Measuring the very distant

Detectors: novel technologies and new markets

In the infrared and submillimeter region as in the X- and gamma ray region, advances in detector design are constantly being made. A number of CEA teams are contributing to such advances, with a view to applications that are forever broader-ranging.



Molecular-beam epitaxy equipment, operated at CEA's Grenoble Center to fabricate the active layer (HgCdTe) used in the new generation of infrared detectors.

Infrared: from HgCdTe crystals to microbolometers

Infrared detector technologies have been seeing constant advances over the past fifteen years or so, and have now achieved industrial maturity, allowing production of detectors usable for thermal imaging (320 × 240, 640 × 480, 1,024 × 1,024 **pixels**) at ever lower costs.

Research work in this area, carried out in the Infrared Laboratory at CEA/LETI (Laboratoire d'électronique et de technologie de l'information: Electronics and Information Technology Laboratory) from 1978 on, at the behest of the French DGA (Délégation générale pour l'armement: General Delegation for Armament) laid the ground for the rise, in France, of an industry, through the activity of Sofradir (a joint subsidiary of Thales, Safran, and Areva), ranking nowadays as one of the undisputed world leaders in the field. Such technologies, hitherto dedicated to military, scientific or space applications, are now finding a considerable civilian market opening up, with the emergence of low-cost, microbolometer-based detector technologies.

Why seek infrared vision?

All bodies, due to their inherent temperature, emit light, at wavelengths that lie beyond the visible region of the spectrum (0.4–0.8 micrometers [µm]), mainly in the 5–10 m range. This infrared radiation is linked to their thermal emission, the behavior of which

is described by Planck's law. For such wavelengths, the Earth's atmosphere exhibits remarkable properties, with very extensive windows of transparency $(3-5 \mu m,$ 8–12 μm). If these low-energy photons can be detected, by means of a suitable sensor, objects may be seen from very far afield, with no need to illuminate them. This type of infrared imaging is know as passive imaging, as distinct from active imaging, which requires a light source to be shone on the objects, to view the light reflected from them, as is the case with the human eye in the visible range.

High-performance infrared detector technology The concept of high-performance infrared detection relies on the direct photovoltaic conversion of photons into electron-hole pairs within a semiconductor, this being the basic principle of solar cells. The most widely used crystal is mercury-cadmium telluride (HgCdTe), which exhibits outstanding properties. This semiconductor, which may be fabricated into monocrystalline thin films, of very high quality, exhibits a direct gap that can be tuned by acting on the compound's composition, for all infrared detection bands, with a steady crystal lattice constant. The mastery achieved at LETI, of HgCdTe growth technology, planar *n*-*p* junction⁽¹⁾ fabrication, and the interconnection of such detector arrays with silicon readout circuits (CMOS: complementary metal-oxide semiconductor) was the key factor in Sofradir's success.

A hybrid architecture is that most widely adopted nowadays for these arrays. The CMOS circuit is used to process the information from the detectors, and turn it into a video signal. Such arrays, which may be fabricated to complexities exceeding the megapixel, for pitches as small as 15 µm, achieve theoretical ultimate thermal resolutions of a few thousandth of a degree Kelvin, provided they are cooled to some – 196 °C. These cryogenic constraints, which represent one factor in the high cost of such components, currently restrict this technology (a few tens of thousand product items per year, worldwide) to applications in the military (missile guidance, surveillance cameras), scientific (most commonly **spectroscopic** analysis through observation of absorption lines in the infrared; see Box D, Chromatography, spectroscopy and spectro*metry*) and space fields (satellite observation of the Earth, other missions).

Infrared detectors for astrophysics In this area, the ISO telescope for ESA, put into space by an Ariane 4 launcher in 1995, featured an infra-



Position, on the US Cassini probe, in orbit around Saturn since 2005. of the CIRS (Composite Infrared Spectrometer) spectrometer, featuring an array of 10 HqCdTe infrared detectors fabricated by CEA/LETI, the associated electronics being made at DAPNIA in partnership with CNES. To the right may be seen the European Huygens probe, which landed on Titan in January 2005.

red camera (ISOCAM), for which the detector had been made by CEA/LETI (gallium-doped silicon elements, cooled to 4 °K, for detection down to 17 µm) (see Infrared, X- and gamma radiation: nonvisible wavelengths to probe the Universe). This type of component has also been fitted to Earth-based telescopes. The US Cassini probe, which has been orbiting Saturn since 2005, also carries a spectrometer (CIRS), featuring an HgCdTe infrared detector array fabricated by CEA/LETI. One of the goals of that mission is to detect the presence of organic molecules in the atmosphere of Titan, one of Saturn's satellites (wavelengths down to 10 µm). Currently, CEA/LETI are fabricating a very-long-wavelength detector array (200-600 µm) intended for the PACS spectrometer on the Herschel satellite (very long wavelengths are used for the purposes of observing very cold objects out in the Universe, close to absolute zero). This component, operating at 0.3 °K, employs a detector architecture based on cooled microbolometers. These space programs are carried out in collaboration with CEA's Astrophysics Department (SAp: Service d'astrophysique), which is responsible for the instruments (see Infrared, X- and gamma radiation: nonvisible wavelengths to probe the Universe).

From the second to the third generation

Only a few groups around the world have shown the ability, over the past twenty years, to bring to industrial maturity these very-high-performance detector technologies. These include, mainly, Raytheon, DRS, and Rockwell in the United States, and, for the rest of the world, Sofradir, along with - to a lesser degree - AIM in Germany, SELEX in the United Kingdom, and SCD in Israel. Other technologies are gradually coming in to compete with the HgCdTe pathway: to wit, technologies based on InSb semiconductors (operating in the 3-5 µm band), or GaAlAs and InAs/GaSb semiconductors, the latter group involving use of quantum wells⁽²⁾ or superlattices,⁽³⁾ and operating in the 3-5 µm or 8-12 µm bands. All of these technologies exhibit performances that are inferior to that of HgCdTe, at comparable operating temperatures.

The major challenge, over the next ten years, will be that of mastering the third generation of components, that of multicolor detector arrays, which will gradually be supplanting single-color arrays. These should have the ability to carry out imaging simultaneously in a number of bands, in order, in particular, to obtain information on the observed objects' absolute temperature. As regards HgCdTe, growth by molecular beam epitaxy is the only way to achieve multilayer structu-

(1) Planar n-p: a semiconductor fabrication process, whereby ultimately three superposed regions are obtained: one consists in the original semiconductor (n-type silicon), a second one is formed by the first diffusion (p-type silicon), and the third is formed by the second diffusion (n-type silicon). Using the planar technique, a large number of transistors may be obtained simultaneously.

(2) Quantum well: a component of nanometric size, in which each electron may only travel in two spatial dimensions, being constrained by a semiconductor of wider band gap. (3) Superlattice: a periodic multilayer structure of atomic

or molecular layers, consisting in the repetition of an elementary pattern comprising a number of chemically different successive layers.

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res with the ability to effect such detection, while conserving spatial coherence for the information. CEA/LETI is conducting major research programs in this area, with support from DGA, in collaboration with Sofradir, for HgCdTe, and Thales, for GaAlAs. Initial prototypes at representative formats (320×256), on a par with best world standards, have already been fabricated.

Low-cost, microbolometer-based infrared detectors

A revolution in infrared imaging occurred about fifteen years ago, when US manufacturers Honeywell unveiled a new detector concept, allowing thermal imaging while not requiring sensor cooling. Taken up by such companies as Raytheon, DRS, BAe and FLIR Systems, this concept uses tiny bolometers, directly fabricated into arrays on CMOS circuit wafers. These microbolometers comprise an extremely thin platelet (0.1 µm vanadium oxide), termed the thermometer, suspended between two connector electrode arms. Such detectors operate on a very different principle from that of quantum detectors making use of direct photovoltaic photon-electron conversion. They are thermal detectors: as it takes up infrared photons, in the 8–12 µm band, the platelet heats up, resulting in a variation in its resistivity, enabling the CMOS circuit to convert this optical signal into an electrical signal, and video imagery. Combining this



2,048-pixel focal plane of the microbolometer infrared detector for the PACS telescope, carried on the Herschel mission, constructed by LETI. This will enable observation to be carried out in the 60–210 μ m range of the far infrared (black-body emission in the 14–50 K range).

extremely simple, batch-production (and hence lowcost) **above IC** technology with freedom from cryogenics made it possible to contemplate very early cost reductions, and availability for civilian applications. The sensitivity of such cameras only attained 1/20 of a degree, this being adequate for most applications not calling for image collection at great distances.

CEA/LETI initiated work very soon after Honeywell's publication, with support from DGA. After ten years' research work, a simpler, more readily industrializable process than Honeywell's was developed. This uses an amorphous silicon platelet, rather than vanadium oxide. The process was transferred to Sofradir in 2000, the company setting up in 2001 a subsidiary, Ulis, to bring it to industrial production, this company now standing as the largest manufacturer of microbolometerbased infrared detector arrays worldwide, outside of the United States.

Major advances have been achieved in terms of performance, and pitch reduction. Arrays in 320×240 format, for a 35-µm pitch, are already available, with sensitivities of a few hundredths of a degree; while 640×480 arrays on a 25-µm pitch are entering production. With regard to this technology, the challenge is to retain thermal resolution when narrowing detector pitch, as it becomes increasingly difficult to retain good thermal isolation of the thermometer platelet, with respect to the connector arms, to guarantee good sensitivity. CEA/LETI is collaborating with Ulis on this technology, for which production is assessed, in the longer term, at several million components per year.

The areas of application for uncooled, microbolometer-based thermal infrared cameras are many. Highly compact as these are, they are already employed by many users, particularly in the area of medicine (screening fever-infected passengers at airports, or monitoring patients in hospitals, early detection of skin cancers...). As regards security, they will allow nighttime viewing of intruders inside premises, monitoring, in industrial sites, the overheating of electrical components or machinery, liable to result in an explosion, or pollution. Firefighters are extremely keen on this type of equipment, allowing them as it does to locate through smoke inert bodies, or to visualize the hot walls of burning buildings. Aircraft pilots could avail themselves of an all-weather landing aid system for small airports. It is, however, car driving aids that should represent the largest application domain, infrared cameras allowing the sighting of obstacles or pedestrians even through fog or smoke, at night and against glare from the lights of incoming vehicles. Prototypes demonstrating their effectiveness have already been validated at CEA/LETI.

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X- and gamma rays: detectors at ambient temperature

The decisive contribution of cadmium telluride To investigate sources in the sky radiating at high energies (from a few keV to several MeV), astronomers require instruments that have the capability not only to provide images, but equally to carry out accurate measurement of the energy (spectral performance) of each photon emitted by the source, and intercepted by the instrument. A gamma ray camera is a collection of pixels, each one of which is a spectral imaging chain, in which every photon is measured individually.

Cadmium telluride (CdTe) and cadmium–zinc telluride (CdZnTe) are materials recognized as being outstanding gamma ray detectors, affording a number of advantages over the more commonly used germanium (Ge)-based detectors. On the one hand, they operate at temperatures close to ambient conditions (typically, in the range from – 20 °C to + 20 °C), whereas germanium is operational at temperatures around–200 °C, requiring a heavy **cryogenic** environment, meaning development of spaceborne detectors is a complex affair.

At the same time, CdTe is composed of heavy atoms (i.e. having a high average **atomic number** *Z*, standing at around 50, as against 32 for germanium), and exhibits high density (around 6), higher than that of germanium (5.3). Such parameter values mean CdTe is an effective material for gamma ray detection, suitable for construction of highly compact detection suites, to be carried in lightweight, sensitive instruments. CdTe and CdZnTe **crystals** are used for a variety of gamma ray spectral imaging applications, whether in the field of astrophysics (see *Infrared, X- and gamma radiation: nonvisible wavelengths to probe the Universe*) or of medical imagery, the monitoring of hazardous materials, or equally in nuclear physics.

The beginnings: the gamma ray camera for INTEGRAL

Two large gamma-ray cameras, employing CdTe or CdZnTe crystals, are presently in orbit. One is carried on the US Swift *gamma ray burst* detection satellite, put into space on 20 November 2004. The other one, IBIS/ISGRI, is on board **ESA**'s INTEGRAL satellite, launched on 17 October 2002. The development, carried out at CEA, of this imager for a high-energy astrophysics application brought the demonstration that highly reliable use of a large number of CdTe crystals was a feasible proposition.

Each individual crystal is used as one pixel in a gamma ray camera: 16 crystals form a Polycell block; 128 of these blocks are assembled in each of ISGRI's 8 modules. Such modular construction for the instrument affords a major advantage as regards reliability, as required for a space application, since any possible failure will remain "compartmented."

Further improvements to CdTe-based systems Research workers are developing solutions to enhance the spectral performance of detector systems, and bring them to the ultimate level feasible for this type of material, bringing them close to that of the best cooled germanium detectors. Efforts are focusing on crystal fabrication. Detector crystal quality (homogeneity) is a limiting factor on crystal size, whereas it would be advantageous to fabricate large crystals, on the one hand to increase production efficiency – and thus bring down production costs – and, on the other, to allow fabrication of detectors with a thickness greater than a few millimeters, enabling detection of higherenergy photons (the thicker the crystal, the greater the chances of intercepting and measuring high-energy gamma photons, which are highly penetrating). Finally, reproducible crystal fabrication is a requisite, if they are to be used in any number in a large spectral imager.

While CdTe as a whole suffers from limitations, due to difficulties relating to CdTe crystal growth, on the one hand, and its electrical properties, investigations on, and employment of, this type of detector may be advanced further, to enhance spectral performance (crystal quality, electrode type and geometry, associated electronics and filters...) and spatial resolution.

To enhance the latter, one must either resort to very small crystals, which are very difficult to handle, or delineate the pixels on the electrode of a larger crystal. In this manner, a pattern of several individual, juxtaposed small electrodes may be formed across one crystal side.

The aim is to make advances simultaneously on all of these points. Research efforts are focusing on securing



Schematic showing the way the IBIS imager, jointly developed at CEA for ESA's INTEGRAL satellite, can reconstruct the image of events such as gamma ray bursts. Gamma rays shed part of their energy in the first detector layer (ISGRI), consisting in mosaics of cadmium telluride detectors, covering the 15 keV-1 MeV range. The rays deflected by Compton scattering may be absorbed by the crystals in the second layer (PICsIT), covering the 300 keV-1 MeV range. The instrument's coded-aperture mask is shown in blue.

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Artist's impression of the SIMBOL-X mission, involving two satellites "flying" in formation. The first satellite carries the grazingincidence high-energy X-ray optics. Photons from the collimated sources will be focused at some 30 m, at the telescope's focal plane, onto the detector plane, fitted with CdTe and other detectors. carried on the second satellite.

concurrent improvements to spectral performance, spatial resolution, and detection efficiency at high energies (MeV region). For that purpose, CEA is conducting an investigation of detectors, characterizing, modeling and testing them, while specifically developing miniaturized readout devices, bringing forward technology to integrate them into larger systems, having the capability to operate as true gamma ray space cameras, reliably, with low energy consumption, and radiation-tolerant.

Ongoing developments and results achieved

Research work on CdTe, initiated at DAPNIA in 1992, resulted in construction of ISGRI. A new research and development drive, on CdTe-based detectors, was launched in 2003, with support from **CNES**. Highly promising results are opening up new prospects, with regard to future experiments in the field of high-energy astronomy.

In particular, a range of microelectronic circuits (IDeF-X, for "imaging detector front end") has been developed, allowing us to demonstrate the CEA teams' ability, through use of suitable pixellized CdTe detectors, to achieve outstanding spectral performance, with no sensor cooling. Moderate cooling further improved the results.

Research workers achieved a number of breakthroughs, improving, by a factor 5, spectral resolution, i.e. measurement precision as regards photons interacting with the detector. Detection threshold the minimum energy for photons to be recorded by the detector - was also improved, coming down from 12 keV for ISGRI to under 2 keV for the latest prototypes. The latter point is essential, insofar as it allows 'gamma astronomers" to investigate, using the same instrument; sources in the X-radiation region, where photons are far more abundant than at higher energies. In the particular instance of searching for gamma ray bursts, detection of low-energy photons significantly improves the chances of detection, thus enhancing chances of observing the most distant bursts.

New space missions in the offing

On the strength of these results, DAPNIA scientists were able to suggest new experiments, taking advantage of use of these new detectors, particularly for the ECLAIRs telescopes, and the SIMBOL-X formationflying mission.

The ECLAIRs telescope, on board the Chinese–French SVOM (Space-Based Multi-Band Variable Object Monitor) satellite, is dedicated to gamma ray burst observation in the 4-300 keV energy band, and will probably be able to view the first star explosions, occurring when the Universe was less than a billion years old. This mission, currently at Phase A (feasibility study) status at CNES and CEA, is scheduled for around 2010. Aside from DAPNIA at CEA, this mission involves many laboratories: **CESR** in Toulouse (France), **APC** and **IAP** in Paris, and **MIT** in Boston (Mass.). The instrument, put into low orbit, should be able to detect and localize gamma ray bursts, measure their spectra in the X and gamma photon bands, alert the scientific community in real time of the occurrence of a burst, and provide its coordinates. Indeed, these very bright celestial objects are short-lived (lasting from a few seconds to a few minutes). Multiwavelength analysis, using e.g. ground-based telescopes or other space telescopes, entails that the ECLAIRs telescope must give the alert, and transmit, in less than one minute, the burst's position in the sky, accurate to some 10 minutes of arc.

To detect gamma ray bursts, the ECLAIRs telescope will comprise a coded-aperture mask, associated to a gamma ray camera using some 1,000 cm² CdTe, with the ability to measure photons from 4 keV. The CEA detectors are ideally suited for such a situation, and have been offered for this experiment.

These pixellized detectors are equally well suited to measuring gamma photons emitted by black holes and other compact objects, which may thus be measured to an accuracy, sensitivity, and angular resolution unequalled to date in this energy region (from a few keV to 80 keV), by the coming SIMBOL-X formation-flying mission. This mainly French–Italian mission, set up at the behest of CNES, on the basis of a CEA proposal, is currently at the Phase A stage. It further involves other laboratories, including in particular the Brera–Milan observatory (Italy), and MPE in Munich (Germany).

The mission will consist in an observatory deploying two satellites, servo-controlled to fly in formation. The first satellite carries the grazing-incidence high-energy X-ray optics. Photons from collimated sources will be focused at about 30 m, at the telescope focal plane, onto the detector plane, fitted with CdTe and other detectors, carried on the other satellite in the formation.

The mission is to be placed into a high-eccentricity orbit, around 2013.

Aside from their employment for astrophysics, CdTe detectors may prove highly advantageous for environmental monitoring, and the monitoring of sensitive activities (hazardous materials), as well as for controls in nuclear work (materials, tests).

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Spectroscopy and spectrometry

Spectrometric methods are subdivided, as a whole, into two main categories, radiation spectrometry – itself comprising absorption spectrometry, emission spectrometry, Raman scattering spectrometry, and nuclear magnetic resonance spectrometry – and mass spectrometry.

Radiation spectroscopy and spectrometry⁽¹⁾ cover a ensemble of analytical methods allowing the composition and structure of matter to be ascertained, based on investigation of the spectra yielded by the interaction between atoms and molecules, and various types of electromagnetic radiation, emitted, absorbed, or scattered by the former.

Depending on their energy, photons interact selectively with the various electron shells, or levels, making up the electronic structure of the atom, or molecule. The electrons involved are *core electrons* (close to the atom's nucleus), for X-rays,^[2] peripheral electrons (furthest from the nucleus, and involved in chemical bonds) for light absorbed, or emitted, in the near ultraviolet and visible region. In the infrared radiation region, it is the leap from one molecular vibration level to another that is involved the switch from one molecular rotation level to another for microwave radiation, and atomic nucleus spin for NMR.

Absorption spectrometry

Those spectroscopy methods that rely on absorption make use of the Beer–Lambert law, setting out the proportional relation between the intensity of light absorbed, and the amount of absorbing matter:

$A = \log \left(|I_0/I| \right) = \varepsilon \mid C,$

where A stands for the **absorbance** of the medium traversed, I_0 for incident light intensity, I for transmitted light intensity, ϵ is the characteristic **molar** extinction coefficient, for a given wavelength, for the substance investigated – expressed in

(2) It should be noted, at the same time, that Xray crystallography is not deemed to be a spectroscopy method, in the strict sense of the term. L mol⁻¹ cm⁻¹ – while l stands for the thickness passed through, expressed in centimeters, and C is the concentration, in moles per liter.

By measuring the medium's absorbance, for a given wavelength, the concentration of a substance, in a sample, may thus be determined.

In an absorption spectrum, as recorded by means of a spectrometer, absorption peaks correspond to the wavelengths the medium is able to absorb. Just as the spectrum from the Sun's light is obtained by making it pass through a prism, which breaks it up, spectrometers analyze the spectral distribution of the whole range of electromagnetic radiations, separating them out according to wavelength, by means of a reflection diffraction grating. Spectra exhibit peaks, each one corresponding to a specific wavelength.

Depending of the type of sample to be analyzed, and the performance level being sought, in the laboratory, **absorption spectrometry** is used either on molecules in liquid or gaseous phase, or on atomic vapor, obtained through thermal breakdown of liquid or solid samples.

Molecular absorption spectroscopy, in the UV-visible region, affords simplicity of use, however it is only applicable to samples of moderate complexity, since, owing to the width of *molecular absorption bands*, absorption spectra, as a rule, do not allow specific discrimination of every constituent, in a complex mixture.

In infrared (IR) spectrometry, absorption is the outcome of molecular vibration and rotation processes. Infrared absorption spectra thus allow the nature of chemical bonds to be determined, that make up a molecule, by ascertaining the bond's elasticity constant (influencing vibration frequency, as for a spring), thus confirming structural hypotheses.

As the number of atoms increases, the spectrum rapidly exhibits growing complexity, and interpretation becomes highly problematical, especially for organic compounds.

Atomic absorption spectrometry, in this respect, brings higher performance, since absorption by atoms yields very narrow absorption lines. Very precise measurements are thus feasible, even when the sample consists in a complex assembly of chemical elements. Atomic absorption is a reference technique for the analysis of trace elements in a wide variety of samples, in particular for biological samples.

Emission spectrometry

Atoms or molecules brought to an excited state may deexcite by emitting radiation, known as *emission radiation*. When the excitation is caused by selective absorption, by the atoms or molecules to be analyzed, of electromagnetic radiation, this represents a **fluorescence** emission (or a **phosphorescence** emission, depending on the electron excitation state involved).

As with absorption, fluorescence may be applied, in the UV-visible radiation region, to molecules, or atoms. X-ray fluorescence spectrometry, on the other hand, refers to the X radiation emitted by atoms excited by absorption of X-radiation. Fluorescence techniques are more complex to implement than is the case for absorption techniques, since they entail that the particle subjected to analysis be selectively excited by a monochromatic radiation. On the other hand, since the radiation emitted is likewise specific to the particle, fluorescence spectrometry involves a double selectivity, resulting in very low background noise, thus making it peculiarly well suited for the measurement of very low concentrations.

Emission of radiation may also occur when atoms are thermally excited, in an environment brought to high temperatures. Emission spectroscopy is based on the fact that atoms, or molecules excited to high energy levels deexcite to lower levels, by emitting radiation (emission, or luminescence). This differs from fluorescence spectrometry in that excitation is not applied selectively, rather it involves indiscriminately all of the particles making up the medium. Emission lines thus correspond to radiation directly emitted by a body brought to a high temperature, and the emission spectrum allows the detection, and quantification, of all atoms present in the emission source.

Raman spectrometry

Interactions between matter and electromagnetic radiation also give rise to scattering processes, such as elastic scattering, and inelastic scattering. Scattering may occur when the interface between

⁽¹⁾ The term "spectrometry," initially used only to refer to recording and measurement techniques, has tended to become synonymous with "spectroscopy," as the eye was supplanted, for observation purposes, by other receptors and instruments, while the visible region now only formed one special region, in analytical terms.

(cont'd)

two media is encountered, or as a medium is passed through. This process, in most cases, is an "elastic" one, in other words it takes place with no change in frequency for the radiation forming the beam involved. Elastic scattering of solar radiation by the atmosphere is, for instance, responsible for the blueness of the sky, observed when the eye is not directed towards the Sun (*Tyndall effect*). Indeed, scattered intensity is all the greater, the shorter the radiation wavelength, which, in the case of the solar spectrum, corresponds to the color blue.

As regards spectrometry, the main use of scattering concerns *Raman spectrometry*. This involves the inelastic scattering of incident radiation by the molecules making up the sample. The difference between scattered radiation frequency, and incident radiation frequency allows the identification of the chemical bonds involved. Raman spectrometry is a technique that is widely used for structural analysis, to complement infrared spectrometry, and mass spectrometry.

Nuclear magnetic resonance spectrometry

The principle of nuclear magnetic resonance (NMR) is based on the fact that an atom has a *magnetic moment*, just like a spinning charge acting as a tiny magnet, governed by quantum mechanics, aligning in a magnetic field as the needle of a compass in the Earth's magnetic field. The principle of NMR consists in inducing, and detecting, the transition, for the nuclear magnetic moment, from the lowest energy level to the highest energy level, through absorption of electromagnetic radiation of a wavelength lying in the radiofrequency region: when the energy of the photon precisely matches the energy difference between the two levels, absorption occurs. Nuclei having numbers of protons, and neutrons that are both even exhibit zero spin. Carbon 12 and oxygen 16 atoms, which are very widespread in nature, thus have zero spin. On the other hand, hydrogen only has one single proton, and its nuclear magnetic moment equals 1/2: it may thus take on two possible energy states, corresponding to the two orientation states of its spin, relative to the magnetic field. Measuring the resonance frequency in the electromagnetic field allowing transition from one of these energy states to the other enables the molecu-



Spectromètre de masse d'ions secondaires utilisé au CEA pour réaliser des mesures isotopiques rapides sur un échantillon par exemple prélevé sur une installation aux activités nucléaires suspectes.

les to be analyzed. This frequency is fixed, however the various nuclei in a molecule do not all resonate at the same frequency, since their magnetic environment is modified by their chemical (electronic) environment.

Many NMR spectra exhibit more peaks than there are protons in the nucleus, owing to the interactions between protons and their neighbors. Two nuclei may interact within the molecule, though they are separated by several chemical bonds: this is known as interatomic coupling. This interaction endows the NMR spectrum with a fine structure.

Mass spectrometry

Mass spectrometry is a highly sensitive *detection* and *identification* technique, allowing determination of molecular structures, and thus of a sample's composition. This is not, strictly speaking, a form of spectrometry, since it is not concerned with discrete energy levels. What is its principle? A compound introduced into the device is vaporized, and subsequently **ionized** by an electron bombardment source (at 70 eV). The ion thus obtained, termed a molecular ion, allows the compound's molar mass to be determined. Breaking chemical bonds within the compound may yield characte-

ristic fragment ions. These are then sorted according to their mass/charge ratio in an *analyzer*, through application of a magnetic and/or electric field, then collected by a *detector*, which amplifies the signal associated to the ions, which arrive with varying delays. A data processing system converts the information from the detector into a mass spectrum, readout of which, by comparing it with reference spectra, allows the identity details of the molecule to be drawn up. Through use of a highresolution mass spectrometer, the exact mass of the compound may be determined, together with isotope percentages for each constituent atom.

Choice of ionization method is directly related to the nature of the sample, and the type of analysis. If mass spectrometry has gradually adapted to meet the growing demands from chemists, and biologists (separation of increasingly complex, highly polarized mixtures, determination of ever higher molecular masses on samples of ever more constricted sizes), this is essentially due to advances in ionization techniques, these including secondary ion mass spectrometry (SIMS), chemical ionization, thermospray ionization, and fast atom bombardment (FAB) sources, further comprising, from the 1980s, matrix-assisted laser desorption ionization (MALDI), and electrospray ionization (ESI), together with advances in *detection* techniques, from time-of-flight (TOF) measurement to "ion traps" (ITs), through quadrupoles (MS or Q).

In proteomics, for instance, only MALDI, ESI and SELDI (surface-enhanced laser desorption ionization) are employed.

Ion mobility spectrometry (IMS) is a chemical analysis technique in the gaseous phase, which consists in subjecting a gas to an electric field. Ionized molecules acquire a velocity that is characteristic for the ion, since this depends on mass, and charge. Arrival of the ions on one of the plates generating the field results in a current, which is recorded. The length of time after which a peak occurs can be related to the nature of the ion causing it.

Scientists often make use of a coupling of devices each belonging to one of the two main families of analytical techniques (see Box E, *What is chromatography?*), e.g. of a chromatograph with a mass spectrometer (or an electron-capture detector [ECD]), particularly for the investigation of trace complex mixtures.

Fundamental interactions and elementary particles

he standard model of particle physics is the reference theoretical framework describing all known elementary particles (see Table 1) and the fundamental interactions these particles are involved in (see Table 2). The basic constituents of matter, known as fermions, are partitioned into two main categories, as determined by their partcipation in the fundamental interactions, or forces (the gravitational, electromagnetic, weak, and strong forces), which are mediated by vector bosons, the fundamental particles which carry out the transmission of the forces of nature^[1] (see Table 2). Whether a particle belongs to the category of fermions, or to that of bosons depends on its spin (i.e. its intrinsic angular moment, or internal rotation moment), depending on whether it exhibits half-integer spin (fermions) or integer spin (bosons).

At the same time, to every constituent of matter is associated its **antiparticle**, a particle having the same *mass*, but the opposite *charge*. The **positron** is thus the positively charged antiparticle of the **electron**, which exhibits a negative charge.

Leptons and quarks

Fermions include, on the one hand, **leptons**, which may travel freely and do not participate in the *strong interaction*, which ensures the cohesion of atomic **nuclei** (it is consequently termed a *nuclear* interaction), and, on the other hand, **quarks**, which participate in all interactions but are not individually observed, enmeshed and confined as they are within **hadrons**, the particles susceptible to strong interaction, of which they are the constituents.^[2]

In the lepton category, charged leptons participate in the *electromagnetic interaction* (which ensures the cohesion of **atoms** and **molecules**, and in the *weak interaction* (which underlies decay processes, in particular β radioactivity). Neutral leptons, or neutrinos, for their part, participate in the weak interaction only. Exhibiting very low mass, there is one type of neutrino for each type of charged lepton.

Independently from their involvement in interactions, the basic constituents of matter are classified into three *gene*- rations, or families, of particles. From one family to the next, quarks and leptons having the same charges only differ by their mass, each family being heavier than the preceding one.

The electron, up quark (symbolized *u*) and down quark (symbol *d*), which belong to the first generation, are the lightest massive particles, and are stable. These are the sole constituents of normal matter, so-called baryonic matter (a baryon is an assembly of quarks), which is made up of protons and neutrons, this however only accounting for 4% of the Universe's energy content! Particles in the other two families are heavier, and are unstable, except for neutrinos, which on the other hand exhibit non-zero mass, but are stable.

These latter particles may only be observed or detected in the final states resulting from collisions effected in accelerators, or in cosmic radiation, and rapidly decay into stable first-generation particles. This is why all the stable matter in the Universe is made up from constituents from the first family. According to quantum mechanics, for an interaction to take place between particles of normal matter, at least one elementary particle, a boson, must be emitted, absorbed, or exchanged. The photon is the intermediate (or vector) boson for the electromagnetic interaction, the W⁺, W⁻ and Z are the intermediate bosons for the weak interaction, and gluons are those of the strong interaction, acting at quark level.

As to the graviton, the putative vector for the gravitational interaction, it has not so far been empirically discovered. The gravitational force, which acts on all fermions in proportion to their mass, is not included in the standard model, due in particular to the fact that quantum field theory, when applied to gravitation, does not yield a viable scheme, as it stands. While gravitational effects are negligible in particle physics measurements, they become predominant on astronomical scales.

Interaction ranges

Quarks and charged leptons exchange photons. The photon having no electric charge, these particles conserve their electric charge after the exchange. Since the photon's mass is zero, the electromagnetic interaction has an infinite range. Having no electric charge, neutrinos are the only elementary fermions that are not subject to electromagnetic interaction.

In the electroweak theory (a unification of the weak and electromagnetic interactions), the weak interaction has two aspects: charged-current weak interaction, for which the interaction vectors are the W⁺ and W⁻; and neutral-current weak interaction, for which the mediator is Z⁰. These two forms of weak interaction are active between all elementary fermions (quarks, charged leptons and neutrinos). The mass of these bosons being very large (about 80 GeV/c² for W^{\pm} , 91 GeV/c² for Z⁰], the range of the weak interaction is tiny - of the order of 10⁻¹⁸ m. Since W[±] bosons have a nonzero electric charge, fermions exchanging such bosons undergo a change in electric charge, as of nature (flavor). Conversely, since the Z⁰ boson has no electric charge, fermions exchanging one undergo no change in nature. In effect, neutral-current weak interaction is somewhat akin to exchanging a photon. As a general rule, if two fermions are able to exchange a photon, they can also exchange a Z⁰. On the other hand, a neutrino has the ability to exchange a Z^0 with another particle, though not a photon.

Only those quarks that have a color charge⁽¹⁾ exchange gluons, these in turn being bearers of a color charge. Thus,

(1) The participation of basic constituents in fundamental interactions is governed by their *interaction charges* (electric charge, color charge), or "conserved quantum numbers." *Color charge*, a quantum number that determines participation in strong interactions, may take one of three values: "red," "green," or "blue" (these colors bearing no relation to visible colors). Every quark bears one of these color charges, every antiquark one of the three anticolor charges. Gluons are endowed with double color–anticolor charges (eight combinations being possible).

(2) To take e.g. **nucleons:** the proton holds two up quarks and one down quark, the neutron two down quarks and one up quark. A **meson** is made up of just two quarks (one quark and one antiquark).

B (cont'd)

when a gluon exchange takes place between quarks, the latter exchange their respective colors. Gluons have zero mass, however, since they do bear a color charge, they are able to interact together, which greatly complicates theoretical treatment of this interaction. The range of the strong interaction is consequently very restricted – of the order of 10^{-15} m.

The quest for unification

The theoretical framework for the standard model is quantum field theory, which allows a quantitative description to be made of the fundamental interac-



tions between elementary particles, while respecting the principles of special relativity, as those of quantum mechanics. According to the latter theory, if one seeks to observe a microscopic structure at high temporal and spatial resolution, this entails transferring to it an amount of energy-momentum, the greater, the higher the resolution being sought. However, according to the theory of relativity, such an energy-momentum transfer is liable to undergo transformation, yielding particles not present in the initial state: fermions may be generated, or annihilated, in particle-antiparticle pairs, while bosons may be so in any arbitrary number.

All processes involving one and the same fundamental interaction are interrelated. The quantum field theory approach, in which properties of **symmetry** play a fundamental part, seeks to describe all of the processes relating to each fundamental interaction, within overarching theoretical constructions.

The strong and electromagnetic interactions are formalized, respectively, in the theories of **quantum chromodynamics**, and **quantum electrodynamics**. The weak interaction, for its part, is not subject to a separate description, being described jointly with the electromagnetic interaction, in the unified formalism of **electroweak theory**. Theories of the *grand unification* of all fundamental interactions do exist, however they remain as yet lacking any experimental validation.

All the predictions of the standard model have been corroborated by experiment, except for just one, to wit, the existence of the Higgs boson(s), which particle (particles?), it is hoped, will be discovered with LHC. The Higgs mechanism is thought to be responsible for the mass exhibited by elementary particles, the eponymous boson making it possible for zero-mass fermions interacting with it to be endowed with mass. This would allow the unification, at high energies, of the weak and electromagnetic interactions within the electroweak theory, while effectively accounting for the breaking of this electroweak symmetry at low energies, taking the form of two interactions, which may be seen as distinct at that energy level (see The electroweak

interaction from one accelerator to the next: the LHC roadmap and the yardstick of LEP measurements, p. 23).

Going beyond, or completing the standard model?

The standard model features a set of parameters (such as the masses of elementary particles, or the intensities of fundamental forces) which are "anchored" in experimental findings. It is, in any event, a theory that is liable to be improved, or further elaborated, or even surpassed and left behind. It does not account in any way for the classification of the constituents of matter into three generations of particles, whereas it is precisely the existence of these three generations which makes it possible to account for CP (charge-parity) invariance violation (meaning that a physical process involving the weak interaction is not equivalent to its own mirror image), a violation that is in all likelihood the source of the matter-antimatter imbalance, running in favor of the former, in the primordial Universe. The model neither allows quantum treatment of gravitation, nor does it fully account for the fundamental property of confinement, which prevents quarks from propagating freely outside hadrons.

To go beyond, or to complete the standard model, research workers are mainly exploring two avenues:

- supersymmetry (widely known as

SUSY) would associate, to every particle (whether a boson or a fermion) in the standard model, a partner from the other series, respectively a fermion or a boson. Supersymmetric partners would, at first blush, be highly massive, the lightest of them being a particle interacting very weakly only. This would be an ideal candidate to account for the hidden matter (or dark matter) in the Universe, accounting as it does for some 21% of the Universe's energy content, the remainder (close to 75%) consisting in a dark energy, the nature of which likewise remains to be determined. These WIMPs (acronym for "weakly interacting massive particles") are actively being sought (see EDELWEISS II, the guest for dark matter particles);

- the substructure path assumes there could be a new level of elementarity, underlying the particles in the standard model (or some of them). This would lead to a veritable blossoming of new, composite particles, analogous to hadrons, but exhibiting masses two to three thousand times heavier.

It should be noted that, whereas supersymmetry theories yield predictions that agree with the precision measurements carried out at LEP, the theories propounding substructures (or their simpler variants, at any rate) fail to do so. As for the more complex variants, these are encountering difficulties at the theoretical level.

fundamental interaction	associated particles (messengers)	actions
gravitation	graviton?	having an infinite range responsible for the mutual attraction of any two masses and for the law of falling bodies
electromagnetic interaction	photon	having an infinite range responsible for the attraction between electrons and atomic nuclei, hence for the cohesion of atoms and molecules
weak interaction	W ⁺ , W ⁻ , Z ⁰	responsible for β ⁻ and β ⁺ radioactivity, reactions involving particles as neutrinos
strong interaction	gluons (there are 8 gluons)	ensures the cohesion of the atomic nucleus

Tableau 2.

Fundamental interactions, their vectors, and effects.

What is chromatography?

Chromatography, together with the various forms of spectroscopy and spectrometry (see Box D, Spectroscopy and spectrometry), represent the two major basic analytical techniques, the former serving for the separation, the latter for the identification of the constituents of a substance.

Chromatography (from the Greek khrôma, "color," and graphein, "to write"), allows the separation of the constituents of a mixture in a homogeneous liquid or gaseous phase, as blotting paper might spread out in concentric rings a liquid poured onto it.

A chromatograph comprises a sample injection device, a column, a detector, and a recording and analysis system. Its principle is based on the equilibrium of compound concentrations, between two phases coming into contact: the stationary phase, in the column, and the *mobile phase*, which moves across it. Separation relies on the differential displacement of constituents inside the column, passing through in times that are proportional to their size, or depending on their structure, or affinity for the stationary phase (polarity...). As they reach the far end of the column, a detector measures, on a continuous basis, the quantities of each constituent.

The most common form of chromatography is gas chromatography, carried out on gaseous samples, or samples that may be vaporized without incurring breakdown. The mobile phase is a gas (helium, nitrogen, argon, or hydrogen), constantly sweeping through the column, which is placed in a thermostat oven. Detectors allow the selective analysis and identification of highly complex mixtures.

If the stationary phase is a nonvolatile, or not highly

tography. If the stationary phase is an adsorbent solid (silica, alumina, zeolites, or **polymers**), this is gas-solid chromatography. Within this same family, of adsorption chromatography processes, **liquid–solid chromatography** is characterized by its stationary phase, this being a polar solid. In high-performance liquid chromatography (HPLC), the sample must be wholly soluble in the mobile phase (elution solvent). The latter must be kept at high pressure (hence the alternative name of *high-pressure* liquid chromatography), to ensure a constant flow rate inside the column, and preclude any loss of head. HPLC involves solute-mobile phase-stationary phase exchange mechanisms, based on partition or adsorption coefficients, depending on the nature of the phases in contact.^[1] A chromatographic analysis yields a chromatogram, this being a graphical representation of the evolution of a parameter (intensity of the detector signal), related to instantaneous solute concentration, as function of time. This exhibits peaks, rising above the *baseline*, which obtains in the absence of any compounds (see Figure).

(1) There are two further types of liquid chromatography, ion chromatography, and exclusion chromatography N.B: This Box reproduces a number of excerpts from a presentation by Pascale Richardin, head of the Datation Group at the Research and Restoration Center of the French National Museums Administration (Musées de France), taken from the pages dealing with analytical methods, as posted on the site : ttp://www.culture.gouv.fr/culture/conservation/fr/ biblioth/biblioth.htm



Figure.

An example of the combined use of mass spectrometry and chromatography: the separation of isomers ("sister molecules") of an explosive molecule (dinitrobenzene [DNB]), after solid-phase microextraction sampling, by gas chromatography, and their detection by mass spectrometry (SPME-GC-MS).