Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 103, No. 3, March 1991, pp. 225–236.

Laser and synchrotron-based sources for excited state intramolecular dynamics studies

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Abstract. Energy ranges and time scales for excitation and relaxation of intramolecular processes are discussed and compared with the operational characteristics of laser and synchrotron radiation sources. The basic physics of synchrotron radiation and undulator emission is presented. It is shown how undulators can be used to generate short wavelength harmonics. Free electron lasers of the Compton and Raman scattering types and the associated electron beam sources are described. The properties and applications of free electron lasers are reviewed.

Keywords. Synchrotron radiation; undulator; free electron laser; intramolecular dynamics.

1. Introduction

This review compares and contrasts laser and synchrotron sources for excitation and interrogation of physical and chemical processes. The general references provide some introductory material on intramolecular dynamics (Jortner and Leach 1980; Leach 1989), lasers (Jortner and Leach 1980; Bass and Stitch 1985; Stitch and Bass 1985; Fleming 1987; Alves *et al* 1988), synchrotron radiation (Margaritondo 1988) and Free Electron Lasers (FEL) (Marshall 1985; Leach 1989). A picture of world-wide FEL development and devices can be obtained from recent conference proceedings. The present review is, in part, a shortened version of a more detailed presentation recently published (Leach 1989). Additional material brings the subject abreast of current activities.

2. Intramolecular dynamics: Ideal source requirements

2.1 *Basic photophysical processes*

An outstanding goal of research is the elucidation of a large class of radiationless processes. These involve energy exchange between and within electronic, vibrational and rotational degrees of freedom, e.g. nonradiative coupling of electronic states and vibrational states and also include processes such as dissociation and ionization in their direct form as well as the indirect processes of predissociation and autoionization. The various intramolecular dynamics processes occur on characteristic energy and time scales. The energy regions for excited state photophysical processes in molecules

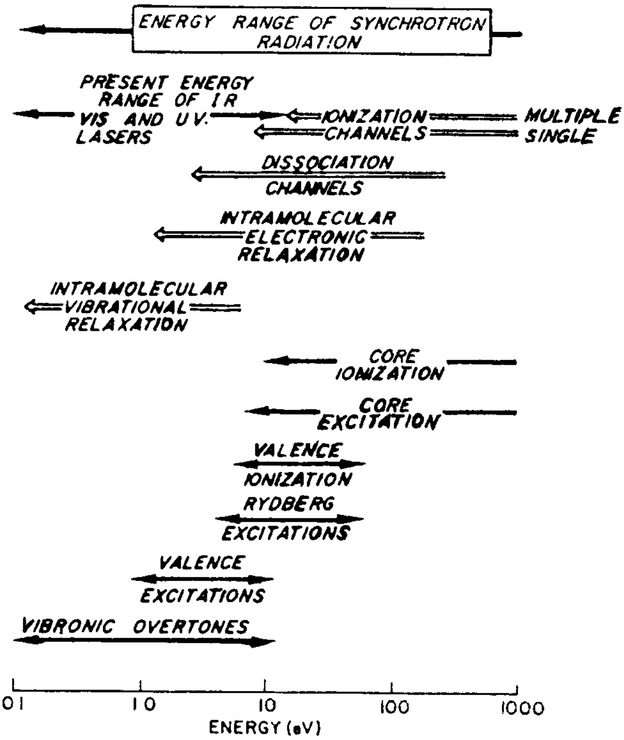

Figure 1. Energy ranges of lasers, synchrotron radiation and of intramolecular processes.

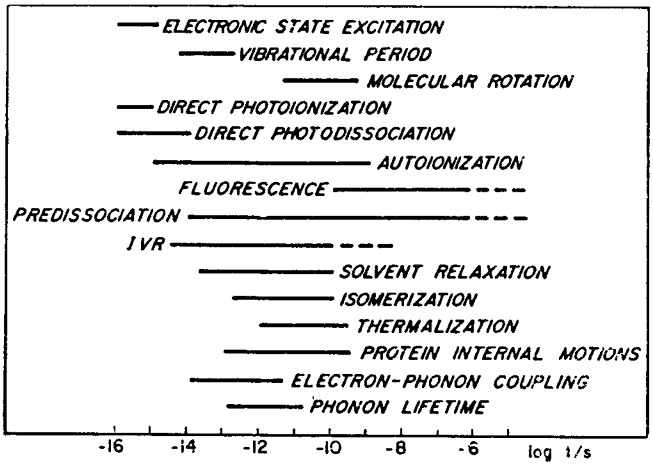

Figure 2. Time scales for excitation and relaxation in physicochemical processes.

is indicated in figure 1, which also shows the present range of synchrotron and laser sources. It is seen that the interesting energy regions of particular processes are mainly within the range 0·1–1000 eV.

A non-exhaustive list of physico-chemical processes and their characteristic times is given in figure 2. The period of electronic motion provides the lower limit for the time scale of electronic autoionization, while the time scale for intramolecular nuclear motion determines the lower limit for a variety of processes which involve nuclear vibrations.

2.2 *Objectives and current situation*

There are two major goals of studies in intramolecular (and intermolecular) dynamics. First, one has to identify and elucidate the various decay channels, the interactions between channels, and the sequence of photophysical (and photochemical) processes (non-dissociative, dissociative, ionization) in excited states. Second, the phase relationships between excited states, as well as between the ground state and the excited doorway state, have to be explored in order to understand intramolecular interference effects, intramolecular dynamic processes, as well as medium perturbations of excited states.

The study of excited state dynamics requires selective, well-defined excitation of the parent molecule. Thus, optical excitation is favoured over alternative techniques such as nonselective excitation by electron or ionic impact, fast neutral bombardment, or excitation by energetic (α, β, γ) particles.

3. Synchrotron radiation sources

An electron in an accelerating field will lose energy by radiation. This is the basis of synchrotron radiation and FEL devices, in which positive or negative electrons undergo radial acceleration, usually by magnetic constraints. A low velocity electron radiates with a pattern close to that of a normal Hertzian electric dipole (figure 3a) but this is severely distorted at high electron velocity, due to relativistic effects. The zeros of the radiation pattern then occur at angles $\theta = (1 - v^2/c^2)^{1/2}$ from the direction of motion. From the viewpoint of a stationary observer, the relativistic (Lorentz) transformation of the electron causes the power radiated to be projected into a very small foward cone of the order of a milliradian in angle, giving the radiation pattern indicated in figure 3b.

The most useful synchrotron radiation device is based on the *electron storage ring*

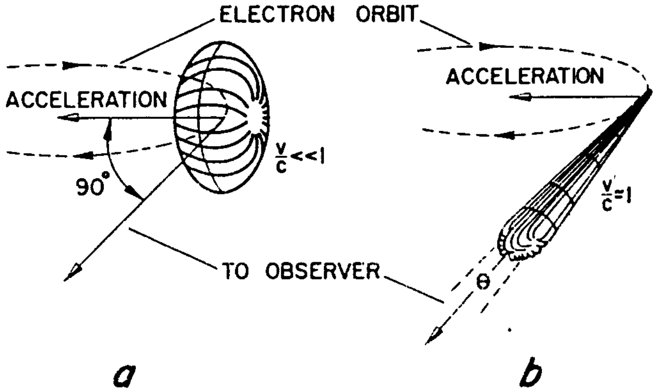

Figure 3. Schematic radiation patterns for electrons in circular orbit (**a**) at low velocities; (**b**) at relativistic velocities, $\theta = (1 - v^2/c^2)^{1/2}$.

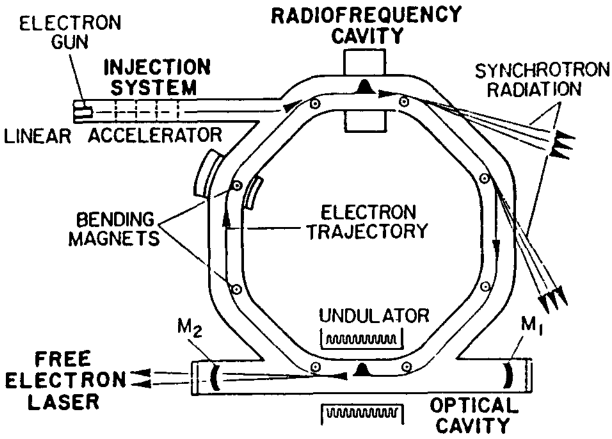

Figure 4. Schematics of an electron storage ring and associated free electron laser. Two electron packets are represented. M1 and M2 are the optical cavity mirrors.

(figure 4). This contains a number of dipole "bending" magnets which force the electrons to undergo a circular trajectory where they radiate. Between the bending magnets are a number of straight sections where reside quadrupole magnets to focus the electron beam, and insertion devices such as undulators. Electron beam correction may require additional, sextupole, magnet coils. Electrons, once injected into the magnet lattice, can have their energy modified or restored by a radiofrequency cavity.

The basic relations between instrumental parameters and synchrotron radiation characteristics are given elsewhere (Leach 1989).

Because of the Lorentz transformation, an observer at a particular angle in the orbit plane will detect synchrotron radiation emitted in the bending magnet region. The power spectrum comprises the Fourier components of the synchrotron radiation pulse and will contain harmonics of the orbit frequency v up to $\omega = v\gamma^3$. The fundamental frequency is Doppler-shifted from the MHz region into higher frequencies; the harmonics blur into a continuum, so that the observed spectrum extends from the far infra-red to the ultraviolet and X-ray regions approximately up to the critical wavelength $\lambda_c = 5{\cdot}59\, R/E^3$ (where R is the magnetic radius of curvature in meters and the electron energy E is in GeV). The divergence of the resulting light, in the vertical plane, is comparable to that of a laser.

Figure 5 gives the radiation spectrum of an electron moving in a curved trajectory, per GeV. This is expressed in terms of the photon flux, which is of practical interest, as a function of the radiation wavelength divided by the critical wavelength. Its peak occurs at $\lambda/\lambda_c \approx 4$. Although the flux falls off rapidly below $4\,\lambda_c$, it is still of useful intensity down to $\approx 0{\cdot}1\,\lambda_c$.

The principal properties of synchrotron radiation of interest as a spectroscopic source or excitation source in physicochemistry are as follows:

(1) tunability over a very broad energy range from below 0·1 eV to above 1000 eV;
(2) pulsed time structure (ps-ns range) enabling time resolved experiments to be carried out;
(3) high intensity (brightness);
(4) high degree of spatial collimation (1 mrad);
(5) quasi-complete linear polarisation; possibility of other polarisations;
(6) temporal and spatial stability.

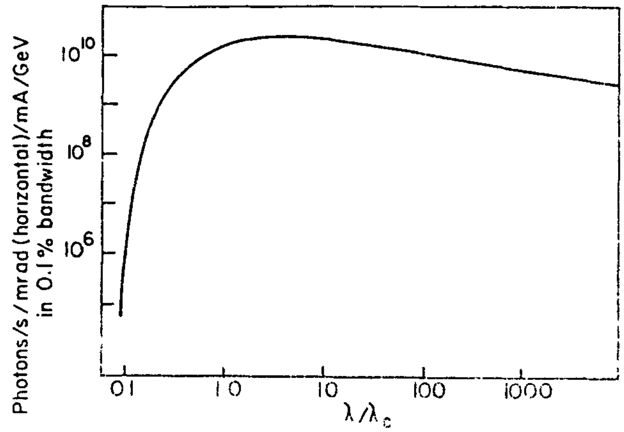

Figure 5. Normalized radiation spectrum of an electron moving in a curved trajectory, per GeV. λ_c = critical wavelength.

Many of these properties carry over to, or are improved upon in, insertion devices and FELs.

Characteristics of present-day and projected synchrotrons and storage rings (about 50 in all) used or useful for synchrotron radiation are listed elsewhere (Leach 1989). The critical wavelengths go from 2800 Å (N-100, Kharkov) to 0·16 Å (PEP, Stanford). Compact storage rings are also being developed, at Berlin (BESSY), the UK (Oxford Instruments) and Japan, mainly for industrial lithography.

4. Laser sources

4.1 *Introduction*

There is a vast literature on lasers. Their development and characteristics can be advantageously followed in a number of handbooks. There are many workshops and conferences devoted to lasers, reported in the standard literature and in proceedings form. Free electron lasers are treated later in the present text. Two of the subjects of main concern here i.e. ultraviolet and VUV lasers (Fleming 1987; Alves *et al* 1988), and short-pulsed lasers, have been the subject of recent reviews. Conventional lasers for the VUV generally involve frequency conversion techniques. These include frequency doubling with anisotropic crystals, and conversion in gas vapours via anti-stokes Raman shifting, 3rd, 5th and 7th harmonic generation, sum and difference frequency mixing. These techniques can provide VUV radiation down to about 600 Å ($\sim$ 25 eV), and even, with 7th harmonic generation in He, to 355 Å.

4.2 *Comparison of laser and synchrotron radiation sources*

It is convenient at this stage to compare and contrast conventional lasers and synchrotron radiation (SR) as sources for studies of intramolecular dynamics. This is examined in detail elsewhere (Leach 1989) and the conclusions can be summarized as follows.

(1) SR sources will undoubtedly be superior to lasers with respect to tunability over the broad energy range required for studies of molecular dynamics.

(2) The time resolution of current SR sources is superior to that of current VUV lasers, but future VUV lasers will achieve subpicosecond time resolution, as has been obtained in the visible and near UV.
(3) The effective energy resolution of many lasers is superior to that obtained by monochromatization of SR sources.
(4) The photon intensity of current visible, UV and VUV lasers is greater than current SR sources, making possible multiphoton excitation by lasers but not by SR.
(5) The polarization characteristics of both SR and laser sources are excellent for molecular dynamics studies.
(6) The temporal coherence of lasers permits interrogation of coherent optical effects which cannot be carried out using SR.

There are, however, a number of inherent limitations of VUV lasers, as compared to SR sources. For example, the output of VUV lasers consists of a single spectral line or is limited to tuning over a narrow energy range. Furthermore, their available energy range is relatively small i.e. 5–13 eV for one photon and 10–30 eV for multiphoton excitation.

The use of VUV lasers in the area of molecular dynamics cannot be considered as an alternative to synchrotron radiation excitation. Rather, the utilization of VUV laser sources will provide useful information concerning one-photon and multiphoton excitation, ultrashort decay times and coherent effects, all interrogated over a narrow energy range, or at various selected energies. Thus synchrotron and VUV laser sources supplement and complement each other for molecular dynamics studies.

5. Undulator emission

In this section a return is made to the area of synchrotron radiation. The discussion concerns magnetic devices inserted in a relativistic electron beam trajectory with the object of modifying and enhancing a synchrotron radiation source.

5.1 *Undulators and optical klystrons*

5.1a *Undulator structure and parameters*: A transverse undulator is a multipole device constituted by a sequence of several magnets with the field alternating in polarity and in a direction perpendicular to the electron orbit (figure 6). The spectral characteristics of an undulator, as of all insertion devices, are largely determined by

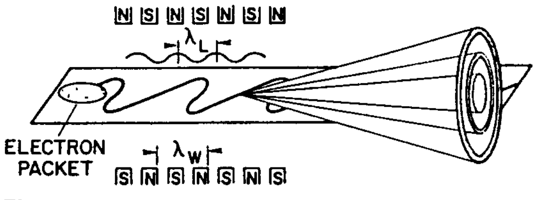

Figure 6. Schematic representation of the passage of a relativistic electron packet in an undulator and radiation emitted at a particular point in the trajectory. λ_w = undulator period; $\lambda_L = \lambda_w/2\gamma^2$ is the fundamental wavelength emitted [cf. (2)].

the dimensionless deflection parameter, or field index:

$$K = \alpha\gamma = eB\lambda_w/2\pi m_0 c = 0{\cdot}0934\, B_0 \lambda_w, \tag{1}$$

where B_0 (Teslas) is the maximum magnetic field on the electron trajectory and λ_w(mm) is the undulator period. K is thus the ratio between the maximum angle of electron deflection α and the radiation emission angle $\theta \approx \gamma^{-1}$ where the relativistic factor $\gamma = E/m_0 c^2 = 1957\,E$). K has a value of the order of unity for most undulators. The photon emission is greatly enhanced in intensity with respect to a single bending magnet. Coherent radiation can be produced by interference effects between photons emitted by the same electron at different points on its trajectory through the undulator.

The synchrotron radiation emitted in the electron trajectory direction is linearly polarised, with the **E** vector in the direction of electron acceleration i.e. polarised in a plane perpendicular to the field. The small value of α means that radiation can be collected from practically the whole electron trajectory in the undulator.

Two undulator configurations are usually considered: (i) a transverse sinusoidal magnetic field with period λ_w and maximum field amplitude B_0, and (ii) a helical magnetic field in which the field amplitude remains constant but the direction of the field vector rotates about the axis of the undulator as a function of the distance along the axis.

5.1b *Undulator emission – the resonance condition*: The wiggling electron in the undulator becomes equivalent to a dipole oscillator in the electron frame of reference. Since these are high velocity electrons, the electron sees the undulator relativistically contracted, so that it is forced to oscillate and emit dipole radiation of wavelength $\approx \lambda_w/\gamma$. The radiation emitted undergoes a Lorentz transformation in the laboratory frame, just as described earlier, the electromagnetic radiation being Doppler shifted to wavelength $\approx \lambda_w/2\gamma^2$ and projected forward in a small cone whose angular dimension is $\approx \gamma^{-1}$. The motion in the electron frame becomes more complex with increasing K, giving rise to the emission of harmonics. The fundamental ($n = 1$) or harmonic ($n > 1$) wavelength of this spontaneous emission is given by the important *resonance condition*:

$$\lambda_n = (\lambda_w/2\gamma^2)(1 + cK^2 + \gamma^2\theta^2)/n, \tag{2}$$

where θ = angle of observation with respect to mean electron trajectory. The constant $c = 1/2$ for a planar undulator, $c = 1$ for helical field undulators. The fraction of the power emitted in the fundamental is given by $(1 + K^2/2)^{-2}$.

The gain in power emitted in a solid angle $2\gamma^{-2} \times 2\gamma^{-2}$, as compared with normal bending magnets, is of the order of N, the number of undulations. An increase of the order of N^2 in spectral brilliance can be obtained for a well-collimated beam. The spectral width W will depend on the number of poles, the angular spread, the electron beam aperture, and the acceptance angle θ. In practice, $\Delta\lambda/\lambda$ is of the order of 1%, so that the use of undulator emission for selective excitation requires further monochromatization.

The fundamental wavelength can be changed either by modifying K, i.e. by varying the undulator gap, or by observing off axis, i.e. θ variation. The range of tunability can be calculated from (2) by putting in suitable practical values of the parameters. The spectral effects of varying K and the angle θ are as follows. For a particular value of K, as θ increases the emitted wavelengths increase in value (blue to red) giving rise to a "rainbow" pattern. Successive patterns correspond to *different harmonics.* For a given value of θ the emitted frequency decreases with increase in K.

Most undulators have a vertical magnetic field so that the polarization of the radiation is then in the ring orbit plane. Circular polarization can be obtained by using crossed undulators, asymmetric wigglers, or helicoidal undulators.

The *time structure* of the emission of an electron in an insertion device also depends on the value of K. The time structure of an actual electron bunch is that corresponding to its length and its repetition rate. The spectral and time structure properties of insertion devices carry over to free electron lasers in which they play a part.

5.1c *Optical klystrons*: Electron microbunching in undulator devices creates coherent spontaneous emission (and also leads to more efficient harmonic generation, see later). The optical klystron, proposed by Vinokurov and Skrinsky (1977), enables electron bunching to be further enhanced. It consists of two undulators, respectively the "modulator" and the "radiator", separated by a dispersive section in which the transit time of the electrons depends on their energy. Thus slower electrons will catch up with faster electrons in the dispersive section, increasing further the microbunching process for a given undulator length. A recent theoretical description of the optical klystron has been given by Elleaume (1986). A number of optical klystrons have been built or are projected.

5.2 *Harmonic generation*

Harmonic generation of radiation via insertion devices promises to have important applications in photophysics and photochemistry. Spatial bunching of electrons serves not only to create coherent radiation but also to enhance the higher Fourier components in the emitted radiation. Harmonic generation may be "intrinsic" i.e. using spontaneous synchrotron radiation as a trigger, or "extrinsic" in which an external source (which may be an FEL) is used to enhance electron density modulation by focussing an external laser source (wavelength λ_l) into an undulator or an optical klystron (Girard *et al* 1984). This technique can thus produce radiation in the vacuum ultraviolet region either in the "intrinsic" mode (Billardon *et al* 1983) or using an external laser source in the visible or near ultraviolet (Prazeres *et al* 1987). In the "intrinsic" mode, radiation down to the 100 Å region has been observed at Orsay (Billardon *et al* 1983) and at Wisconsin (Hansen *et al* 1990). In the "extrinsic" mode, coherent radiation at $\lambda_3 = 1773$ Å and $\lambda_5 = 1064$ Å was observed in an experiment at Orsay in which radiation of $\lambda_l = 5320$ Å (0·4 J in 6 ns, $\Delta\lambda = 0{\cdot}35$ Å) from a frequency doubled Nd-YAG laser was focussed into the modulator of an optical klystron (Prazeres *et al* 1987). These experiments require very precise superposition of the external photon beam on the electron beam.

6. Free electron laser

6.1 *FEL types and characteristics*

Free electron lasers (FEL) operate on free–free transitions i.e. by energy changes of *unbound* electrons, so that any state of electron motion or energy value may be involved.

The basic elements of an FEL are a high velocity (relativistic) electron beam, a device (e.g. undulator) enabling the electrons to undergo oscillatory motion so as to generate – and interact with – photons, and a resonant optical cavity, the latter having the same feedback function as in a conventional laser (figure 2). The undulator field enables coupling to occur between the electrons and the electromagnetic waves which they emit as a result of their oscillatory motion.

There are two main types of FEL: (i) the low electron density, high energy ($E > 20$ MeV) FEL in which electrons individually experience the undulator magnetic field and the photon fields, and (ii) the high electron density (usually kA current), low energy ($E < 10$ MeV), FEL in which electrons interact collectively (plasma modes) with the undulator and photon fields. These types are distinguished by their electron scattering regimes, Compton for the low and Raman for the high electron density versions. The first is mainly useful from the XUV to the IR while the Raman FEL is of value for the centimeter to millimeter wavelength region.

The Raman-FEL gain process can be thought of as a convective three-wave parametric process in which the pump photon ω_0 decays into a plasmon ω_p and a scattered photon ω_s. In this parametric device the virtual photons corresponding to the undulator field act as the pump mode ω_0 and the space-charge wave ω_p plays the role of an idler wave mode that absorbs the energy remaining from inelastic Raman scattering. The scattered light is the signal mode.

The three familar processes occurring in conventional lasers, i.e. spontaneous emission, stimulated emission, and amplification, all occur in FELs.

The FEL beam has spatial and time structures that reflect the electron beam structure. The radiation pulse length is proportional to the electron bunch length l_e, and the radiation frequency width is given by $\delta\omega = 2\pi c/l_e$. The laser power $P_L = G_{\max} \times P_{RF}$, where P_{RF} is the power given to the electron beam by the RF cavity.

The gain in an FEL is inversely proportional to the square of the linewidth of spontaneous radiation. The maximum gain $G_{\max}$ is proportional to a number of factors:

$$G_{\max} = k\rho_e B_0^2 \lambda_w^{3/2} \lambda^{3/2} N^2 L, \tag{3}$$

where k is a proportionality constant, $L = N\lambda_w$ is the undulator length and ρ_e is the electron density (assuming that the electron energy distribution is Gaussian). Gain measurements on the Orsay FEL are described elsewhere (Deacon *et al* 1981, 1982).

FEL experiments were carried out at Orsay with an optical klystron of 1·3 m length and 2 × 7 periods and an optical cavity 5·5 m long. Time structure and Q-switching studies were made (Billardon *et al* 1985, 1986). The Orsay FEL has operated in the following wavelength regions: 6450–6550 Å (Billardon *et al* 1983; Elleaume *et al* 1984), 5750–6440 Å (Billardon *et al* 1986) and 4630–4860 Å (Billardon *et al* 1987).

Gain measurements and laser operation over a wide spectral range (2400–6900 Å) have very recently been made using an optical klystron installed on the VEPP-3 electron storage ring (Drobyazko *et al* 1989). This is the first FEL operation in the ultraviolet region.

6.2 *Electron accelerators*

The electrons entering the FEL should have optimum characteristics for maximizing the gain [cf. (3)] and avoiding effects leading to line broadening. The feasibility of

FEL is intimately linked to the quality of electron accelerator technology. The most common accelerator devices, their typical beam energies and useful wavelength ranges of FEL using these as electron sources, are as follows:

(1) electron storage rings, $E > 200\,\mathrm{MeV}$, $\lambda = 500\,\mathrm{A}$–$1\,\mu\mathrm{m}$;
(2) radiofrequency Linac: $E > 20\,\mathrm{MeV}$, $\lambda = 1$–$20\,\mu\mathrm{m}$;
(3) induction Linac: $E \approx 0{\cdot}1$–$50\,\mathrm{MeV}$, $\lambda =$ mm–cm range;
(4) Van der Graaff electrostatic accelerator: $E < 10\,\mathrm{MeV}$, $\lambda = 1\,\mu\mathrm{m}$–$1\,\mathrm{mm}$;
(5) classical microtron: $E < 40\,\mathrm{MeV}$, $\lambda = 10$–$500\,\mu\mathrm{m}$;
(6) racetrack microtron: $E = 10$–$500\,\mathrm{MeV}$, $\lambda = 10$–$500\,\mu\mathrm{m}$;
(7) pulse-line: $E \approx 0{\cdot}1$–$5\,\mathrm{MeV}$, $\lambda = 80$–$3000\,\mu\mathrm{m}$.

6.3 *Free electron laser facilities*

Free electron laser facilities and their typical parameter values are listed elsewhere (Leach 1989). At the present time about twenty FEL have operated successfully as lasers in the oscillator mode or as amplifiers of an external source. Others are in various stages of conception, design and achievement.

The FEL can be grouped as a function of electron beam technology, which largely determines the spectral range for amplification and oscillation and whether they are repetitive or single pass devices. Detailed accounts of each FEL can be obtained from the references cited by Leach (1989).

6.4 *Summary of FEL properties and applications*

The properties of FEL which are considered to be possible with existing or foreseen improved technology can be summarized as follows. The operating wavelength range is from the millimeter region to the vacuum ultraviolet, with $\lambda = 500\,\text{Å}$ being a lower wavelength limit beyond which it would be difficult to achieve sufficient gain using an optical resonator. It should be possible to tune the emitted radiation over about one octave in the IR, visible and UV regions. The best electron source varies with wavelength region: storage rings in the visible and UV, microtrons in the IR, and Van de Graaff machines in the millimeter region. Average powers greater than 1 kW have been obtained and much higher values, MW and even GW, are reached or contemplated with improved technology; overall net energy conversion efficiencies of the order 1–30% are achieved or expected. Picosecond pulses can be obtained at high repetition rates (10 MHz–1 GHz). All the usual laser techniques used to minimize linewidths can be applied to the FEL. An important advantage of the FEL is the possibility for it to operate simultaneously at different frequencies, or with a set of independent undulators. Furthermore, a storage ring FEL also generates significant amounts of broadband incoherent synchrotron radiation in addition to the emitted (laser) coherent radiation; this SR could be of interest for independent experiments or for use as a secondary source in conjunction with the laser.

Some possible uses for free electron lasers in spectroscopy, intramolecular dynamics and other studies and applications are summarized as follows.

(1) *Far infrared*: interesting wavelength range; useful for saturation pumping, multiphonon processes, surface state spectroscopy, solid state spectroscopy and photophysics.

(2) *UV–VUV*: advantage can be taken of flexibility, power density, polarisation and wavelength range for studies on spectroscopy, multiphoton ionization, high energy-vibronic states, low density targets such as transients e.g. radicals, ions, muonium, positronium.
(3) *Pump and probe experiments* could be carried out by FEL + SR, FEL + separate laser, or FEL operating in multifrequency mode.
(4) *Study of laser assisted collisions and general photochemistry*, in particular state and/or species selective photochemistry using the multifrequency resources. Selective purification; laser initiated chain reactions; laser isotope separation.
(5) *Industrial applications* of photophysical and photochemical processes, e.g. microfabrication of semiconductor circuits by lithography.

Free electron lasers must still undergo much development before becoming competitive with other laser sources but they are already of some practical use in the infrared and millimeter wave regions. Possibly the immediately most promising area discussed in this review concerns the enhancement of synchrotron radiation by undulators and optical klystrons able to generate harmonics. This can provide a useful tunable source in the VUV region which is of interest for high energy optical excitation of molecules.

References

Alves A C P, Brown J M and Hollas J M (eds) 1988 *Frontiers of laser spectroscopy of gases* (Dordrecht: NATO-ASI, Kluwer)

Bass M and Stitch M L (eds) 1985 *Laser handbook* (Amsterdam: North Holland) vol. 5

Billardon M, Deacon D A G, Elleaume P, Ortega J M, Robinson K E, Bazin C, Bergher M, Madey J M J, Petroff Y and Velghe M 1983 *J. Phys. (Paris) Colloq.* **44** Cl-29

Billardon M, Elleaume P, Ortega J M, Bazin C, Bergher M, Couprie M E, Lapierre Y, Prazeres R, Velghe M and Petroff Y 1987 *Europhys. Lett.* **3** 689

Billardon M, Elleaume P, Ortega J M, Bazin C, Bergher M, Petroff Y and Velghe M 1985 *IEEE J. Quantum Electron.* **QE-21** 805

Billardon M, Elleaume P, Ortega J M, Bazin C, Bergher M, Velghe M, Petroff Y, Deacon D A G, Robinson K E and Madey J M J 1983 *Phys. Rev. Lett.* **51** 1652

Billardon M, Elleaume P, Ortega J M, Lapierre Y, Petroff Y, Bergher M, Bazin C and Marilleau M 1986 *Nucl. Instrum. Methods* **A250** 26

Deacon D A G, Madey J M J, Robinson K E, Bazin C, Billardon M, Elleaume P, Farge Y, Ortega J M, Petroff Y and Velghe M 1981 *IEEE Trans. Nucl. Sci.* **NS-28** 3142

Deacon D A G, Robinson K E, Madey J M J, Bazin C, Billardon M, Elleaume P, Farge Y, Ortega J M, Petroff Y and Velghe M 1982 *Opt. Commun.* **40** 373

Drobyazko I B, Kulipanov G N, Litvinenko V N, Pinayev I V, Popik V M, Silvestrov I G, Skrinsky A N, Sokolov A S and Vinokurov N A 1989 *Proc. Int. Congress Optical Sci. Eng.* (Paris), (in press)

Elleaume P 1986 *Nucl. Instrum. Methods* **A250** 220

Elleaume P, Ortega J M, Billardon M, Bazin C, Bergher M, Velghe M, Petroff Y, Deacon D, Robinson K and Madey J 1984 *J. Phys. (Paris)* **45** 989

Fleming G R 1987 *Chemical applications of ultrafast spectroscopy* (Oxford: Clarendon Press)

Girard B, Lapierre Y, Ortega J M, Bazin C, Billardon M, Elleaume P, Bergher M, Velghe M and Petroff Y 1984 *Phys. Rev. Lett.* **53** 2405

Hansen R W C, Bissen M, Pruett C, Korpela E, Filipponi A, Green M, Marsi M, Trzeciak W, Wallace D, Welnak J and Margaritondo G 1990 *Phys. Scr.* **41** 409

Jortner J and Leach S 1980 *J. Chim. Phys., Phys.-Chim. Biol.* **77** 7

Leach S 1989 *Vibrational spectra and structure* (eds) H D Bist, J R Durig and J F Sullivan (Amsterdam: Elsevier) vol. 17B p. 187

Margaritondo G 1988 *Introduction to synchrotron radiation* (Oxford: University Press)

Marshall T C 1985 *Free electron lasers* (New York: MacMillan)

Prazeres R, Ortega J M, Bazin C, Bergher M, Billardon M, Couprie M E, Fang H, Velghe M and Petroff Y 1987 *Europhys. Lett.* 4 817

Stitch M L and Bass M (eds) 1985 *Laser handbook* (Amsterdam: North Holland) vol. 4

Vinokurov N A and Skrinsky A N 1977 Preprint INP77-59, Novosibirsk (1977); N A Vinokurov *Proc. 10th Int. Conf. High Energy Charged Particle Accelerators*, Serpukhov, vol. 2, p. 454