IAU Colloquium No. 8

Experimental Techniques for the Determination of Fundamental Spectroscopic Data

Reported by

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INTRODUCTION

The last ten years have brought significant changes to the venerable disciplines of astronomy and spectroscopy. Traditionally astronomers sought wavelength catalogues of identified spectra lines. Under this impetus spectroscopists laboured to provide very accurate wavelength measurements and estimates of emission line intensity. Physicists and astronomers alike are now recognizing interest not only in such properties of isolated atoms as energy levels (or spectral-line wavelengths) and oscillator strengths, but also those atomic properties which depend upon the surroundings of a radiating atom: spectral-line profiles, excitation rates, and level populations. In turn, new uses of lasers and interferometers, fast time resolution, and simple but significantly different absorption and emission samples are altering experimental spectroscopy almost beyond recognition. The present colloquium, chaired by *A.H.Cook* (University of Edinburgh) and held at Imperial College, London, on September 1–4 1970, aimed to identify the means by which astronomers can now obtain fundamental atomic data.

ASTRONOMICAL NEEDS

To set the stage, *J.C.Phillips* (University of California, Berkeley) reviewed a number of astronomical problems which require laboratory observations. Foremost of these remains the traditional task of identifying the atoms or molecules responsible for spectral lines. The ultra-violet and infra-red spectra gained from rockets and satellites provide a wealth of unidentified lines. (Roughly half the ultra-violet lines and three-quarters of the visible lines have been identified in the Sun, for example). Many of the ultra-violet lines undoubtedly

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originate in ionization stages which have been observed incompletely, if observed at all. Infra-red features of stellar spectra have been identified with CO and H_2O and with Fe, Si, Ca, C, and rare earths; unidentified features may be due to CO, CN, HCN and C_2H_2. Diatomic molecules, particularly oxides and hydrides, are prominent in the atmospheres of cool stars and in sunspots, and further data are needed on their spectra and dissociation energies. Astronomers would like to know more about negative-ion molecules, in order to assess their contribution to the opacity of cool stars. Specific needs include electron affinities of HS, CN, and H_2O, and photon-absorption cross-sections for SH^-, OH^-, H_2O^-, H_2S^-, C_2^- and CN^-. Triatomic molecules (H_2O, C_3 and NH_3 for example) and polyatomic molecules (H_2CO and HC_3N for example) occur not uncommonly in astronomical objects. Better knowledge of molecular spectra is required in order to ensure unambiguous identification, to permit further searches for molecular lines in the radio spectrum, and to ascertain whether molecules can be responsible for 26 hitherto unidentified broad interstellar absorption lines.

Astronomers' needs for theoretical studies of atomic structure were emphasized by *R.H.Garstang* (JILA, Boulder). Little is known about the spectra of highly ionized atoms, such as Fe XXV seen in the spectra of solar flares. We require laboratory analysis, together with better relativistic treatment of many-electron atoms, particularly calculations appropriate to nuclear charge, Z, intermediate between 1 and 137. Among the many interesting effects expected in the spectra of highly ionized atoms will be the increased intensity of magnetic multiple forbidden lines. The advent of high-resolution X-ray spectra underscores the need for a better understanding of how X-rays affect atoms, particularly the details of excitation and subsequent de-excitation of inner shells. In more traditional spectroscopy, there is still need for study of the hyperfine structure of lines which show very broad line profiles in stellar spectra (e.g. vanadium and gallium lines). Unfortunately our understanding of the theory of line broadening is still rudimentary. In particular we have no adequate theory to treat atoms which have a large hyperfine structure.

OSCILLATOR STRENGTHS

Traditionally, atomic oscillator strengths (or transition probabilities, or lifetimes) and wavelengths of spectral lines have been the two basic atomic properties used by astronomers. Apart from a report by *M.C.Artu* (Meudon) of measurements of 33 new ultra-violet emission lines of Mg IV (done in collaboration with *V.Kaufman* NBS, Washington) there was little discussion of wavelength determination.

Even routine revisions of oscillator strengths can have far reaching astronomical consequences. As pointed out by *S.Bashkin* (University of Arizona), the spectrum of neutral iron illustrates the sometimes indirect influence of oscillator strengths in astrophysics. Recent work suggests that iron lifetimes are a factor of 10 longer than previously assumed, leading to a factor of 10 greater iron abundance in the Sun. In turn, this increased abundance enhances by some 25 per cent the opacity in the solar interior, leading to higher temperature. Nuclear reactions are extremely sensitive to temperature (variations with the *twentieth* power of temperature, for example) so that one now predicts a greater rate of reactions and an increased production of neutrinos. But this revised neutrino radiance conflicts with observed upper limits to the neutrino irradiance received by the Earth. Thus assuming the new oscillator strengths are correct, astrophysicists must now re-examine their theories of solar structure.

W.L.Wiese (NBS, Washington) reviewed the status of data on atomic oscillator strengths. For very simple atomic systems (one and two electrons) the best oscillator strengths now come from theoretical calculations. For more complex atoms, emission spectroscopy is the major source; it provides large numbers of oscillator strengths although it is not the most accurate possible method. The hook method (mentioned below) provides a complementary method applicable to fewer lines. At present the most accurate measurements of oscillator strengths are those based on observations of atomic lifetimes. However, these methods are restricted in application to far fewer lines than the numbers observed in emission spectra. Thus a combination of lifetime and emission measurements will prove important in the future, with lifetimes serving to normalize the numerous relative values obtained from emission spectra. Looking ahead to the future, *Wiese* predicted the extension of emission spectroscopy to heavy elements, using say, metal chlorides; extensions into the ultra-violet and infra-red; and extension to the study of more highly ionized species.

An absolute determination of an oscillator strength from observation of emission spectra requires an absolute determination of both the light intensity (or radiance) and the number of emitting atoms. In making absolute measurements of light, one can deal with either a calibrated source of light (a standard of *radiance*) or with a calibrated detector (a standard of *irradiance*), as pointed out by *R.P.Madden* (NBS Washington). The tungsten lamp, which serves as a radiance standard in the visible spectrum, is not usable in the ultra-violet. Wall-stabilized hydrogen arcs provide a satisfactory continuum emission for wavelengths longer than 1215 Å. It is desirable to develop other electrodeless rare gas discharge lamps, preferably small and portable, to serve as secondary standards. A second possibility is

offered by synchrotron emission, which provides a continuous spectrum with a peak between 150–500 Å for a 180 Mev accelerator. However, the radiation is highly polarized and confined to a narrow sheet, so one must be cautious in making comparisons with thermally excited blackbody radiation. Basically, the use of an absolute standard of radiance relies on a theoretical prediction of light intensity. This means knowing the temperature of a blackbody source or, for synchrotron radiation, the number of electrons in the beam. Work on ultra-violet irradiance standards at NBS has relied in large measure upon thermopiles calibrated in the visible and extended into the ultra-violet. However, thermopiles are very slow, and so considerable work is underway to develop photo-diodes as secondary standards. Various diode configurations are being examined (transmission cathodes, opaque cathodes, and windowless diodes) in order to surmount such diffiulties as charge build-up on windows, wall effects, and non-uniform response across the cathode surface.

Ambiguities and uncertainties in the determination of particle density have been responsible for errors of orders of magnitude in oscillator strengths. As *W.L.Wiese* pointed out, spectroscopists have traditionally dealt with this determination by employing light sources whose excitation was presumably governed by the Boltzmann distribution. Application of this distribution, which may be regarded as a partial Local Thermodynamic Equilibrium (LTE), allows one to parameterize the atomic populations in terms of a single number, the temperature. Many of the earlier results are incorrect because authors failed to account for departures from LTE, self-absorption, spatial inhomogeneities, high-density corrections, contributions from background and wings of distant lines, and unreliable diagnostics. There are also discrepancies within modern work. Although some of these can be traced to the use of different diagnostic techniques, other discrepancies remain unexplained.

In recent years there has been considerable interest in more direct measurement of radiative lifetimes, thereby eliminating the need for density measurements. *S.Bashkin* reviewed these methods. First, there are several methods based on magnetic field splitting of energy levels: the Hanle effect, level crossing, and double resonance. These techniques have been used on a relatively few lines (about 50) with an accuracy of 10 per cent or better. The recognized sources of error include radiation trapping (lifetime enhancement) and pressure broadening (lifetime shortening). Results are generally limited to resonance levels of atoms, although a few experiments have been done on low-lying levels of singly-ionized atoms.

Lifetimes can also be measured directly by observing the radiative decay following a pulsed excitation by either electrons or photons.

The excitation need not be an impulse: one can use a sinusoidally varying excitation and observe the phase delay of the emergent sinusoidally modulated de-excitation. In applying these techniques, one must account for the possibility of cascading radiative decays. Delayed coincidence measurements eliminate the effects of cascading. Some 100 atomic lifetimes and an equal number of molecular lifetimes have been obtained by delayed-coincidence methods.

A very promising technique for measuring lifetimes is the beam-foil technique, discussed at length by *Bashkin*. Accelerated ions, passing through a foil, are impulsively excited; moving away from the foil at constant velocity, they radiatively decay. A measurement of distance downstream from the foil is equivalent to a measurement of time subsequent to excitation. Thus the lifetime can be found by following the intensity diminution of a spectral line with downstream distance. The method permits study of large numbers of lifetimes for all elements, in many stages of ionization, throughout all wavelength regimes. Densities are quite low (say 10^4 cm^{-3}) so that density effects are negligible. However, not all spectral lines follow the simple exponential decay law expected for direct radiative de-excitation: some lines are in fact unresolved blends of two or more lines with different lifetimes, and some transitions are fed by radiative cascade. These, and other difficulties, cause disagreement between different laboratory determinations, and so it is essential to have independent observations at several laboratories.

Molecular spectroscopy is, in many respects, much more complicated than atomic spectroscopy and it provides a great challenge for both experimenter and theorist. The strengths of molecular lines depend, in addition to molecular populations, on the product of three factors: an electronic factor, a Franck–Condon factor (dependent upon vibrational quantum numbers), and a Hönl–London factor (dependent upon angular momentum quantum numbers). The Hönl–London factors, though simple in principle, permit ambiguity of definition; as a result, the literature contains a confusing variety of definitions. *J.B.Tatum* (University of Victoria, British Columbia) spoke for the meeting concensus in pleading for a definition based on unit normalization (as discussed in *Astrophys. J. Suppl*, **124**, 1967). The Franck–Condon factors are more difficult to calculate, but the advent of high speed computer codes has now made their computation a routine matter.

It seems clear that major contributions to atomic and molecular physics will be made by laboratories which draw together both experiment and theory. *R.W.Nicholls* (York University, Toronto) outlined such a concerted programme of studies on molecular spectra now being carried out at the Centre for Research in Experimental Space

Science (CRESS) at York University. The laboratory studies include (a) preparation of line-identification atlases; (b) observation and measurement of wavelengths and intensity structure (e.g. in O_2, NO, CO, SO, BeO, AlO, TiO and VO); (c) the determination of dissociation energies; and (d) application of computer codes to the Loomis–Wood method of analysing band systems. These endeavours are supported by a parallel programme of theoretical work including (a) studies of diatomic molecular potentials and the concomitant vibration-rotation wavefunctions; and (b) studies of line strengths in molecular spectra. Computer codes play an indispensable role in the CRESS programme, both to unravel observed spectra and to produce synthetic spectra.

EMISSION AND ABSORPTION SOURCES

In view of the astrophysical importance of highly ionized atoms, *A.H.Gabriel* (Culham) reviewed the techniques which are available for producing and analysing the spectra of these atoms. The techniques have advanced noticeably during the last decade. The simplest procedure, a vacuum spark, produces a spectrum of the electrode material. Though this technique is applicable to a wide range of elements, it is poorly reproducible and very inhomogeneous. An improvement, the sliding spark, uses an insulator between the electrodes to guide the spark and improve stability and reproducibility. Low-inductance sparks, which employ a third, triggering, electrode, have been used for low-excitation. This type of device can also produce high ionization stages, as a result of a recently discovered instability. In recent years, a variety of plasma devices, wherein trace elements are added to hydrogen filler gas, have been used as sources of ions. Quite a different approach is provided by laser-produced plasmas: a Q-switched laser, focused on to a solid, produces a very pure, small, hot source. The plasma expands and cools after the laser is switched off, so that one can isolate by spatial resolution the radiation from successive stages of ionization. As *Gabriel* pointed out, excitation conditions vary markedly amongst the several types of sources. At one extreme, in sources of high density, atomic levels are brought into equilibrium with thermal particles. Such conditions produce highly excited levels and levels which radiate intersystem lines and two-electron transitions. At the other extreme, in a source of low density, atoms are excited by single collisions followed by radiative decay. These conditions are similar to those prevailing in the solar corona; they favour the excitation of resonance lines and single-electron excitation, whilst failing to produce many of the transitions seen in a thermal source.

Plasma emission and absorption sources, though viewed with some distrust in the past, have proven extremely reproducible and reliable. A variety of experimental techniques, discussed by *D.D.Burgess* (Imperial College), now provide consistent diagnostics of these sources. These techniques include the measurement of continuum intensity (providing a measure of T^4 for thick sources, or a measure of electron density for a thin source), the observation of reference-line profiles (the Hβ line is customarily used) and measurement of the refractive index (from which one deduces the plasma frequency). A laser interferometer can be an excellent device for determining refractive index, particularly for pulsed sources: the measurement then consists of counting the number of fringes which sweep past a fixed detector during the course of the pulse.

Conventional arc sources are also capable of improvement. *E.W.Foster* (University of London Observatory) described his work using an arc surrounded by a liquid vortex. The evaporating liquid can generate turbulence and thereby ensure plasma mixing, although the mixing is not complete when alcohol is used. *Foster* has used vortex arcs in determining oscillator strengths for selected lines of O I, C I, Cl I, Cl II, S I and S II.

For years, the spectroscopist's ideal has been a steady, reproducible, homogeneous source—sharply defined in spatial extent, and of precisely defined and regulatable temperature. This ideal is very closely approached in the heat-pipe oven described by *C.R.Vidal* (NBS, Boulder). The device (*J. appl. Phys.*, **40**, 3370; 1969) is based on the evaporation of a sample at the centre of a tube under pressure of an inert noble gas. The sample condenses at the tube ends, and is drawn by capillary action of a stainless steel wick back to the tube centre for re-evaporation. The temperature of sample evaporation, which is within 1° C of the temperature of condensation, is set by the pressure of the inert gas, and it may be readily determined from the vapour-pressure curve of the sample. The source vapour purifies itself during operation. The absence of confining end-walls makes the device a suitable absorption cell for the vacuum-UV spectral region. Use of a double heat-pipe promises still further improvement in oscillator strength determinations.

LINE PROFILES

Lists of wavelengths and oscillator strengths do not exhaust the atomic data required in astrophysics. One must also be able to predict the frequency dependence of the absorption coefficient for spectral lines. However, as *D.D.Burgess* pointed out, a spectral-line profile cannot be characterized by an atomic damping constant which can be

tabulated once and for all. Line profiles depend sensitively upon the nature of the medium which surrounds the radiating atom; any damping factor must vary with temperature, pressure, and composition, and will depend upon whether electrons, ions, or neutral particles most influence the radiating electron. More specifically, the relative importance of these different types of perturbers varies over the frequencies of the spectral line: in the centre of the line, the profile is primarily influenced by impulsive collisions between the radiator and fast particles, whereas in the line wings the profile is primarily determined by random quasi-static fields. The latter fields also induce satellite lines attributable to transitions which would be forbidden in the absence of static fields. Furthermore, different mechanisms dominate different spectral regions: shorter wavelength lines are primarily influenced by strong binary collisions, whereas infra-red lines are more sensitive to collective effects in the plasma medium. Thus one should keep in mind that a satisfactory theory of line shapes must combine atomic theory (for the calculation of collision cross-sections) with statistical theory (to incorporate particle correlations within the medium). There exist a variety of prescriptions for calculating line profiles, or portions of line profiles, and these have been able to account for the essential features of line profiles under selected conditions. However, there are known failures: a quantitative description of the induced forbidden (satellite) lines has not yet been satisfactorily produced. (Theory also predicts too much structure in the centre of the Balmer lines, according to *W.L.Wiese*.) In view of all these comments, it is essential to carry out observations under conditions which closely mimic astrophysical conditions, and to make such observations for a range of densities, temperatures and compositions. It is at present very risky to extrapolate results into very different regimes.

Studies of the influence of a neutral noble-gas atmosphere upon line shapes of impurity atoms have been a traditional source of information on pressure broadening. *W.R.Hindmarsh* (University of Newcastle) pointed out that the present theoretical descriptions of line broadening produced by impacts of neutral perturbers are restricted to elastic collisions with projectiles which follow straight paths. Such theories provide a connection between line shapes and intermolecular potentials. There is a need not only for better knowledge of intermolecular potentials, but also for a theory which includes the effects of inelastic collisions and close encounters.

Although studies of line shapes in noble-gas atmospheres provide an interesting field of investigation, they have no direct application to the line profiles required in astrophysics. Astronomical spectral lines are formed in media where either neutral hydrogen atoms or ions and electrons predominate. Hydrogen, with its half-filled electron shell,

does not have the same influence as a neutral closed-shell atom. Unfortunately, a source of hot hydrogen, mimicking the solar conditions of 5000°K and 10^{18} atoms cm^{-3} has not been available hitherto. Now, as announced by *W.H.Parkinson* (Harvard College Observatory), just such a source has been developed. The device, developed in collaboration with *J.Grindlay* and *D.D.Burgess*, is quite simple in principle: a piston is driven, by impulsive expansion of pressurized gas, down a hydrogen-filled cylinder. The hydrogen, heated by compression, yields few free electrons, so that line shapes are not dictated by electron impacts or Stark effects. The Harvard investigators routinely monitor a variety of concurrent diagnostics in order to ensure that the gas conditions are well understood. Measurements include gas pressure (as a function of time), continuum emissivity, and laser-interferometer determination of electron and neutral particle density. Line profiles are observed by means of a rapid-scanning Fabry–Perot interferometer or with light-pipe photomultiplier detectors. The first observations have disclosed widths for the sodium lines which are eight times greater than theoretical predictions had indicated.

CROSS-SECTIONS

In many astronomical sources, atomic populations depart significantly from the Boltzmann law of thermal equilibrium. Populations are governed instead by a set of coupled equations which balance gains and losses of population. Laboratory studies of excitation and ionization rates are required if one is to understand such gases.

Conceptually, the most direct measurements of cross-sections are obtained from the observation of intersecting streams of particles, as in the work of *K.Dolder* (University of Newcastle), who studies electron-impact induced ionization using crossed ion-electron beams. At present, theoretical results lag far behind experiments: the commonly-used Coulomb–Born approximation is accurate only for electron energies in excess of 20 times threshold; the proportionality between cross-section and the square of the ionization potential—which classical theory predicts—has been found to be in general accord with observations of several isoelectronic sequences, but it fails for the neon sequence (Ne, Na$^+$, Mg^{+2}). The quantitative influences of autoionizing resonances and of electron correlation are, as yet, not known.

G.E.Chamberlain (NBS, Boulder) emphasized that published excitation cross-sections show alarmingly large discrepancies between different experimenters, far exceeding quoted experimental error. He stressed the importance of detailed documentation with attention to the calibration of gas pressure and radiometry, careful construction of electron guns without magnetic fields, and measurements at low density with dual determinations of density.

Given values for excitation and ionization cross-sections, one can, in principle, predict atomic populations and, in turn, line intensities for arbitrary plasmas. *R.W.P.McWhirter* (Culham) described such comparisons carried out over the last few years at Culham. Observed intensities are within ± 50 per cent of those predicted with the use of theoretical cross-sections. Further progress will require cross-sections accurate to ± 10 per cent.

In order to know the rates at which atomic and molecular processes occur in the Earth's atmosphere, or in interstellar clouds, we require a more quantitative description of the cross-sections for absorption of photons with subsequent ionization or dissociation. As *J.A.R. Samson* (University of Nebraska) emphasized, we need not only the total photon attentuation cross-section (as obtained from traditional absorption measurements) but also the partial cross-sections for producing ions in their various energetically allowed excited states. Present techniques, reviewed by *Samson*, permit collection of the photon-produced ions or else collection and energy analysis of photoelectrons.

OTHER NEW DISCOVERIES AND NEW TECHNIQUES

New discoveries continue to be announced in spectroscopy. High-lying atomic levels, with principal quantum numbers of one or two hundred, have been known for several years from radio observation. (The transition between $n = 110$ and $n = 109$ is a well-known feature of the radio spectrum from interstellar clouds.) Now, for the first time, optical observations have been extended into this realm of high quantum numbers: *W.R.S.Garton* (Imperial College) announced the observation of principal series in Barium out to a transition originating at $n = 103$. These observations, carried out with *F.S.Tomkins* (Argonne National Laboratory) using the Argonne 30 ft spectrograph, mark a new record for optical-series observations.

Both iron and hydrogen are prominent elements in the Sun, and so it is not unreasonable to anticipate that iron hydride might be present. Unfortunately, the spectrum of FeH has never previously been observed, although numerous workers have sought it for years. Now, using a King furnace and high resolution, *P.K.Carroll* (Dublin) has seen some 200 lines, both in emission and absorption, which can be attributed to FeH. Furthermore, some 30 of these lines correlate with lines in the Revised Rowland Atlas of solar lines. Although the lack of well-defined band systems has thus far prevented an analysis of the FeH spectrum, the identification of FeH in the solar atmosphere appears secure.

The reliance of spectroscopists upon those venerable tools, the spectrograph and the photographic plate, is being eclipsed by imaginative new devices for examining spectra. Although fast shutters for spectrographs have extended their usefulness by permitting time resolution of pulsed emission and absorption spectra, it appears that interferometers will, in the years ahead, become basic spectroscopic instruments. Reported applications of interferometry ranged from the far infra-red to the ultra-violet.

A.Costley (NPL and Imperial College) described the development of an interferometer to obtain the spectrum of plasma emission in the far infra-red. This spectrum is obtained from the Fourier transform of the interference function obtained by varying the path length within a Michelson interferometer. This technique, applied to pulsed sources with *D.D.Burgess*, provides useful information for plasma diagnostics: the far infra-red spectrum yields measures of plasma frequency, of blackbody temperature, and of optical thickness. In turn, such diagnostics are essential in studies of line broadening and of molecular kinetics.

Looking towards the opposite end of the spectrum, *G.H.C.Freeman* (National Physical Laboratory) described a Michelson interferometer which he is using to study wavelengths and line shifts in the ultra-violet spectrum of mercury.

Illustrative of the new approaches to spectroscopy are the refractivity studies, reviewed by *M.C.E.Huber* (Harvard College Observatory). Basically the studies are based on the connection between the absorption coefficient and refractivity: the occurrence of a Lorentz-profile spectral line seen in emission or absorption must be accompanied by a dispersion-profile variation of the refractive index. In application, light is passed through an interferometer containing the sample gas in one arm. The emerging intensity, when analysed with a spectrograph, forms an interference pattern of fringes. At wavelengths where absorption lines occur, the fringes follow a characteristic hook pattern; the wavelength separation between hooks is proportional to oscillator strength, and so provides an alternative to measurement of light intensity. The hook method for determining oscillator strengths works best for strong (optically thick) well-separated spectral lines. For such lines, the method is insensitive to line width. However, it is difficult to apply the method to weak lines. Though conceived in 1912, the method is still little used. At Harvard, measurements are carried out simultaneously of absorption and refractivity of shock-heated gases, and a computer code is used to analyse the data incorporating the refractivity of a hundred spectral lines. Particular attention has been paid to the measurement of Fe I oscillator strengths; results of high precision have been obtained. Looking to the future, *Huber*

mentioned the significance of examining the refractivity associated with autoionizing lines, whose Beutler–Fano absorption profiles should produce characteristic refractivity profiles distinct from ordinary lines.

Further applications of the hook method, to molecular spectroscopy, were discussed by *Lady Anne Thorne* (Imperial College), who pointed out two advantages of this method over conventional absorption spectroscopy: one does not measure intensity, and one does not require high resolution. In application to molecular spectra, the primary limit to accuracy comes from ignorance of molecular dissociation potentials, leading to uncertainty in populations. Hydride spectra, with their characteristic open structure where individual rotational lines are readily discerned, are well adapted to the hook method. *Lady Anne* has examined the ultra-violet system of OH. Because of the astrophysical importance of hydrides, it may be worth while to undertake a major investigation of hydrides, using the hook method. In more crowded molecular spectra, where only the band heads can be discerned, the hook method provides a measure of the total oscillator strength within the band. *Lady Anne* has analysed bands in NO in this way.

Work by *T.McIlrath* (Harvard College Observatory) with laser-exited states suggests a seemingly endless list of potential applications. His basic procedure makes use of a tunable dye laser to populate one or more excited states. Present laser technology permits one to apply megawatts of power in a predetermined bandwidth (which can be fixed between 100 cm^{-1} and $0 \cdot 01$ cm^{-1}) centred on an arbitrary wavelength (between one micron and 3000 Angstroms) during a controlled time interval (variable from picoseconds to tens of microseconds). It is possible to obtain a source in which half the atoms in the line of sight are excited to a pre-selected level. The excitation initially produces a coherent state whose properties differ significantly from a thermally excited state. The excited system can then be examined using standard absorption-spectroscopy techniques. *McIlrath* has applied this technique to study the absorption spectrum of excited calcium by selectively populating the $4s4p\ ^3P_1$ level with a 30 nanosecond pulse which produced some 10^{16} excited atoms. The absorption spectra show, as one expects, series of absorption lines originating with the excited level, including autoionizing lines and photoionization. In addition, a variety of more subtle effects can be seen. For example, the initial coherent state relaxes toward a thermal distribution of populations; measurements of this relaxation time provide values of cross-sections for electron-impact induced transitions between fine-structure levels.

In summary, the colloquium heard of new techniques and new observations, and of refinements in more traditional work. The overall picture was of a subject offering broad opportunity for significant research by physicists with imagination and who are able to make full use of sophisticated instrumentation, data-reduction techniques, and advanced computer codes.