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MOLECULAR SPECTROSCOPY PROBED BY SYNCHROTRON RADIATION AND ELECTRON SCATTERING

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

Molecular spectroscopy is fundamental to many aspects of atmospheric and astrophysical science including the new scientific discipline of astrobiology (and the search for possible existence of extraterrestrial life). The construction of a 'Spectral Atlas' is therefore essential to the development of these fields of research. However at present our knowledge of the spectroscopy of many molecular systems is incomplete, particularly in the UV spectral region. In this review modern experimental techniques utilising both synchrotron radiation and electron impact are reviewed and their impact upon the collection of a comprehensive spectroscopic database discussed.

1. Introduction

Molecular spectroscopy is fundamental to many aspects of atmospheric and astrophysical science. The absorption spectrum of a molecule provides a unique fingerprint covering a wide spectral range. Molecular spectroscopy may be broadly divided into three wavelength regions. The first, and that requiring the least energy transfer, is due to the molecules ability to rotate, such molecular transitions dominate at microwave and far infrared frequencies. Within astronomy microwave emissions provide the most direct evidence for the existence of molecules in the interstellar medium (ISM). The second involving molecular vibrations is dominant in the infrared range. Infrared spectroscopy is paramount in the study of the 'greenhouse effect' in planetary atmospheres and those processes leading to possible 'global warming' within the terrestrial atmosphere. The third wavelength region involves excitation of molecular excited states and requires the higher energies of visible and ultraviolet radiation. This is the major spectroscopy of interest when studying the absorption of solar radiation within any planetary atmosphere and in the formation and destruction of the Earth's stratospheric ozone layer. The ability of light to 'break' molecular bonds through the absorption of visible and ultraviolet light (the process of photodissociation) provides the main energetic process for the formation of molecules in the atmosphere and interstellar space and may ultimately determine the formation of those molecules that lead to the development of life.

Spectroscopic studies therefore underpin not only basic atomic, molecular and optical research and astronomy, but much of modern environmental science and increasingly plays a role in the life sciences. For example UV induced degradation of skin tissue (eg the condition known as 'erythema' or sunburn) is intrinsically linked to the molecular spectroscopy of key biological molecules such as DNA. The construction of a 'Spectral Atlas' for molecular systems is therefore essential to our understanding of atmospheric, astrophysical, environmental and the life sciences.

However despite exhaustive studies of molecular spectroscopy there remain significant gaps in the available database. These arise either from the difficulty in producing adequate samples of the molecular compound in question, or the need to study molecular targets in physical regions beyond those commonly encountered in the laboratory. For example molecular absorption cross sections needed for studies of the terrestrial ozone layer require data to be collected at a temperature of typically 200 K, while in the ISM temperatures may vary from 4 K in deep space to 10000 K (in regions of shocks). Therefore there has been a major effort to develop new methodologies to measure molecular spectra over a wide temperature and wavelength range.

2. Spectroscopic Techniques

Three major techniques are currently being used to probe the spectroscopy of molecular systems: (1) Photo-absorption spectroscopy, (2) Electron energy loss spectroscopy and (3) Laser spectrosocopy. Laser spectroscopy is the most selective of the three techniques and unlike the others may be used for field studies. However in order to utilise the maximum sensitivity of laser techniques the basic spectroscopy of the molecule to be monitored must already be known. Thus photo-absorption spectroscopy and electron energy loss spectroscopy provide the most fundamental data upon any system and will be the subject of the remainder of this brief review.

2.1. Photo-absoption spectroscopy

Many of the experimental studies of photo-absorption have involved measurement of the attenuation of a beam of photons traversing a gas-filled absorption cell. Such an arrangement may be easily established in any laboratory using commercial UV-VIS or FTIR instrumrnts allowing spectra to be recorded from the infra-red to the near ultraviolet (200 nm). For studies in the far UV such a gas cell may be incorporated into one of the user beam lines at a synchrotron facility [1]. Synchrotron radiation falls on a rotatable diffraction grating where it is dispersed. The dispersed radiation is then focused into the absorption cell with a single exit slit between the grating and the absorption cell selecting the resolution of the incident radiation.

The intensity of the incident radiation is then recorded by a photo-multiplier placed a the exit of the gas cell (to convert UV radiation into visible radiation a sodium salicylate window may be placed between the gas cell and the photo-multiplier). If light of flux I_0 is recorded with no gas in the gas cell the measured intensity falls to some lower value I when gas in introduced. If X is the path length in the cell and then these two intensities are related by the equation

$$I = I_0 \exp(-\mu x) \ ,$$

where μ is the absorption coefficient for the particular wavelength in use. μ may be related to the photo-absorption cross section σ_{pa} by $\mu = \sigma_{pa}N$ and N is the number density of the gas. There are however two conditions on the validity of this equation. First the radiation must be so nearly monochromatic that there will be no change in effective absorption as the radiation progresses through the gas, then μ will be independent of the value of x chosen, and Lambert's law will be obeyed. Secondly μ must also be independent of temperature and pressure, so that Beer's law is obeyed. If either of these conditions is broken then so-called 'line saturation' phenomena may occur resulting in erroneous absolute photo-absorption cross sections. It is therefore necessary to measure apparent σ_{pa} at different incident resolutions and gas pressures if absolute cross sections are to be derived. Provided these constraints are met such simple apparatus it is therefore possible to study the spectroscopy of most atomic and molecular systems.

2.2. Electron energy loss spectroscopy

Photoabsorption measurements are necessarily restricted to those transitions of an 'allowed' nature, forbidden transitions (those not obeying the simple dipole radiation $\Delta l = \pm 1$) will therefore only have weak absorption cross sections, often too low for detection with conventional light sources. Forbidden transitions produce long lived excited states which are amongst the most chemically reactive species in the atmosphere. Such states are produced by photodissociation, recombination and collisional excitation in the stratosphere and ionosphere and are also responsible for the emissions in airglow and the aurora. However, to date there have been few experimental studies on the spectroscopy of such forbidden states. Therefore another experimental technique has been applied to probe the spectroscopy of aeronomic molecules. This is the technique of electron energy loss spectroscopy (EELS).

When an incident electron (kinetic energy E_{in}) inelastically scatters through an angle θ from a molecular target, the kinetic energy lost (ΔE) is provided to the target for rotational, vibrational and electronic excitation i.e.

$$e_{Ein} + ABC \rightarrow ABC^{**}(J',\upsilon) + e_{Ein-\Delta E} .$$

Measurement of the electron energy after the collision (E_{in}-ΔE) will allow the energy transferred to be calculated and thence which electronic states have been excited in the target molecules. This EELS method has been used to probe the spectroscopy of molecular targets for nearly thirty years. It is a flexible approach since all the electronic states of the target may be excited by electron impact since, in contrast to optical spectroscopy, there are no selection rules. However certain collision geometries favour certain types of transitions [2].

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. The electric field acts most strongly with the transition dipole of the molecule such that electric dipole (or optically allowed) transitions are predominantly excited, hence the inelastic electron scattering process simulates the photo-absorption 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 ($T >> E_L$, the electron energy loss) 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.

In contrast at low impact angles and large scattering angles ($\theta > 90^{\circ}$), i.e. the conditions of large momentum transfer within the collision event, structure observed in the 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 which are not able to be observed in one photon absorption experiments, but which may be excited in the Earth's atmosphere.

3. Molecular spectroscopy probed by synchrotron radiation and electron impact

The remainder of this article will consist of a few case studies where photoabsorption and electron energy loss studies of the spectroscopy of molecular systems have provided important data for applied sciences community.

3.1. Ozone: The Earth's UV filter

Ozone is only a minor constituent of the Earth's atmosphere forming but 0.2% of the terrestrial atmospheric mass, such that if all the atmospheric ozone was collected at the Earth's surface it would form a ring only 3mm thick around the Earth. It is the presence of ozone in the atmosphere that shields the Earth's surface from harmful solar UV radiation since uniquely amongst those molecules in the Earth's atmosphere ozone has a strong 'absorption band' (the so-called 'Hartley Band') between 210 and 300 nm. Hence ozone 'filters' out the Sun's ultraviolet radiation below 300nm preventing these wavelengths from reaching the Earth's surface [3].

Biological molecules have evolved under conditions of such 'filtering' and thus while they do not absorb visible light they can safely absorb ultraviolet light since such radiation does not reach the Earth's surface. Figure 1 shows the solar emission spectrum reaching the Earth's surface for wavelengths below 340nm together with the absorption spectra of two important biomolecules, DNA, the carrier of the genetic code, and α-crystallin the major protein of the mammalian eye lens. The absorption of light by both these biological molecules is essentially zero in the region $320<\lambda<400$ nm, the near-UV or UV-A region but it is intense in the region $200<\lambda<290$ nm, the far UV or UV-C region. The presence of ozone in the terrestrial atmosphere ensures that the absorption spectrum of these biological molecules only overlaps the solar spectrum at the Earth's surface in the wavelength region $290<\lambda<320$ nm, the mid-UV or UV-B region.

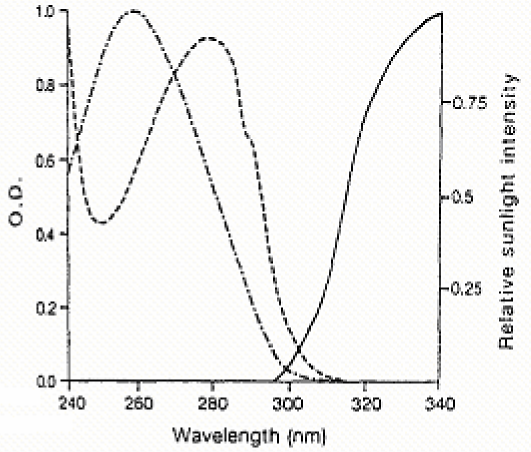

Fig. 1. Absorption spectra of DNA and α-crystallin with the spectrum of the solar flux reaching the Earth's surface when a complete ozone layer is present in the stratosphere.

However should the Earth's ozone layer become thinner larger fluxes of both UV-B and UV-C radiation will penetrate the Earth's atmosphere reaching the Earth's surface where it will be absorbed by such biological molecules, leading to mutagenesis (cell death) and hence irreversible tissue damage, manifest for example in skin cancers and cataracts.

In 1974, Molina and Rowland [4] suggested that the uncontrolled release of chlorofluorocarbons (CFC's) into the terrestrial atmosphere would lead to the catalytic destruction of ozone. Although chemically stable within the troposphere, in the stratosphere the CFC's can be broken down by solar radiation and release chlorine atoms which in turn form ClO catalytic species such that one ClO radical may destroy several hundred ozone molecules before it itself is removed form the ozone chemical cycle. Thus Molina and Rowland suggested even trace (ppm) amounts of any CFC in the stratosphere could have a dramatic effect upon stratospheric ozone concentrations.

Such predictions were confirmed in 1985 Joe Farmer, Brian Gardiner, and Jonathan Shankin [5] of the British Antarctic Survey discovered a sharp reduction in ozone concentrations above Antarctica; this was soon termed the ozone 'hole'. Satellite monitoring of the ozone 'hole' has shown it is expanding and its depth increasing and there is now evidence of similar but less marked changes over the Arctic and the more densely populated northern latitudes. The consequences of such ozone loss are great and therefore swiftly led to global treaties to halt the manufacture of CFCs but due to their long lifetime in the terrestrial atmosphere the consequences of their emissions over the last forty years is such that the ozone hole may continue to grow for another two decades and it is therefore important to quantify the effect of such ozone loss on human, mammelian and plant life. Therefore it is essential to have detailed information on the spectroscopy of ozone and those molecules that lead to its destruction.

Ozone photo-absorption spectroscopy

The most important spectroscopic measurement in ozone depletion studies is that of the ozone molecule itself. Figure 2 shows the absorption 'cross section' of ozone recorded at the UK Daresbury synchrotron facility [6]. The main optical absorption band in ozone is the Hartley Band ($200 < \lambda < 300$ nm) attributed to the excited $^1B_2$ state its characteristic band shape arising from a symmetric stretching progression with subsequent dissociation along the asymmetric stretching mode, the resultant products being excited molecular oxygen $O_2(a^1\Delta g)$ and excited atomic oxygen $O(^1D)$. It is this band that 'filters' out the Sun's ultraviolet radiation below 300 nm preventing these wavelengths from reaching the Earth's surface thus it is probably the most accurately measured absorption cross section for any molecular excited state cross sections being know to 1% accuracy over a temperature range from 77 to 400 K.

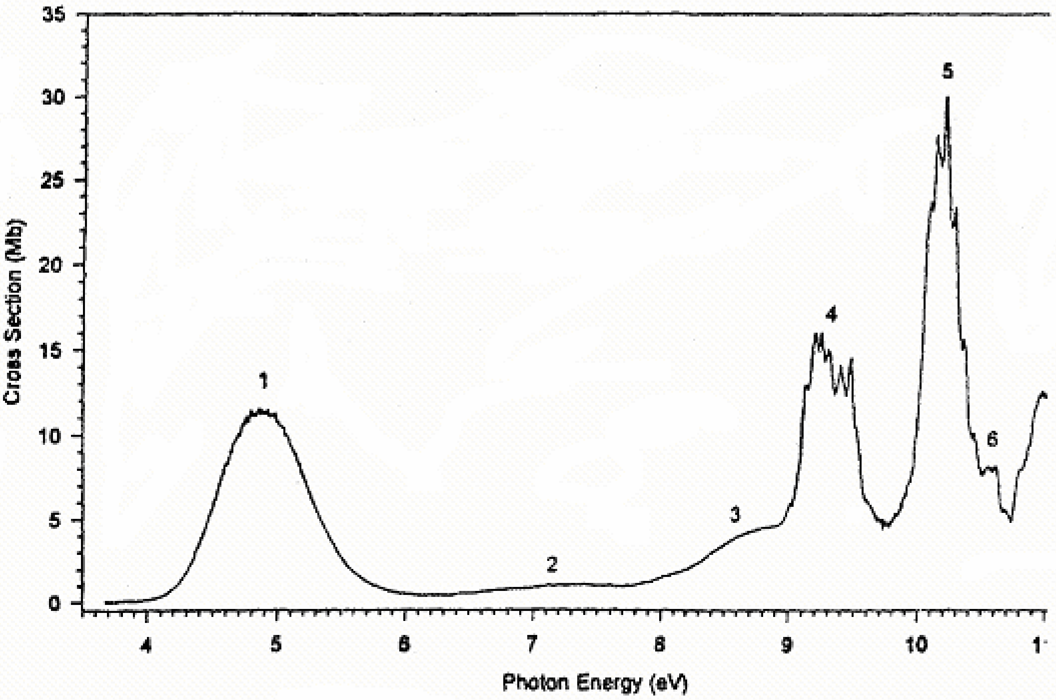

Fig. 2. Photoabsorption spectrum of ozone recorded using the UK synchrotron facility

Ozone forbidden states

Ozone is an unusual triatomic molecule in that it is a spin-paired biradical having weak bonding between the singly occupied π orbitals on the terminal oxygen atoms. This biradical electronic structure leads to a small energy separation between the Highest Occupied Molecular Orbital (HOMO) and the Lowest lying Unoccupied Molecular Orbital (LUMO) and hence there exist several *low lying* electronically excited states, several of which may be of a repulsive character ($O_3 \to$ $\to O_2 + O$), resulting in an unusually low dissociation energy for a triatomic species. This low dissociation energy explains why ozone is so difficult to produce within laboratory discharges since low energy electrons within the discharge may easily reduce ozone to molecular oxygen.

Considerable theoretical efforts have been made to calculate the excitation energies and dissociative properties of the electronically excited states of ozone in an attempt to understand the spectroscopy, photochemistry and dissociation pathways. However until recently the results have been conflictory, and the ordering of the lowest lying states, and thence the assignment of observed absorption band structures, have remained ill-determined.

The method of electron-energy loss spectroscopy finally answered several of the remaining uncertainties on the order, nature and excitation energies of the lowest lying optically forbidden states of ozone [7]. Figure 3 shows an electron energy loss spectrum under scattering conditions favouring triplet (forbidden) state excitation, while the Hartley band is still clearly evident between 4 and 6 eV new structure is observed at low energies comprising of a band with superimposed vibrational structure. The vibrational structure can be plausibly, but not unambiguously divided into two progressions labelled I and II. The first has an origin at 1.29 +/- 0.1eV the second progression at 1.528 +/- 0.01eV thus suggesting that at least two of the low lying states of ozone are capable of supporting bound states and therefore are likely to be 'metastable' in character. Thus if such states are excited in collisional processes within the atmosphere, or if they are populated during ozone formation processes, they will act as an energy 'sink', while providing the nascent ozone with sufficient internal energy to overcome certain chemical reaction barriers previously regarded as impenetrable. The role of such 'metastable states' in the ozone depletion mechanisms will therefore need to be evaluated by atmospheric modellers.

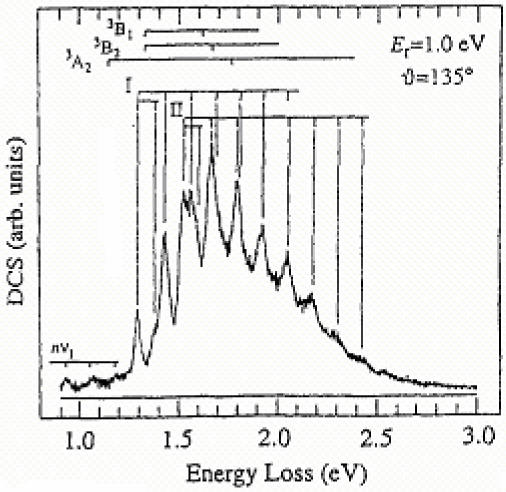

Fig. 3. The forbidden states of ozone observed using electron energy loss spectroscopy.

3.2. *Large polyaromatic hydrocarbons in Space*

When observing the interstellar medium there are several distinct features that appear throughout the sky. Within the infrared region there are discrete bands of emitted radiation at 3.3, 6.2, 7.7, 8.6 and 11.3 µm while within the ultraviolet region there is an absorption 'bump' centred at 217.5 nm. Such features have intrigued astronomers for over twenty years but their cause remains unknown. Modern theory ascribes these features to the presence of large polyaromatic hydrocarbons (PAHs) comprising of sets of aromatic benzene rings with possible methyl or ethyl groups attached. Any such compounds present in these regions must be extremely stable to ultraviolet radiation, hence the suggestion of PAHs [8]. Furthermore PAH compounds are characterised by a single large UV absorption peak arising from the $\pi \rightarrow \pi^*$ transition in such compounds. Figure 4 shows the photoabsorption spectrum for several of the smaller PAH compounds recorded using synchrotron radiation [9].

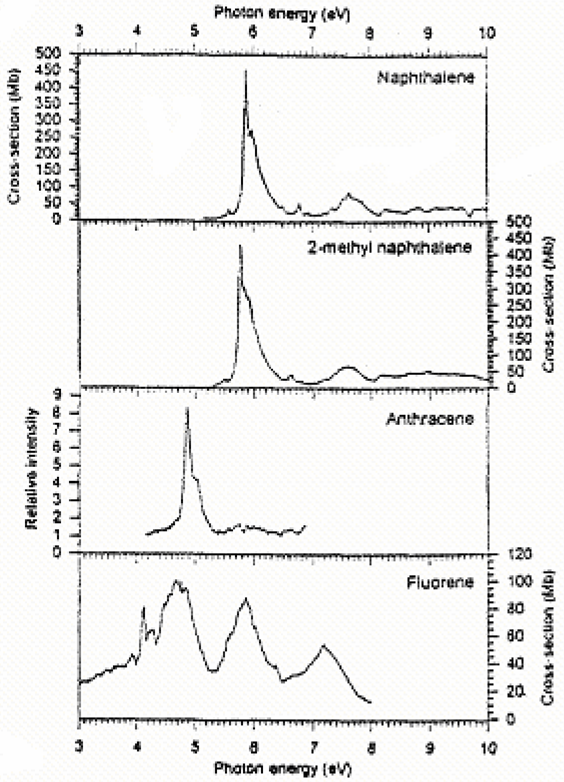

Fig. 4. Photoabsorption spectra of selected polycyclic aromatic hydrocarbons (PAHs)

However recent experiments [10] have shown that when irradiated by UV light PAH compounds do not emit with the characteristic infra red signal observed in space. It was therefore proposed that all such compounds may be positively ionised and hence their emission lines shifted from the neutral line wavelengths to those observed in space, but recent experiments have shown this not to be the case. Therefore the present hypothesis is that the PAHs may in fact be present as cations, whose emission signature is unknown. However this is still an unsatisfactory argument since an ensemble of PAHs and their cations would still be required to explain the observations and there is no theory to explain why such a molecular mixture should be constant throughout the universe.

Therefore it is necessary to continue to study the photoabsorption (and infra emission) of larger hydrocarbons capable of forming in space. These may include long C–C chain molecules: five membered ring compounds and molecules composed of both five and six membered rings since these make up the most stable of all PAHs – Carbon 60; the buckeyball.

New molecules are being found in space at the rate of 5 to 6 every year such that at present some 75 polyatomic molecules have been observed. Most recently the precursors of simple sugars and amino acids have been identified in the ISM. Such discoveries have led to the development of the new field of *astrobiology*. Astrobiology aims to determine how and where the those molecules essential to the development of life formed and may one day seek to answer the most profound question of all - how and where did life as we know it begin and are the conditions for the development of life common across he universe. Such studies can only be answered by probing ever deeper into the universe and studying other solar systems galaxies and the ISM, all such studies rely upon our knowledge of spectroscopy and therefore require us to complete a comprehensive 'Spectral Atlas'.

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МОЛЕКУЛЯРНА СПЕКТРОСКОПІЯ З ВИКОРИСТАННЯМ СИНХРОТРОННОГО ВИПРОМІНЮВАННЯ ТА РОЗСІЮВАННЯ ЕЛЕКТРОНІВ

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

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

Молекулярна спектроскопія є фундаментальною в багатьох аспектах атмосферної та астрофізичної науки, в тому числі й у такій новій науковій галузі, як астробіологія (і пошук можливого існування позаземного життя). Тому для розвитку цих галузей досліджень важливим є створення "спектрального атласу". Однак, сьогодні наші знання зі спектроскопії багатьох молекулярних систем неповні, зокрема в ультрафіолетовій спектральній області. Нами зроблено огляд сучасних експериментальних методик, що використовують як синхротронне випромінювання, так і електронний удар, обговорюється їх вплив на формування широкої спектроскопічної бази даних.