

Photoionization Studies of Reactive Intermediates

using Synchrotron Radiation:

an overview of the work performed by the Southampton PES group at the SRS at Daresbury
1993-2000

by

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Introduction

The Southampton photoelectron spectroscopy (PES) group was initially attracted to using the SRS at Daresbury because, when studying a reaction by conventional PES with an inert gas discharge photon source, the photoelectron signals from the reaction (or reactive) intermediates are usually much smaller than the signals from the reactants or reaction products. This problem could be partly addressed by using synchrotron radiation as the photon source, as the early work of W.C.Price (1,2) on NO and O₂ had demonstrated that if the photon energy could be tuned to a resonant Rydberg state above the first ionization energy then the first PE band recorded at this resonant photon energy would be more intense and may exhibit extra vibrational structure. However, very soon after we started work at Daresbury in 1993 we soon realised that the use of synchrotron radiation in PES studies of reactive intermediates had other advantages (see later).

All our work was carried out at Daresbury on beamline 3.2, using a 5m normal incidence McPherson monochromator, during the period 1993-2000. It was performed using a spectrometer designed and built by Alan Morris to study reactive intermediates, with significant advice and input from John West, with financial support from EPSRC (via a grant to A.Morris, J.B.West and J.M.Dyke). During our beamtime runs during this period, the Southampton group was ably supported by Daresbury staff scientists notably John West, David Holland and Mike MacDonald. We spent 7 productive years at Daresbury up until 2000, when we found that we could no longer obtain beamtime at the SRS (on BL3.2) because our applications were not awarded any "tickets" to use the facility. At this time, we took the decision to apply for time at another synchrotron. Elettra was selected and the team (and the spectrometer) continued research on reactive intermediates at this synchrotron facility in Trieste. The project is still on-going. At the time of writing (April 2016), the four most recent studies from this work are studies of hydrogen peroxide (3), CF₂ (4) and vibrationally excited nitrogen (5) with threshold photoelectron spectroscopy and a study of the angular distribution and photoionization cross-sections of the valence ionizations of iodine atoms (6). It was clear at an early stage that the project would require theoretical support, mainly in the form of quantum chemistry calculations. Ed Lee has provided this support (since 1978) and he continues to support the project in this way.

Background and Motivation

If a reaction occurs in more than one step, it must go through an intermediate, which like the reactant and the product, corresponds to a minimum on the reaction surface. If the intermediate has a short lifetime because it is reactive then the intermediate is termed a “reactive intermediate”. As reactions of this type are very common, such reactive intermediates are found in all areas of chemistry. Although they are often present in low concentrations and may have short lifetimes, reactive intermediates play key roles in determining the products and the branching ratios between different product channels, as they represent branching points with paths leading from a local minimum to two or more sets of products. Understanding the ratio of the products from different channels often necessitates understanding the properties of the reactive intermediates. Photoionization followed by detection of the electrons or the ions produced is an excellent way of monitoring reactive intermediates and reaction products from the different channels, to measure product branching ratios.

Two methods are often used, PES and PIMS, depending on whether electrons or ions are detected. In photoelectron spectroscopy (PES) (7) the electron energy distribution is measured at fixed photon energy. It gives information on the electronic and geometrical structure of the molecular species ionized. In photoionization mass spectrometry (PIMS) (8) ion intensities are measured at fixed photon energy. If too high a photon energy is used, fragmentation of the parent ion will occur with the ions observed being lighter fragments of the parent ion. However, if the parent ion is observed, its intensity can be monitored as a function of photon energy to obtain an ionization efficiency curve. This can be used to estimate the associated adiabatic ionization energy (AIE) by determining the parent ion intensity at photon energies just above the ionization energy and extrapolating the ionization efficiency curve back to the onset of ionization. In the absence of fragmentation, and effects arising from autoionization resonances, the photoionization efficiency curve for a selected neutral molecule is essentially the integral of its photoelectron spectrum.

Photoionization processes of reactive intermediates are of fundamental importance, and find application in a large number of scientific areas, including astrophysics, planetary science, the chemistry of the earth's atmosphere, radiation chemistry, physics and biology. Researchers in these fields require ionization energies and information on electronic excited neutral states and low-lying ionic states, as well as measures of intensities (relative and absolute cross-sections) for photoabsorption, photoionization, and photofragmentation processes over a wide spectral range. One way of studying reactive intermediates and ions produced from them is by spectroscopic means, supported by electronic structure calculations, and this helps to understand their structure and reactivity in environments such as plasmas, flames, the earth's

atmosphere and in solution. Also, measurements of ionization energies of reactive intermediates leads to determination of key thermochemical quantities such as heats of formation and bond dissociation energies, which are valuable in calculations relevant to these environments (9-13).

For example, the first AIE of a molecular reactive intermediate is equal to the difference in the heats of formation of the cation and the neutral molecule. If the heat of formation of the cation is available from other sources, for example from proton affinity studies, the heat of formation of the neutral molecule is obtained. Also, if a stable molecule ABC is considered with reactive fragments AB and C, which are usually fragments with unpaired electrons called free radicals (a very important group of reactive intermediates), then the following ionization processes are possible:-



If the AIEs of ABC and AB can be measured for processes (1) and (3), and the appearance energy (AE) of AB^+ can be measured for step (2), then from the AE of AB^+ and the AIE of ABC, the dissociation energy of AB

+

-C, $D(AB$

+

-C), can be calculated, using equation (4):-

$$D(AB^+ - C) = AE(AB^+) - AIE(ABC) \quad \text{-----(4)}$$

Also, from the $AE(AB^+)$ in equation (2) and the AIE of AB in equation (3), the neutral dissociation energy $D(AB-C)$ can be calculated

$$D(AB-C) = AE(AB^+) - AIE(AB) \quad \text{-----(5)}$$

Thermodynamic cycle calculations of this type have been used extensively to determine heats of formation of reactive intermediates and bond strengths in molecules and ions (11-13). This information is important in modelling the atmosphere and other environments, and in benchmarking theoretical methods used to calculate these quantities.

For example, modelling of ozone in the stratosphere requires its ionization energy and electron affinity, and also modelling the role of ozone in the lower ionosphere requires knowledge of direct and dissociative ionization by photons and electrons. The first adiabatic ionization energy of ozone was not unambiguously determined until 2005 (14). Prior to that, in u.v. photoelectron spectroscopy (PES) studies, a weak component was observed at (12.44 ± 0.01) eV, on the low IE side of the first PE band, which was assigned to ionization to the vibronic ground state of the cation (15,16). This weak feature was not observed in other studies (17,18), which reported a value of 12.52 eV for the AIE in agreement with the result of (12.519 ± 0.004) eV obtained by photoionization mass spectrometry (19). A value near 12.52 eV has also been suggested on the basis of an analysis of relevant thermochemical cycles (20,21). In more recent work, this discrepancy was resolved in a pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron study of jet-cooled ozone (14) which gave a value for the first adiabatic IE of ozone as (12.52495 ± 0.00006) eV, indicating that the earlier value of (12.44 ± 0.01) eV arises from ionization of vibrationally excited ozone. The highly precise value of the AIE determined in this PFI-ZEKE study also allowed a determination of a more accurate value for the lowest dissociation threshold of O_3^+ , $D(O_2^+--O)$ as (4898 ± 3) cm⁻¹.

The study of reactive intermediates with PES using vuv radiation from an inert gas low-pressure discharge photon source is now an established method (9-12) and the method has been applied to measure rate coefficients and branching ratios of gas-phase reactions (22,23), by interfacing a flow-tube operated under Langmuir flow conditions to a photoelectron spectrometer. However, using monochromatized synchrotron radiation allows more information to be obtained on the molecular ionic states and the associated photoionization processes than a PES study with a constant energy vuv photon source. In particular

- (i) because the synchrotron photon source is tunable it is possible to identify autoionization resonances, and, once identified, a photoelectron band recorded with photons at these resonance energies can have added intensity in the adiabatic region and extra vibrational structure at higher energy compared to that observed in a PE spectrum recorded off resonance,
- (ii) because the photon source is polarized, angular distribution measurements are possible and this allows information on photoionization dynamics to be obtained ,
- (iii) a study of the relative band intensities in the valence PE spectra of an atom or molecule as a function of photon energy can provide valuable information to assist in band assignment, and
- (iv) by sweeping the photon energy and detecting threshold electrons, threshold photoelectron (TPE) spectra can be obtained. These are higher resolution than conventional PE spectra and hence provide more information on the ionization process and the ionic states accessed.

As stated in the Introduction, it was the first feature which initially attracted the Southampton group to use synchrotron radiation because in a number of previous investigations some of the valence PE bands of the reactive intermediate studied, when recorded with a inert gas discharge source, showed an intense adiabatic component with very little intensity in other vibrational components. This is the case for reactive intermediates such as OH, SH, N₃ and CH

³
O. Such an observation for the first PE band of a reactive intermediate is particularly disappointing, since measurement of the vibrational level separations in the ground ionic state is usually one of the main experimental objectives. Also, as stated earlier, the intensity of a PE band from a reactive intermediate, recorded at a non-resonant photon energy, in a given reaction system may be low and monitoring it at a photon energy corresponding to an autoionization resonance should enhance its intensity.

A PE spectrometer has been built in the Southampton group to study reactive intermediates with synchrotron radiation (24-26). Three types of spectra can be recorded with this instrument:-

- (a) angularly resolved PE spectra;

(b) angularly resolved constant-ionic-state (CIS) spectra; a CIS spectrum is obtained by monitoring the intensity of a selected PE band as a function of photon energy.

(c) threshold PE spectra.

In angle resolved PES and CIS measurements, which allow the angular distribution parameter (β) to be measured as a function of photon energy, the photoionization dynamics of a reactive intermediate can be probed. These measurements can determine the angular momentum of the free electron and the phase difference between the continuum waves of this outgoing electron, and information can be derived on the angular momentum transferred between the initial state (the target and the photon) and the final state (the ion and the photoelectron). Also, angular distribution measurements of the β -parameter for vibrational components of a molecular photoelectron band recorded as a function of photon energy have shown that the β -parameter can change significantly at molecular resonances. This is useful to separate the non-resonant and resonant contributions to the vibrational envelope, and investigate fundamental issues such as the applicability of the Born-Oppenheimer approximation in autoionization from such molecular resonances. When the spectrometer was first built and used at Daresbury, spectra of the type (a) and (b) could be recorded. The ability to record threshold PE spectra was added later after the spectrometer had been moved to Elettra (this was supported by an EPSRC grant awarded to A.Morris, G.C.King, S.Stranges and J.M.Dyke).

Many reactive intermediates have unpaired electrons and are therefore classed as open-shell. Studying open-shell reactive intermediates by these experimental methods is important as although extensive studies have been made of the photoionization behaviour of closed-shell atoms and molecules few attempts have been made to investigate the photoionization dynamics of open-shell atoms and molecules because they are so reactive and often difficult to prepare in sufficient number densities. However, these preparative problems have now been overcome by using techniques developed by the Southampton group and other research groups. Studying reactive intermediates, particularly open-shell reactive intermediates, in this way allows an investigation of effects such as electron correlation, and inter-and intra-channel coupling, and provides important tests of theories that take these interactions into account.

The work carried out at Daresbury represents important advances in the study of reactive intermediates with synchrotron radiation using the PES and CIS methods with angular resolution. This is summarised in the papers listed in the next section (labelled as A1-A10).

Summary of the papers published arising from work at the SRS Daresbury 1993-2000

A1. Studies of Reactive Intermediates with Synchrotron Radiation: $\text{SO}(\text{X } ^3\Sigma^-)$

J.M. Dyke, D. Haggerston, A. Morris, S. Stranges, J.B. West and A.E. Wright

J.Elect. Spec. Rel. Phen. **76**, 1995, 165-170

Abstract

Constant ionic state (CIS) and photoelectron spectra have been recorded for the $\text{SO}(\text{X } ^3\Sigma^-)$ molecule using a photoelectron spectrometer specifically designed for the study of short-lived molecules in the gas-phase with synchrotron radiation.

A2. A Study of the SO Molecule with Photoelectron Spectroscopy using Synchrotron Radiation

J.M. Dyke, D. Haggerston, A. Morris, S. Stranges, J.B. West, T.G. Wright and A.E. Wright

J. Chem Phys **106**, 1997, 821-830

Abstract

The SO molecule has been studied by photoelectron spectroscopy using vacuum ultraviolet radiation from a synchrotron as the photon source. Both constant ionic state (CIS) and photoelectron spectra have been recorded. Resonances which appear in the CIS spectra recorded for selected vibrational levels of $\text{SO}^+ X^2\Pi$ in the photon energy region $h\nu = 11.5\text{-}15.0$ eV have been assigned to excitations to Rydberg states which converge to the SO^+

$a_4^-\Pi$ and $A_2^-\Pi$ states and autoionize to $\text{SO}^+ X^2\Pi$. Also, resonances which appear in the CIS spectra recorded in the photon energy region $15.0\text{-}16.4$ eV for selected vibrational levels of $\text{SO}^+ b_4^-\Sigma^-$ have been assigned to excitations to Rydberg states which converge to $\text{SO}^+ B_2^-\Sigma^-$ and autoionize to SO^+

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. Photoelectron spectra recorded at selected resonant photon wavelengths show that autoionization can dramatically alter the intensities of the vibrational components in a photoelectron band and may allow extra vibrational structure to be observed. The additional information obtained from using this method to study short-lived molecules is discussed.

A3. A Study of the CS molecule with photoelectron spectroscopy using synchrotron radiation

J.M. Dyke, S.D. Gamblin, D. Haggerston, A. Morris, S. Stranges, J.B. West, T.G. Wright and A.E. Wright

J. Chem Phys **108**, 1998, 6258-6265

Abstract

The CS molecule has been studied with constant ionic state (CIS) spectroscopy in the photon energy range 11.2-19.5 eV using radiation from a synchrotron source. The spectra were obtained by monitoring the intensities of the first three vibrational components in the first photoelectron band as a function of photon energy, The structured spectra obtained have been analyzed in terms of excitation to and autoionization from Rydberg states with A $^2\Pi$, B $^2\Sigma^+$ and C $^2\Sigma^+$

ionic cores. Photoelectron spectra of the first band of CS recorded at selected resonant energies showed extended vibrational structure which was used to obtain improved ionic state vibrational constants for CS

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X
2
Σ
+

compared to those derived from an off-resonance spectrum.

A4. A study of $O_2(a^1\Delta_g)$ with photoelectron spectroscopy using synchrotron radiation

J.D. Barr, A. De Fanis, J.M. Dyke, S.D. Gamblin, A. Morris, S. Stranges, J.B. West, T.G. Wright and A.E. Wright

J. Chem Phys **109**, 1998, 2737-2747

Abstract

The atmospherically important species $O_2(a^1\Delta_g)$ has been studied by photoelectron spectroscopy using vacuum ultraviolet radiation from a synchrotron as the photon source. Constant-ionic-state (CIS) spectra, recorded for vibrational levels of O

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= 0,1,2,3 accessed from O

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^g
) $v'' = 0$, exhibit intense signals in the photon energy region 14.0-15.5 eV which are shown to arise from autoionization from a Rydberg state with an O

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(C
²
 Φ
^u
) core. On the basis of the results obtained and earlier evidence derived from vacuum ultraviolet absorption spectroscopy, this state is assigned as a (C

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,3s σ
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)
¹
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Rydberg state. Photoelectron spectra recorded for O

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^g
) at positions of strong resonances have allowed extended vibrational structure to be obtained in the first photoelectron band. The relative vibrational component intensities in the resonant photoelectron spectra are in good agreement with computed relative intensities obtained via Franck-Condon calculations, confirming the vibrational numbering of the resonances in the

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^u
state. Competition between autoionization and predissociation in the

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Rydberg state is discussed on the basis of the results obtained. Weaker structure is observed in CIS spectra recorded in the photon energy regions 12.5-13.5 and 15.0-20.0 eV. Suggestions are made for the nature of the highly excited states of O

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associated with this structure, based on available ionization energies and spectroscopic constants of known ionic states accessible from O

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) . For example, two broad bands centered at approximately 16.4 and approximately 17.75 eV
 are assigned to excitation to Rydberg states arising from the configurations (D
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 Δ
^g
 ,3p
 π
^u
) and (D
²
 Δ
^g
 ,4p
 π
^u
) respectively.

A5. Study of the OH and OD radicals with photoelectron spectroscopy using synchrotron radiation

J.D. Barr, A. De Fanis, J.M. Dyke, S.D. Gamblin, N. Hooper, A. Morris, S. Stranges, J.B. West and T.G. Wright

J. Chem Phys **110**, 1999, 345-354

Abstract

Photoionization of the OH and OD radicals, produced from the H + NO₂ and D + NO₂ reactions, has been studied in the gas phase in the photon energy region 13.0–17.0 eV using constant

ionic state (CIS) and photoelectron spectroscopy (PES) employing synchrotron radiation. Structure in the CIS spectra, recorded for the first and second photoelectron bands, has been assigned to excitation to ($\sigma^*_{1/2}$)

($\sigma^*_{1/2}$) and ($\sigma^*_{3/2}$) Rydberg states. A comparison of vibrationally specific OH and OD CIS spectra, and photoelectron spectra recorded at resonant wavelengths, has allowed a more complete assignment of structure observed in earlier photoionization mass spectrometric measurements.

These assignments have been supported by the results of Franck–Condon calculations. The CIS spectra have been shown to be dominated by structure arising from excitation from the outermost valence molecular orbitals of OH [the nonbonding 1π ($O\ 2p$) orbital and the bonding 3σ orbital] to $O\ n$ Rydberg orbitals. Photoelectron spectra recorded for the first bands of OH and OD at resonant photon energies have allowed more extensive vibrational structure to be obtained than has previously been recorded by PES experiments performed with inert gas discharge photon sources.

A6. Photoelectron Spectroscopy of Reactive Intermediates

J.M. Dyke, S.D. Gamblin, A. Morris, J.B. West and T.G. Wright

(American Institute of Physics, New York, 1998)

Resonance Ionization Spectroscopy 1998, 81-88

Abstract

The advantages of using synchrotron radiation to study reactive intermediates are described

and likely future developments are outlined. Examples of studies on O_2 $a^1\Delta_g$, OH and SO are used to show that the use of synchrotron radiation in this research area allows more information to be obtained on the molecular ions and the associated photoionization processes.

A7. A photoelectron spectrometer for studying reactive intermediates using synchrotron radiation

J.M. Dyke, S.D. Gamblin, A. Morris, T.G. Wright, A.E. Wright and J.B. West

J. Electron Spec Rel Phen **97**, 1998, 5-14

Abstract

The construction of a photoelectron spectrometer, designed for studying reactive intermediates with synchrotron radiation, is described. The principal features are the inclusion of several stages of sample pumping, necessary to provide the required gas throughput and to protect the electron optics of the storage ring and spectrometer. The facility to rotate the whole spectrometer is also included in the design. Some data are presented which demonstrate the use of the instrument for obtaining photoelectron spectra, constant-ionic-state (CIS) spectra, and near-threshold photoelectron spectra of reactive species.

A8. Photoelectron spectroscopy of short-lived molecules using synchrotron radiation.

J.B. West, J.M. Dyke, A. Morris, T.G. Wright and S.D. Gamblin

J. Phys. B, **32**, 1999, 2763-2782

Abstract

In this paper, examples are given of recent measurements made at the Daresbury Synchrotron Radiation Source on four short-lived diatomic molecules. The equipment designed to overcome the difficulties of interfacing reactive species with the ultra-high vacuum environment of a synchrotron radiation source is described. The measurements presented have been selected to show the advantage of using a continuum source of radiation in identifying new structure in the photoionization continuum of these molecules.

A9. Angle Resolved Photoelectron Spectroscopy of $O_2(a^1\Delta_g)$ with Synchrotron Radiation.

L. Beeching, A. De Fanis, J.M. Dyke, S.D. Gamblin, N. Hooper, A. Morris and J.B. West.

J. Chem. Phys., **112**, 2000, 1707-1712

Abstract

Angular distribution of photoelectrons for the photoionization processes $O_2^+ X (^2\Pi_g, v+ = 0-3) + e^- \leftarrow O_2 (a^1\Delta_g) + h\nu$ has been studied at the photon energy of 21.22 eV and in the photon energy range 13.8-15.2 eV where the cross-sections for these processes show strong enhancement due to the presence of resonant transitions to a Rydberg state (C

2

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u
 $, 3s\sigma$

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u
 $)$. It has been found that the plot of the asymmetry parameter, β , against photon energy shows structure at energies corresponding to O

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 1

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 $v') \leftarrow O$

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 $) v'' = 0$) excitations. The O

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 $, v_+)$ $\leftarrow O$

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 $) v'' = 0$) ionizations have also been investigated in the photon energy range 18.0-19.2 eV, where the presence of unassigned resonances was observed in earlier photoelectron spectroscopic work. In this energy range the plot of asymmetry parameter (β) against photon energy also shows resonant structure. Suggestions for the excited states associated with these resonances have been made on the basis of constant-ionic-state spectra recorded at different angles.

A10. Photoelectron spectroscopy of reactive intermediates using synchrotron radiation

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, and T.G.Wright

J.Elec.Spec. Rel. Phen. **108** , 2000, 47-61

Abstract

Experiments performed with a purpose built spectrometer to study reactive intermediates with synchrotron radiation are described. Results are presented for some short-lived molecules of atmospheric and combustion importance. Constant ionic state (CIS) and photoelectron spectra were recorded. In each case, the observation of resonant structure in the CIS spectrum enabled the identification and characterisation of Rydberg series associated with excited neutral states to be carried out. Examples of window resonances (SO) and possible competition between autoionisation and predissociation ($O_2(a^1\Delta_g)$) are encountered. Photoelectron spectra recorded at selected resonant energies exhibited extended vibrational structure, which led to improved estimates of ionic state spectroscopic parameters (ω_e , ω_x , ω_e , ω_x , ω_e).

Franks-Condon calculations for both CIS and PES data provided confirmation of resonant state assignments. Preliminary angular distribution measurements performed on $O_2(a^1\Delta_g)$ are presented, where the asymmetry parameter (β) showed structure at energies corresponding to neutral state resonances.

ω_e
 ω_x
 ω_e
 ω_x
 ω_e

Δ

ω_e are presented, where the asymmetry parameter (β) showed structure at energies corresponding to neutral state resonances.

Acknowledgements

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