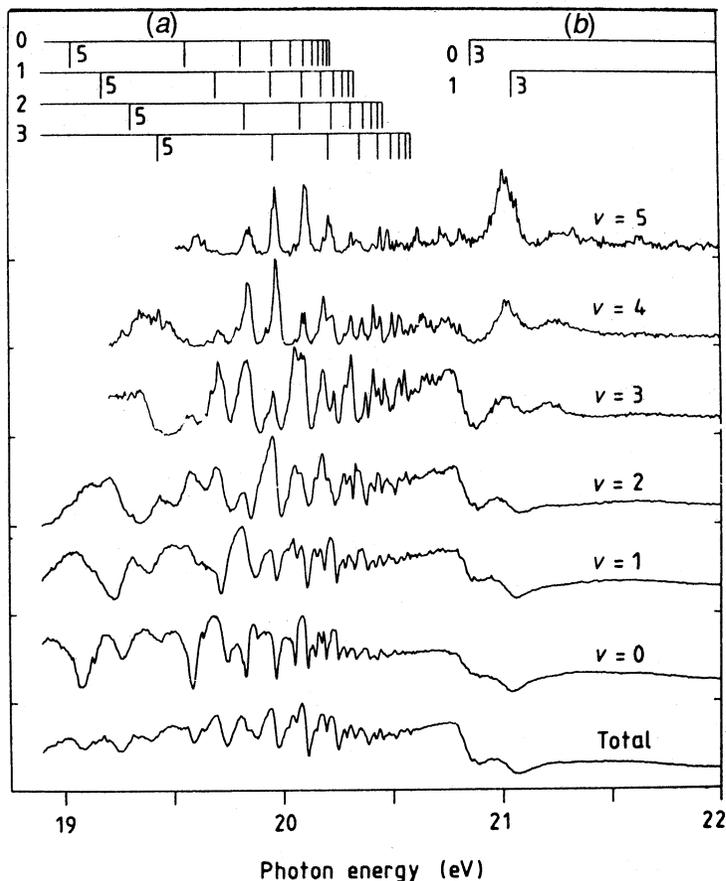


Fig. 2. Total and vibrationally resolved excitation functions of O_2^+ : (a) Rydberg states $\nu' = 0-3$ converging to $O_2^+ B^2\Sigma_g^-$ and (b) Rydberg states, $\nu' = 0, 1$ converging to $O_2^+ c^4\Sigma_u^-$.

These lines can be assigned as at least six vibrational bands, which are inner valence states of HCl. Each one of these shows changes in intensity as a function of photon energy due to the presence of autoionising states. These are measured with a resolution of 0.075 eV and represent the first vibrationally resolved measurements of inner valence states of HCl^+ . The spectrum can be used to deduce parameters for their potential curves. The assumption that there are members of Rydberg series converging on states of HCl^{++} leads to information about the potential curves of the corresponding doubly charged ion states. A significant advantage of the technique of two dimensional spectroscopy is that a range of lines are measured in the same experiment, together with backgrounds, so that normalisation is more reliable. A further advantage is that the technique often reveals other processes which may be difficult to identify in conventional one dimensional spectra. An example of this is illustrated in Fig. 4 which shows a photoelectron surface of HCl. The photon energy is lower than that of Fig. 3

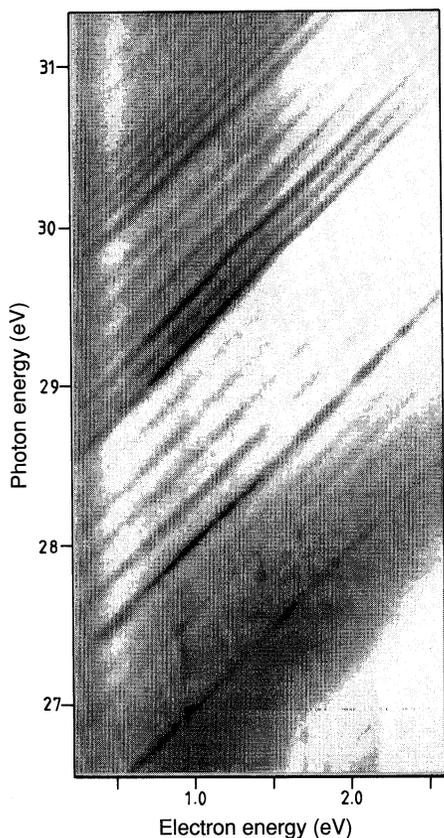
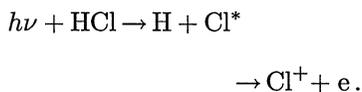


Fig. 3. Photoelectron surface for HCl showing diagonal lines due to molecular photoionisation.

and in this case shows lines of constant electron kinetic energy. These are due to neutral photodissociation producing, in this case, a neutral ground state hydrogen atom and a neutral chlorine atom in an autoionising state. The fragment then decays giving electrons with an energy which is independent of photon energy:



The technique of two dimensional spectroscopy distinguishes clearly between the two processes discussed above. It is also possible to measure the onset of fragment autoionisation which can assist in the identification of the lines (Wills *et al.* 1991*a*, 1991*b*).

An alternative technique for studying autoionising states is electron impact and it is possible to examine excitation by electron energy loss spectroscopy or to study decay by measuring the kinetic energy spectrum of emitted electrons. The former technique has the advantage of specifying the energy of the autoionising state. The latter does give information about decay routes and has been employed particularly in the case of the atoms, but the spectrum can be extremely complicated for molecules because of the range of possible intermediate and final vibrational states. Fig. 5 shows an example of an electron energy loss spectrum

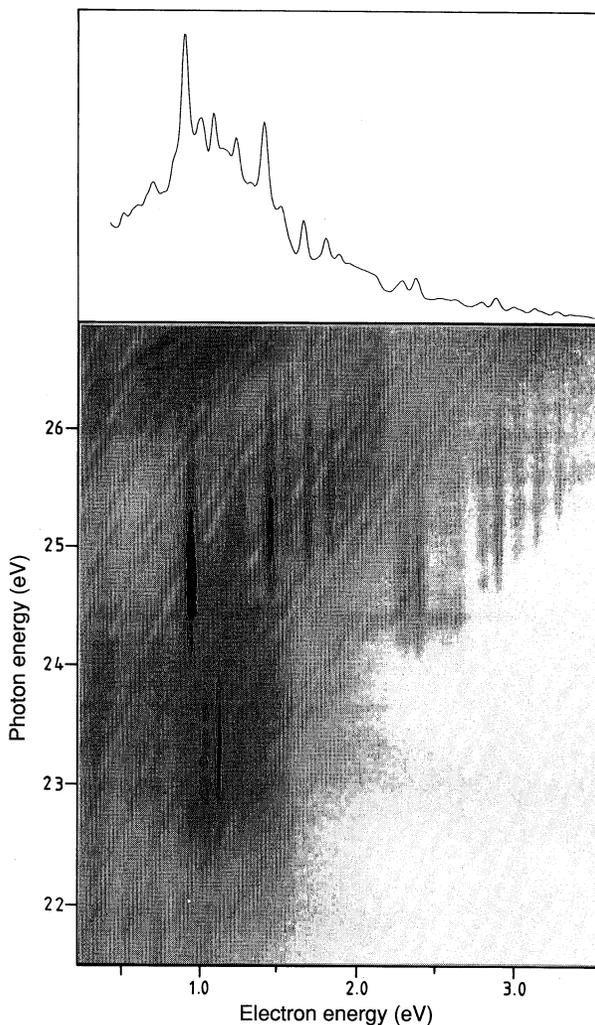


Fig. 4. Photoelectron surface for HCl showing lines due to fragment autoionisation.

for argon (Currell *et al.* 1991) in the region of the lower double ionisation potentials. This is an interesting region because of the possibility of highly correlated Rydberg states with two electrons converging on the double ionisation potential.

4. Conclusions

A number of techniques for investigating autoionising states have been discussed. Measurements on autoionisation by photoelectron spectroscopy and electron impact are complementary in that the former provides good information on decay processes while electron impact measurements have the possibility of exciting optically forbidden transitions which are strong, particularly at low energy and high scattering angle. A recent development is the investigation of the autoionisation of fragments produced in neutral photodissociation using tunable synchrotron radiation.

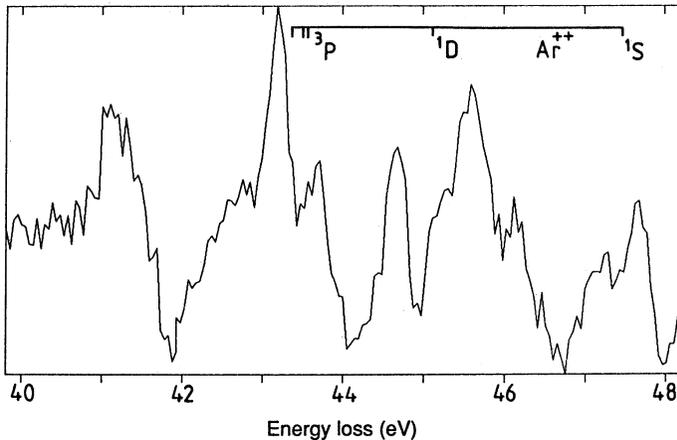


Fig. 5. Electron energy loss spectrum of argon taken at a scattering angle of 12.5° and a constant residual electron energy of 10 eV.

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