

Vibrational Spectroscopy 29 (2002) 27-43

### VIBRATIONAL SPECTROSCOPY

www.elsevier.com/locate/vibspec

# High resolution Fourier transform spectroscopy with the Imperial College (IC) UV-FT spectrometer, and its applications to astrophysics and atmospheric physics: a review

### Juliet C. Pickering

Blackett Laboratory, Imperial College, London SW7 2BZ, UK
Received 31 August 2001; received in revised form 5 December 2001; accepted 5 December 2001

#### **Abstract**

The improvements in astronomical telescopes and their spectrographs, and in spectrographs used for studies of the earth's atmosphere have created a requirement for matching improvements in the laboratory atomic and molecular database needed in the analysis of the astrophysical and atmospheric spectra. The technique of Fourier transform spectroscopy (FTS) is described and its suitability in improving the atomic and molecular databases is discussed. The extension of the wavelength range of the Fourier transform (FT) spectrometry into the vacuum ultraviolet to 140 nm is described. Examples are given of recent atomic and molecular spectroscopy research using the Imperial College (IC) UV-FT spectrometer and applications to astrophysics and atmospheric physics are given. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Fourier transform spectroscopy; Ultraviolet; High resolution; Atomic and molecular databases

### 1. Introduction

Atomic and molecular spectra in the ultraviolet obtained in the laboratory are required for three main applications: studies of basic atomic and molecular physics, interpretation of astrophysical spectra, and in observations of the earth's and other planetary atmospheres. In this paper, in particular, the applications to astrophysics and atmospheric physics are considered.

There have been great advances in the capabilities of astronomical telescopes and their spectrographs during the last decade. The inadequacies of the existing laboratory atomic database were, and continue to be, highlighted by the high resolution spectra being obtained with the new generation of high resolution spectrographs: the Hubble space telescope (HST)

E-mail address: j.pickering@ic.ac.uk (J.C. Pickering).

spectrographs formerly the Goddard high resolution spectrograph (GHRS) and the current space telescope imaging spectrograph (STIS) (resolving power  $R \sim 105,000$ ), The University College London Echelle spectrograph (UCLES) and the ultra high resolution facility (UHRF) ( $R \sim 10^6$ ) on the Anglo–Australian telescope (AAT), and they will be further exposed with future spectrographs (e.g. the high resolution optical spectrograph (HROS)/GEMINI, target  $R \sim 120,000$ ).

The great improvement in quality of high resolution stellar spectra can be seen in Fig. 1—a section of the  $\chi$  Lupi spectrum is shown recorded with the international ultraviolet explorer (IUE) and is compared with the more recent GHRS/HST spectrum.

The atomic database for the astrophysically important 3d transition group (iron group) elements was, prior to the last decade, based on grating spectra

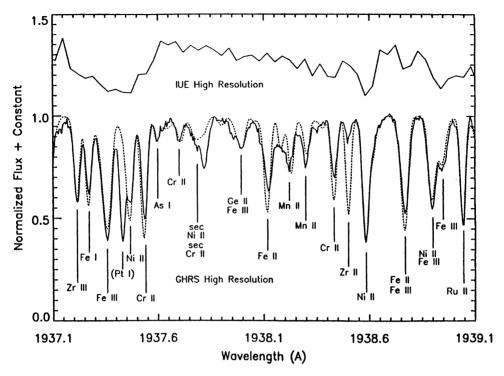


Fig. 1. High dispersion spectra of  $\chi$  Lupi obtained with the international ultraviolet explorer (IUE) satellite (top), and with the GHRS/HST (bottom). Solid curves are the observations, dashed curve is a theoretical synthetic spectrum (taken from [1]).

and often dated back over 50 years. Intensities were based on eye estimates of photographic plate blackening. Improvements were needed of an orderof-magnitude in accuracy of the atomic data and can now be achieved, i.e. wavelengths to at least 1 part in  $10^7$ , and oscillator strengths (f-values) to a few percent. Knowledge of these complex spectra is essential in stellar spectroscopy because the large number of energy levels of these species combined with their high abundance make them, within the appropriate temperature ranges, responsible for most stellar opacity. Accurate wavelengths, energy levels, f-values, hyperfine structure (HFS) and isotope shift data are vital for the synthetic spectrum fitting procedure used by astronomers to analyse astrophysical spectra. These synthetic spectrum calculations are only as reliable as the atomic data they are based on; where these are poor or missing, the model will also be poor.

Atomic data for heavier element spectra are also important in many cases; it is especially important to have a broad atomic database in undertaking analyses of the many chemically peculiar stars currently of such great interest. Studies of the bizarre abundance and isotope anomalies in many hot stars are constrained by the accuracy of the abundance determinations which are only of high quality if accurate *f*-value, hyperfine structure, isotope shift, and wavelength data are available.

Semi-empirical theoretical atomic and molecular structure calculations are underpinned by accurate atomic and molecular data giving approximate predictions of transition probabilities, absorption cross-sections and wavelengths where no laboratory measurements exist.

There have also been improvements in spectroscopic observations of the earth's atmosphere, and the atmospheres of objects in our solar system, and improvements are required in the laboratory molecular database in order to correctly interpret these observations.

In this paper, the achievements of UV-FT spectroscopy in improving spectroscopic data for astrophysics and atmospheric physics will be discussed.

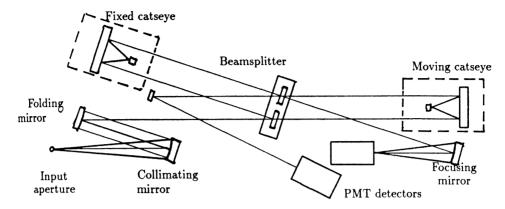


Fig. 2. Schematic diagram of an FT spectrometer layout (Imperial College).

### 2. Fourier transform spectroscopy (FTS) and atomic spectroscopy

The Fourier transform (FT) spectrometer [2] is based on the Michelson interferometer. The input beam is amplitude divided by the beamsplitter into two beams, each then following different paths before recombining and reaching the detector (see Fig. 2). The detector signal recorded by scanning one of the mirrors, the interferogram, is sampled at equal intervals of path difference, determined using the fringes of a He–Ne laser following the same path through the interferometer. This interferogram is the Fourier transform of the source spectral distribution and an inverse Fourier transform is thus carried out to produce the spectrum. Atomic spectra are observed in emission, and molecular spectra are observed both in emission and absorption.

In the past decade, FTS has become an established technique not only in the IR and the visible but also now in the ultraviolet spectral regions, and progress is continuing into the vacuum ultraviolet (VUV), with the short wavelength limit currently at 140 nm [3]. The main challenges going to shorter wavelengths are the higher optical and mechanical tolerances required, and the design and building of a UV-FT spectrometer at Imperial College (IC) [4] was a ground-breaking advance. Although the multiplex and throughput advantages over grating spectroscopy are no longer relevant in the UV, the advantage in terms of resolution and wavenumber accuracy is still significant. Initially, the short wavelength cut-off was

limited by the use of a silica beamsplitter to about 178 nm. The development of a MgF<sub>2</sub> beamsplitter [5] has now pushed the short wavelength cut-off for FTS down to 140 nm, the current limit [3]. Work at Imperial College is continuing to further extend the VUV range.

FTS now covers the IR-VIS-VUV spectral range, and is thus ideally matched to studies of spectra of neutral, singly and doubly ionised transition group elements, as well as to studies of molecular species.

### 2.1. Main properties of FTS

The main properties of Fourier transform spectroscopy include the following.

### 2.1.1. High resolution

The spectral resolution is determined by the maximum path difference, and is given by the reciprocal of twice the path difference. For example, the IC-FT spectrometer has a maximum path difference of 20 cm and this corresponds to a maximum resolving power of  $2 \times 10^6$  at  $50,000 \, \mathrm{cm}^{-1}$ . This resolving power is sufficient to fully resolve a line of a 3d transition element emission spectrum in a hollow cathode discharge at  $50,000 \, \mathrm{cm}^{-1}$  where the line widths are typically a few hundreths of a wavenumber. FTS, thus, provides Doppler-limited resolving power in an instrument a fraction of the size of a large grating spectrograph (typically 6–10 m focal length). This high resolution allows studies of hyperfine structure [6] and isotope shifts [7,8] to be carried out.

### 2.1.2. Linear wavenumber scale and high wavelength accuracy

With FTS, the wavenumber scale is linear due to the properties of the Fourier transform and is derived from the intervals at which the interferogram is sampled. Although the fringes of a stabilised He-Ne laser are used to produce the sampling intervals, small angular differences between the source and laser beams through the interferometer means that the laser wavelength may not be used for absolute wavenumber calibration. In principle, just one reference line is needed to vield the small correction factor to make the wavenumber scale accurate [9]. In practice, a small set of interferometrically measured Ar II lines [10] are commonly chosen as wavelength standards. In comparison, grating spectroscopy requires a set of reference wavelengths distributed through the spectral region.

For a line in an FT spectrum the wavenumber accuracy is given by the uncertainty in the calibration and by the statistical uncertainty of the measurement of the line position. The uncertainty in line position measurement of a well-resolved symmetric line of width FWHM has been shown to be given by FWHM/(2×SNR) [11] . So, for a strong unblended line with SNR (signal-to-noise ratio) of 100, a Doppler

width of 0.2 cm<sup>-1</sup> (typical of a hollow cathode lamp emission line in the UV), the uncertainty is about 0.001 cm<sup>-1</sup> plus the calibration uncertainty, which amounts to a total uncertainty of approximately 0.002 cm<sup>-1</sup>. This high accuracy easily matches with that needed for analysis of stellar spectra recorded.

### 2.1.3. Large and variable-free spectral range

The FT spectrometer has a unique combination of a large free spectral range with high resolution. Laser and Fabry–Perot spectroscopic techniques may surpass FTS in resolution but they are very much line-by-line techniques and are not suitable for studying spectra consisting of thousands of lines covering a broad spectral range. Although the wavelength range may be large with a grating spectrometer the resolution cannot match that of FTS. Fig. 3 shows as an example of a section of broadband FT spectrum of Fe III (27 nm wide) with a small 1.4 nm section expanded.

### 2.1.4. Slowly varying photometric response

A slowly varying photometric response combined with a wide free spectral range, ensures that FTS can be used for reliable measurements of relative intensities of emission lines and hence branching ratios.

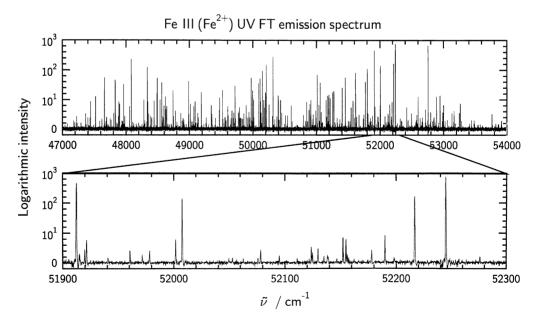


Fig. 3. A broad section of Fe III FT spectrum recorded in the VUV at IC with a small 1.4 nm section expanded.

Since an interferogram is a simultaneous measurement on all spectral elements, any small drifts in source intensity will not lead to big errors in branching ratios as would be the case with a sequentially scanned grating monochromator. The branching ratios when combined with measured [12] or calculated level lifetimes yield transition probabilities which are used by astronomers to determine elemental abundances in astrophysical objects.

### 2.2. Light sources

A dc hollow cathode discharge (HCD) is the light source commonly used for FTS observations of transition group spectra. This principally emits neutral and singly ionised emission spectra. Since with FTS the resolution is such that the line widths are Doppler limited, water-cooled hollow cathode lamps are often used to reduce the Doppler line widths. Although the HCD is ideal for neutral and singly ionised spectra, it cannot be used to excite doubly ionised spectra. Increasing the light source ionisation is possible either:

- by using a pulsed source and increasing the current density. There are many difficulties involved with a pulsed source and very accurate synchronisation of the pulses with the interferogram sampling is essential along with reliable pulse repetition;
- or by increasing the path length travelled by the electrons between anode and cathode as is the case with a Penning discharge (PD) [13]. The PD can be operated with very low buffer gas pressures (e.g.  $3 \times 10^{-5}$  mbar) as the electric and magnetic fields confine the charged particles very effectively. Discharge voltages are of the order of 1 kV and intense lines are emitted of the cathode material and buffer gases. This source is very stable and is proving to be ideal for studies of doubly ionised spectra of the 3d transition group.

### 2.3. Steps in processing FT spectra

After transform of the interferogram to yield the spectrum, the production of a linelist is the first stage of the spectral analysis process. The linelist consists of wavenumber, intensity, signal-to-noise ratio and width. Commonly used programs are those of J. W. Brault, DECOMP [11] and its successors GREMLIN and XGREMLIN (developed by U.Griesmann and G. Nave), which can be used to fit Voigt profiles to the lines. Where HFS is present and the lines no longer show Voigt profiles, centre-of-gravity wavenumbers are found. Wavenumber calibration is carried out as described in Section 2.1.2 using standard lines. These could be either the 26 Ar II lines in the visible if the carrier gas in the source is Ar, or other standards such as Fe or Ni lines whose wavelengths are already accurately known and based on the Ar standard lines. The wavelength calibration is extended to the VUV and IR by overlapping broadband spectra. Any grating spectra also to be included in an analysis can then be calibrated from Ritz wavelengths determined from the FT spectra. For intensity calibration a line intensity standard is used to determine the response of the FT spectrometer, and this is applied to the linelist.

### 3. Examples of atomic spectroscopy projects carried out by UV-FTS

The complexity of the spectra, in particular of the 3d transition group elements, means that different project strategies are needed depending on the particular astrophysical application; in this section, examples of large and small scale studies are presented.

### 3.1. Large scale studies

### 3.1.1. Wavelengths and atomic energy levels: term analysis

3.1.1.1. Analyses of 3d element FT spectra. FTS covers the entire wavelength range of the spectrum of a particular neutral 3d transition element species, consisting of many thousands of emission lines, fully resolved. However, for singly and doubly ionised transition elements although most of the strongest transitions do fall in the FTS range, grating spectra are needed below the short wavelength cut-off, 140 nm, of the FT spectrometer.

A full term analysis of a complex spectrum involves identifications of thousands of lines, improving the known atomic energy levels and searching for new energy levels and is an extremely time-consuming undertaking. Initially, the known energy levels are

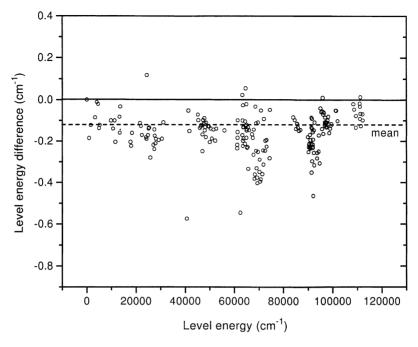


Fig. 4. Co II energy level differences between those based on grating spectra and FT spectra.

investigated; these subsequently typically improve in accuracy by at least an order-of-magnitude when accurate FT lines are used in their determination where previously only grating lines were available. The level values are improved by a least squares fitting procedure using all the identified lines. Some of the "old" levels may simply be incorrect, due to spurious chance coincidences of combinations of levels and grating spectral lines where the uncertainties were far larger than with FT data. Fig. 4 gives an example of the improvements possible in energy levels. The differences between the older grating-based energy levels and the improved FTS-based levels of Co II are plotted. Since the accuracy of the levels based on FTS measurements is usually between 0.001 and  $0.006 \,\mathrm{cm^{-1}}$  (depending on the strengths of the lines used in finding the level values) the errors in the grating-based levels are clearly seen to be large.

Once the known energy levels have been improved, new and missing levels can be searched for. In this procedure, predictions of energy level values and expected transitions based on theoretical calculations are very useful. LS labels are assigned to existing levels and using semi-empirical calculations the search can be very effectively narrowed down. In a

search for a new level the unidentified lines of the spectrum linelist are used together with selected levels which are expected to be involved in transitions with the level being searched for. When a possible level is found, the transition intensities can be compared with transition probabilities predicted by calculation—a very important check on the validity of the new level.

The recent work on Co I and Co II carried out at IC is a good example of the kind of improvement possible in the atomic data; FT spectra acquired in the VUV-VIS with the VUV IC-FT spectrometer and in the IR with the Kitt Peak FT spectrometer were used in an extensive study of the Co I and Co II spectra. In Co I, accurate wavelengths (0.002 cm<sup>-1</sup> for strong lines) of 2442 Co I transitions were found, 300 known energy levels were revised and 64 new levels reported [14]. In Co II, 215 known energy levels were revised and 222 new energy levels were found [15-17]. The number of identified lines was doubled. Fig. 5 shows a small portion of cobalt spectrum recorded as part of this project. As a result of newly found energy levels most of the lines in this spectrum segment were identified for the first time, and were due to 4d-4p transitions in Co II; many of the 4d levels were previously unknown.

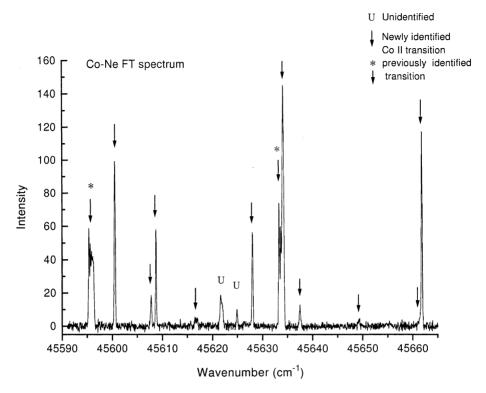


Fig. 5. Co-Ne high resolution Fourier transform spectrum showing transitions identified for the first time as a result of recent work [15].

In Fig. 6 a schematic diagram of the energy level structure in Co II is shown. Each box represents the energy levels, described by LS and J quantum numbers for that subconfiguration. The solid boxes represent the levels newly found as a result of the Co II spectrum analysis.

This kind of large scale term analysis has been carried out or is being currently undertaken for all the neutral and singly ionised 3d transition group element spectra mainly by either the group at Imperial College, or by the atomic spectroscopy group at Lund University, Sweden.

The atomic data from these large scale term analyses are fed into atomic databases used in calculations of stellar atmospheres and synthetic spectra. They are also of importance in atomic structure calculations, yielding better predictions of energy levels, improved level eigenvector compositions, and calculated transition probabilities which are used by astronomers where no laboratory life-time or branching ratio measurements exist.

### 3.1.2. Hyperfine structure and isotope shifts

Knowledge of hyperfine structure and isotope shifts are of great importance to astrophysics [18,19] to facilitate accurate abundance and velocity determinations and line broadening parameters. The high resolution and wide wavelength coverage of FTS enables large scale studies of HFS and isotope shifts to be undertaken. Other techniques may give greater resolution (such as Doppler-free laser spectroscopic methods), but FTS has the advantage of recording many hundreds or thousands of line profiles in one spectrum. Analysis of hundreds of line profiles is therefore possible unlike the handful-of-lines approach of other methods [6].

3.1.2.1. Hyperfine Structure. The fine structure levels are split by the hyperfine interaction between the nuclear spin and the orbital angular momentum of the electrons. In neutral and singly ionised 3d transition group spectra the HFS splittings are typically 0.1 cm<sup>-1</sup> in size. An example of HFS in

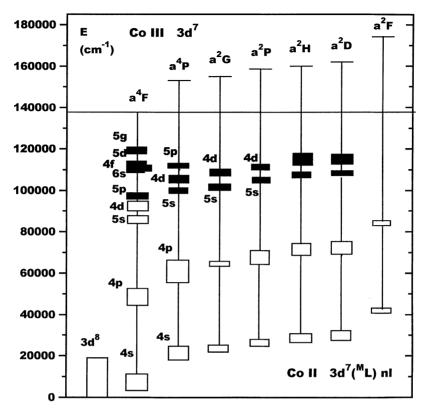


Fig. 6. Schematic diagram of the energy level structure in Co II. Solid boxes represent newly found energy levels.

Co I is shown in Fig. 7. However, these well-resolved components will not be seen in a stellar spectrum; the higher temperature of the star, its rotation or turbulance will all combine to produce a broad, and possibly assymmetric, line profile. To correctly fit such a line in a synthetic spectrum it is essential to know the HFS splitting factors, and wavelengths of the components and their intensities, and a good centre-of-gravity line wavenumber.

It is only with FTS that large scale studies of HFS are possible; an example is the dramatic increase in the knowledge of the hyperfine structure splitting factors, A, in Co I. The splitting of each fine structure level (with designated quantum number J) into hyperfine levels (with quantum number F) is given predominantly by the hyperfine structure splitting factor A for that fine structure level. Cobalt exhibits pronounced hyperfine structure which is well-observed by FTS. An analysis of over 1020 Co I line profiles yielded HFS A splitting factors for 297 of the 364 energy levels [6].

For 208 of these levels no previous HFS measurements were known.

It is only recently that large scale studies of HFS have been carried out and much still remains to be done, especially for the singly ionised species where few, if any, data on HFS exist.

3.1.2.2. Isotope shifts. The energy levels of different isotopes are slightly different because of two effects:

- the difference in nuclear masses leads to a "normal mass shift" and a "specific mass shift" [20] and
- the difference in nuclear volume leads to a "volume isotope shift" since the electrons are less tightly bound the larger the nuclear volume. The effect is appreciable especially for orbitals which represent an appreciable electron density at the nucleus, i.e. s electrons. Since the volume isotope shift varies depending on the configuration it can also be useful as an aid in level identifications.

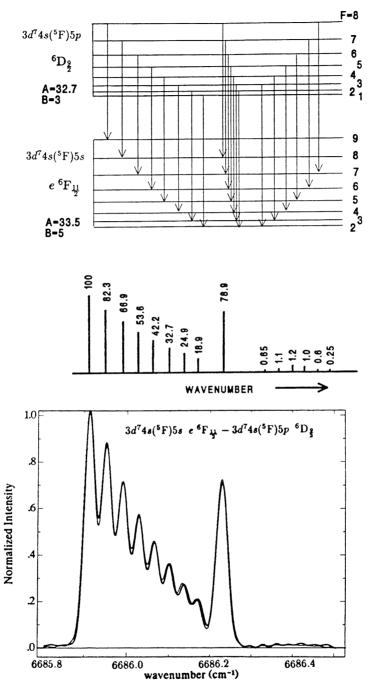


Fig. 7. IR Co I transition exhibiting hyperfine structure. The observed (bold trace) line profile is shown together with the fitted line profile (lighter trace) established by analysis of the HFS splitting factors of the levels involved in the transition. Also shown are the individual hyperfine components and the transition diagram.

So at high resolution, instead of one transition, a set of transitions is seen. The scale of the effect depends on the particular atomic state. In order to produce accurate synthetic spectra the absolute wavelengths of the components are needed, and the relative isotopic abundances determine the relative intensities. Sometimes the situation is further complicated when HFS and isotope shifts are simultaneously present.

An example where knowledge of isotope shifts is important and is seen in the analysis of chemically peculiar star γ Lupi [21]. Many stars have abundances of chemical elements that are close enough to the standard cosmic abundances that astronomers call them "normal". Sometimes, however, astronomers find stars where the observed abundances are so far from the so-called normal abundances that they are designated as chemically peculiar and y Lupi is one of these stars. Fig. 8a shows a portion of the emission spectrum of Pb III recorded with the IC VUV-FT spectrometer. In Fig. 8b, a segment of the stellar absorption spectrum of  $\chi$  Lupi is seen with the isotopic components of the same Pb III transition indicated. Whereas the 208 isotopic component is most intense in the laboratory spectrum, as expected since this has the greatest terrestrial abundance, in the stellar spectrum it is the normally weak 207 isotopic component, consisting of two HFS components, that shows the strongest absorption. This would indicate that the relative abundances of the Pb isotopic components in the atmosphere of  $\chi$  Lupi are completely different to the terrestrial relative abundances.

### 3.1.3. Oscillator strengths

Oscillator strength data (transition probabilities) are needed to approximately 10% accuracy [1] for astrophysical purposes. FTS is ideal for measuring relative line intensities, and hence branching ratios which when combined with level life-times yield oscillator strengths. If the emitting plasma is optically thin, then the transition probability of a transition k is given by [2]

$$A_k = \frac{(\mathrm{BF})_k}{\tau},$$

where the branching fraction  $(BF)_k$ , based on the measurement of relative intensities  $I_j$  of all transitions from a particular upper level with life-time  $\tau$ , is

given by

$$(BF)_k = \frac{I_k}{\Sigma I_i} = \frac{A_k}{\Sigma A_i}$$

and

$$\tau = \frac{1}{\sum A_i}.$$

Life-times are measured experimentally, usually by laser-induced fluorescence methods [12]. Although FTS is ideal for measuring BFs, there are, however, many challenges involved in making accurate measurements [22]. Intensity calibration of the spectra is carried out either with a standard lamp or a set of internal standard lines. For the BFs to be reliable, the emission lines should not be affected by self-absorption, i.e. the plasma must be optically thin. To avoid problems of self absorption which often affect stronger lines to the ground state, several spectra need to be recorded at a range of lamp currents: very low (to avoid self absorption of the resonance lines), medium (suitable for the majority of lines) and high (to detect the weaker lines). However, there will still be some lines which are predicted by calculation but which are not seen because they are too weak. The fractional contribution of these can be estimated by calculations of transition probabilities and needs to be included. It is also essential that all the stronger transitions fall within the spectral region covered. Much work has been carried out on branching ratios using FTS; recent examples of large scale studies include the following.

3.1.3.1. Ti II transition probabilities. The relative intensities of 694 emission lines of Ti II between 187 and 602 nm from 89 levels were measured using the IC-FT spectrometer. The branching ratios were combined with 39 measured and 44 computed life-times to give absolute transition probabilities for 624 lines [22].

3.1.3.2. Fe II transition probabilities: the FERRUM project. Accurate transition probabilities for Fe II re important in many astrophysical objects and until recently very few measurements had been made in the laboratory. As part of the FERRUM project [23], an international collaborative project to measure Fe II transition probabilities, the Imperial College VUV Fourier transform spectrometer and Penning discharge

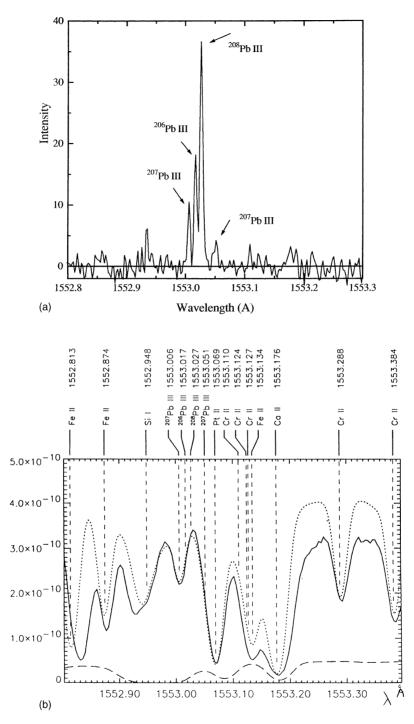


Fig. 8. (a) Section of high resolution lead spectrum, acquired using the Imperial College VUV-FT spectrometer, showing the different isotopic components of the 155.3 nm Pb III transition. (b) Section of spectrum of the chemically peculiar star  $\chi$  Lupi measured with the HST GHRS. The Pb III 155.3 nm transition is shown and it is noticeable that the stellar isotopic abundances are distinctly different to the terrestrial abundances (spectrum: D. Leckrone, S. Johansson, G. Wahlgren, C. Proffitt, private communication).

source have been used to measure the relative intensities of about 100 emission lines of Fe II between 160 and 350 nm (62,168–28,564 cm<sup>-1</sup>) from seven levels. The measured line relative intensities were used to determine the line branching fractions, which were then combined with accurate experimental radiative life-time measurements measured at Lund University to give absolute transition probabilities for around 100 lines. Typical uncertainties in the transition probabilities are less than 12% for strong lines and better than 20% for the majority of weaker lines. This work represents the first complete measurement of oscillator strengths of transitions from the four  $3d^6(a^3F)4p$ levels:  $y^4F_{7/2}$ ,  $x^4$  D<sub>7/2</sub>,  $y^4G_{9/2}$ , and  $y^4G_{7/2}$  [24], as well as new accurate data for f-values of transitions from the three  $3d^{6}(a^{3}F)4p \ y^{6}P_{3/2,5/2,7/2}$  levels.

### 3.1.4. Third spectra

Much progress has been made in the neutral (first) and singly ionised (second) spectra of the 3d transition

group elements. However, the atomic data for the third spectra of these elements is exceedingly poor. Third spectra dominate in hot star spectra, an example of which is shown in Fig. 9.

The current database for the 3d transition group element third spectra has insufficient spectral coverage, in many cases two orders-of-magnitude improvement in wavenumber accuracy is needed, there are almost no useful intensities or hyperfine structure data and, in many cases, an analysis includes only the lowest configurations. The strongest transitions of these third spectra fall in the VUV, where the IC-FT spectrometer has unique coverage. A program of observations and analysis is underway using the combination of PD source and VUV-FTS at IC. Studies have focused initially on Fe III in the UV-VUV at IC, and VIS-IR measurements were carried out with the new VIS-IR FT spectrometer of G. Nave at NIST. Full analyses of these spectra require grating spectra beyond the FTS cut-off.

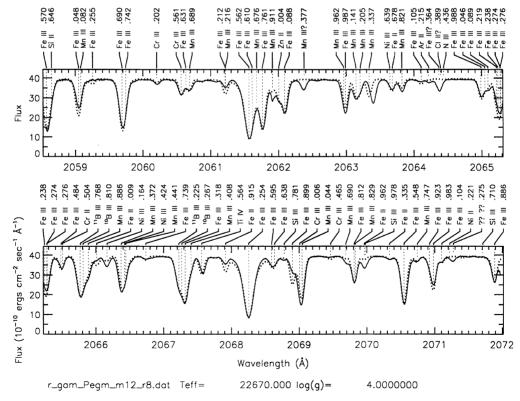


Fig. 9. A section of the high resolution spectrum of hot star γ Pegasus recorded using the HST (courtesy of C. Proffitt).

#### 3.2. Small scale studies

Here specific astrophysical problems can be targeted; examples include the following.

### 3.2.1. The thorium neodymium stellar chronometer

This is an example of when a particular line is needed for an accurate abundance estimate for that species but it may be blended with several lines of other species. This was the case for the ThNd stellar chronometer method where the ratio of Th to Nd abundance could be used as a key to the age of the Galaxy. The Th line chosen was blended with Fe, Ni, V and two Co lines with HFS [25]; the accuracy of the atomic data for these lines was vital in order to give meaningful estimates of the Th abundance and hence

Galactic age. The two Co I lines involved in the blend are shown in Fig. 10.

## 3.2.2. Wavelength measurements for determination of a possible time variation in the fine structure constant, $\alpha$

In another example, accurate FTS measurements of wavelength separations between selected transitions in the spectra of Mg I and Mg II, Cr II, Zn II, Fe II, and Ni II were made for applications in cosmology [26,27]. These separations depend on the value of the fine structure constant,  $\alpha = 1/hc(e^2/4\pi\epsilon_o)$ . By comparing measurements of the wavelength separations in the laboratory with those observed in distant high red-shift quasar spectra and in gas clouds along the line of sight to the quasars space—time variations in the fine structure

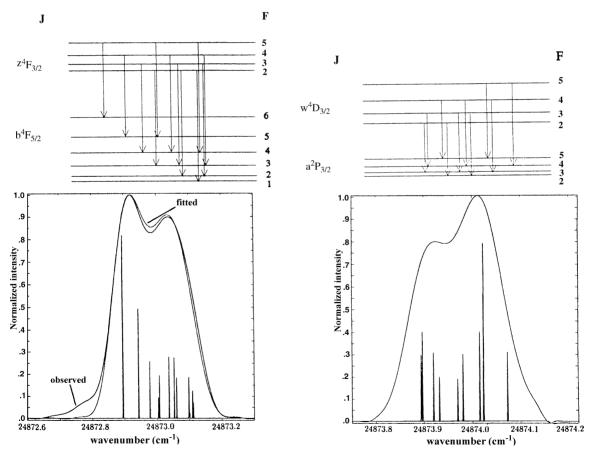


Fig. 10. The two Co I transitions at 401.9 nm which are blended with the thorium transition in stellar spectra used in the ThNd stellar chronometer technique.

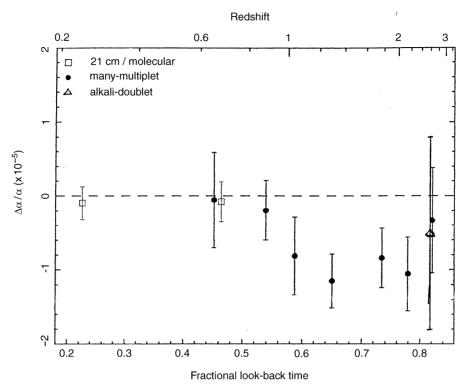


Fig. 11.  $\Delta \alpha/\alpha$  vs. red-shift and fractional look-back time to the big-bang (0: present day, 1: beginning of time). A total of 72 quasar absorption systems contribute to this binned data plot. The hollow squares correspond to H 21 cm and molecular absorption systems. The seven solid circles are binned results from 49 quasar absorption systems using the "many-multiplet" method. The hollow triangle represents the average over 21 quasar absorption systems using the alkali-doublet method. (From [28]).

constant can be determined. But these small differences are only meaningful if the accuracy of the laboratory atomic data is comparable and ideally better than that of the astrophysical spectra, which is the case for the new FTS measurements. Recent results reported by Webb et al. [28] made using quasar spectra indicate that there may indeed be evidence for cosmological evolution of the fine structure constant. Fig. 11, taken from [28], shows the change in  $\alpha$  with red shift and fractional look-back time. There is now evidence that  $\alpha$  has evolved by 1 part in 100,000 over the last 10 billion years.

Only a couple of examples of small scale studies are given here, there are however countless other studies made.

### 4. Molecular absorption spectroscopy by UV-FTS

UV absorption spectroscopy carried out at Imperial College has been primarily concerned with: the

penetration of UV solar radiation into the earth's atmosphere, the study of pollutants, and the study of spectra of importance in planetary atmospheres. Examples of work undertaken include the following.

# 4.1. Measurement of SO<sub>2</sub> reference spectra for remote monitoring using a dual beam FT spectrometer technique

The spectra of pollutants such as  $SO_2$  are required for interpretation of observations made using downward looking satellites. The UV absorption bands of  $SO_2$  can also be used to monitor volcanic activity on Io, one of the moons of Jupiter, as well as being important in studies of the atmosphere of Venus [29]. Two continuum sources were used in this work: a xenon arc continuum lamp for wavelengths greater than 213 nm and a high power deuterium lamp for wavelengths less than 213 nm. The continuum

radiation was first passed through a zero-dispersion double-prism premonochromator before entering the FT spectrometer. The choice of relatively narrow bandpass meant that the SO<sub>2</sub> column densities were optimised for each wavelength region and individual integration times for a high signal-to-noise absorption spectrum were reduced. It is important to establish an accurate baseline corresponding to zero absorption when absorption spectra are to be used to determine photoabsorption cross-sections. In the UV SO<sub>2</sub> spectra recorded with the IC-FT spectrometer it was realised that it was impossible to establish this baseline between the bands of transitions. The usual procedure of determining a baseline by repeating the experiment with an empty absorption cell could not be used since there were drifts in the xenon and deuterium lamp continuum spectra over time. To resolve this difficulty, in addition to the interferogram recorded with the absorption cell at the first output, the second output of the FT spectrometer was used to simultaneously record the spectrum of the lamp alone. The

two outputs could then be normalised from a run with the absorption cell empty, and so the ratio of the two spectra then gave the true transmission spectrum of SO<sub>2</sub> [29]. Figs. 12 and 13 shows a low resolution overview and a small high resolution segment of the photoabsorption cross-sections of SO<sub>2</sub> measured at 295 K.

### 4.2. Absorption spectra of $O_2$ in the UV above 205 nm

In the spectral region above 205 nm and below the ozone absorption bands the absorption of the atmosphere is dominated by the continuum adjoining the three systems of Herzberg bands of O<sub>2</sub>. Measurements of these very weak forbidden bands in the region 250–230 nm was carried out using a 3 m multi-pass absorption cell in front of the IC-FT spectrometer. The spectra have been analysed giving huge improvement in the data on wavelengths and absorption cross-sections [30–33].

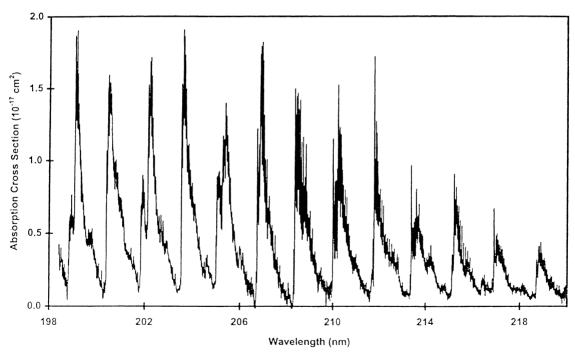


Fig. 12. Low-resolution overview of photoabsorption cross-sections for SO<sub>2</sub> measured with the IC FT spectrometer. For the purposes of the plot, the FT cross-section data have been convolved with a 60 mA\*Gaussian filter, and so the displayed peak cross-sections are lower than the measured peak cross-sections (figure from [29]).

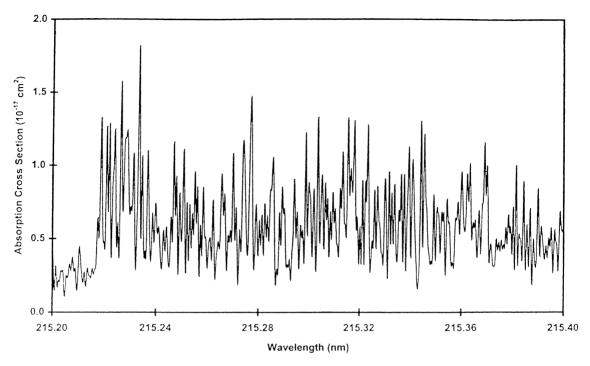


Fig. 13. Small segment of high resolution SO<sub>2</sub> photoabsorption cross-section (from [29]).

### 4.3. Absorption spectra of $O_2$ and NO below 200 nm

Below 200 nm the discrete absorption lines in the Schumann–Runge bands of  $O_2$  and the band systems of NO control the penetration of solar radiation in the earth's atmosphere. This process can be modelled if accurate wavenumbers are known, and high resolution is used to obtain true line profiles and absolute cross-sections. In the VUV reasonably intense laboratory background continuum sources are not available; synchrotron radiation is the ideal source of photon flux in the VUV. The IC VUV-FT spectrometer was taken to the Photon Factory (KEK) in Japan, and in collaboration with the Harvard–Smithsonian Center for Astrophysics, the spectra of  $O_2$  and NO were measured between 160 and 195 nm at resolution sufficient to resolve the line profiles [34–37].

#### 5. Conclusion

With FTS vast progress has been made in the last 10 years in improvements to the atomic and molecular

databases for astrophysics and atmospheric physics. For the atomic database much still remains to be studied, notably transition probabilities, more hyperfine structure and isotope shifts, and the spectra of the doubly-ionised transition group elements.

### Acknowledgements

The research reported in this paper has been funded by the Royal Society, PPARC and NERC of the UK, and NASA. JCP is funded by the Royal Society.

#### References

- D.S. Leckrone, S. Johansson, G. Wahlgren, C.R. Proffitt, T. Brage, Phys. Scripta T65 (1996) 110.
- [2] A.P. Thorne, U. Litzen, S. Johansson, Spectrophysics: Principles and Applications, Springer Verlag, 1999.
- [3] A.P. Thorne, Phys. Scripta T65 (1996) 31.
- [4] A.P. Thorne, C.J. Harris, I. Wynne-Jones, R. Learner, G. Cox, J. Phys. E 20 (1987) 54.
- [5] A.P. Thorne, G. Cox, R.C.M. Learner, P.L. Smith, W.H. Parkinson, Astron. Soc. Pacific Conf. Ser. 81 (1995) 235.

- [6] J.C. Pickering, Astrophys. J. Suppl. 107 (1996) 811.
- [7] G. Kalus, S. Johansson, G. Wahlgren, D.S. Leckrone, J.C. Brandt, A.P. Thorne, PASP 143, (1998) 326.
- [8] U. Litzen, J.W. Brault, A.P. Thorne, Phys. Scripta 47 (1993) 628.
- [9] R.C.M. Learner, A.P. Thorne, J. Opt. Soc. Am. 5 (1988) 2045.
- [10] G. Norlén, Phys. Scripta 8 (1973) 249.
- [11] J.W. Brault, Mikrochim. Acta (Wien) III (1987) 215.
- [12] J.E. Lawler, S.D. Bergeson, R.C. Wamsley, Phys. Scripta 47 (1993) 29.
- [13] C. Heise, J. Hollandt, R. Kling, M. Kock, M. Kühne, Appl. Opt. 33 (1994) 5111.
- [14] J.C. Pickering, A.P. Thorne, Astrophys. J. Suppl. 107 (1996) 761
- [15] J.C. Pickering, A.J.J. Raassen, P.H.M. Uylings, S. Johansson, Astrophys. J. Suppl. 117 (1998) 261.
- [16] J.C. Pickering, Phys. Scripta 57 (1998) 385.
- [17] J.C. Pickering, Phys. Scripta 58 (1998) 457.
- [18] R.L. Kurucz, Phys. Scripta T47 (1993) 110.
- [19] H. Hühnermann, Phys. Scripta 47 (1993) 70.
- [20] R.D. Cowan, The Theory of Atomic Structure and Spectra, University of California Press, Berkeley, 1981.
- [21] D.S. Leckrone, C.R. Proffitt, G. Wahlgren, S. Johansson, T. Brage, Astrophys. J. 177 (1999) 1454–1470.
- [22] J.C. Pickering, A.P. Thorne, R. Perez, Astrophys. J. Suppl. 132 (2001) 403–409.
- [23] S. Johansson, in: H. Rickman (Ed.), Highlights of Astronomy 12, 2002, in press.
- [24] J.C. Pickering, S. Johansson, P.L. Smith, Astron. Astrophys. J. 377 (2001) 361–367.
- [25] J.C. Pickering, J.I. Semeniuk, Mon. Not. Roy. Astron. Soc. 274 (1995) L37–L42.

- [26] J.C. Pickering, A.P. Thorne, J.W. Webb, Mon. Not. Roy. Astron. Soc. 300 (1998) 131–134.
- [27] J.C. Pickering, A.P. Thorne, U. Litzen, J.K. Webb, V. Zilio, Mon. Not. Roy. Astron. Soc. 319 (2000) 163–167.
- [28] J.K. Webb, M.T. Murphy, V.V. Flambaum, V.A. Dzuba, J.D. Barrow, C.W. Churchill, J.X. Prochaska, A.M. Wolfe, Phys. Rev. Lett. 87 (2001) 091301-1-4.
- [29] G. Stark, P.L. Smith, J. Rufus, A.P. Thorne, J.C. Pickering, G. Cox, J. Geophys. Res. 104 (1999) 16585–16590.
- [30] K. Yoshino, J.E. Murray, J.R. Esmond, Y. Sun, W.H. Parkinson, A.P. Thorne, R.C.M. Learner, G. Cox, Can. J. Phys. 72 (1994) 1101–1108.
- [31] K. Yoshino, J.R. Esmond, J.E. Murray, W.H. Parkinson, A.P. Thorne, R.C.M. Learner, G. Cox, J. Chem. Phys. 103 (1995) 1243–1249.
- [32] K. Yoshino, J.R. Esmond, W.H. Parkinson, A.P. Thorne, R.C.M. Learner, G. Cox, J. Chem. Phys. 111 (1999) 2960–2967.
- [33] K. Yoshino, J.R. Esmond, W.H. Parkinson, A.P. Thorne, R.C.M. Learner, G. Cox, A.S.-C. Cheung, J. Chem. Phys. 112 (2000) 9791–9801.
- [34] K. Yoshino, A.P. Thorne, J.E. Murray, K. Ito, T. Matsui, K.W.-S. Leung, A.S.-C. Cheung, T. Imajo, Phys. Chem. Earth 25 (2000) 199–201.
- [35] K. Yoshino, J.R. Esmond, W.H. Parkinson, A.P. Thorne, J.E. Murray, R.C.M. Learner, G. Cox, A.S.-C. Cheung, K.W.-S. Leung, K. Ito, T. Matsui, T. Imajo, J. Chem. Phys. 109 (1998) 1751–1757.
- [36] T. Imajo, K. Yoshino, J.R. Esmond, W.H. Parkinson, A.P. Thorne, J.E. Murray, R.C.M. Learner, G. Cox, A.S.-C. Cheung, K. Ito, T. Matsui, J. Chem. Phys. 112 (2000) 2251–2257.
- [37] J. Rufus, K. Yoshino, J.R. Esmond, A.P. Thorne, J.E. Murray, T. Imajo, K. Ito, T. Matsui, J. Chem. Phys. 115 (2001) 3719– 3723.