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LINEAR AND CIRCULAR DICHROISM IN THE VACUUM ULTRAVIOLET REGION

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1. Introduction. — Polyatomic molecules with only a pure rotational point symmetry exhibit a mirror-image type of structural isomerism, as was first recognized by Pasteur [1] from a correlation between the enantiomorphous crystal forms of optical isomers and their respective positive and negative circular birefringence, i.e. optical rotation, in the visible region when randomly oriented in the fluid phase. Pasteur termed a structure which is not superposable upon its mirror-image disymmetric, although the term chiral, introduced by Kelvin [2], is now the more commonly employed.

Circular birefringence in the transparent wavelength regions implies the differential absorption of left- and right-circularly polarized radiation at higher frequencies and the expected effect, the Circular Dichroism (CD) of chiral molecules in solution, was discovered by Cotton [3] in 1895. It was only some seventy years later, however, that CD measurements became routinely practicable [4], following pioneer studies of the Cotton effect, notably by Lowry [5], Kuhn [6], and Mathieu [7], which demonstrated the potential of the CD technique in applications to spectroscopic and stereochemical problems.

The basic limitation of CD measurements on randomly-oriented chiral molecules is the generally small magnitude of the CD relative to the average light-absorption, expressed by Kuhn’s dissymmetry factor [6], \( g = (\varepsilon_L - \varepsilon_R)/\varepsilon \), where \( \varepsilon \) expresses the extinction coefficient. The \( g \)-factor of chiral molecules in the fluid phase has a magnitude which, at most, corresponds to the ratio of molecular dimensions to the wavelength of the light absorbed, rarely exceeding \( 10^{-2} \) and often several orders of magnitude smaller.

The \( g \)-factor becomes large, of the order of unity, for axial propagation of the radiation through chiral molecules oriented in a uniaxial single crystal belonging to one of the enantiomorphous space groups, or in a cholesteric mesophase. The corresponding Linear Dichroism (LD) ratio, \( r = (\varepsilon_{\parallel} - \varepsilon_{\perp})/\varepsilon \), is similarly large for anisotropic molecules well-oriented in a single crystal with lower than cubic symmetry, or in a nematic mesophase, or in an oriented film. However, LD measurements on solutions of anisotropic molecules with only a small degree of statistical orientation, such as that produced by the application of an electric field in the case of dipolar solutes, or by streaming the solution in the case of long-chain oligomeric solutes, involve small \( r \)-factors and are attended by the same metrological problems as those encountered in determining the \( g \)-factor of chiral molecules in the gas phase or isotropic solutions.

2. Instrumentation. — The classical CD studies generally were carried out by separate measurements of the sample-absorption of left- and of right-circularly polarized light followed by subtraction [5-7]. The first-reported CD spectrum in the vacuum ultraviolet region (VUCD), that of S-(+)-3-methylcyclopentanone (I), was obtained by this method, employ-
ing separate photomultipliers for the left- and right-circularly polarized beams and a d.c. bridge circuit for the subtraction [8]. Details of the measurements are not yet available, but it is inferred that a double-image polarizing prism in MgF₂ was employed, together with a static quarter-wave retarder, either a birefringent crystal section of MgF₂ or sapphire [9], or a stressed LiF plate [10], or a Fresnel rhomb [11] in CaF₂ or LiF.

Subsequent VUCD instruments [11-14] adopt generally the method of double-beam in time, rather than in space, using the piezo-optical modulator developed by Kemp [15] (Fig. 1). In the four instruments described [11-14] radiation from a VUV one-metre concave grating f/10 monochromator, equipped with either a cold-cathode or hot-filament hydrogen-discharge lamp, passes through a linear polarizer, either a Wollaston or Rochon MgF₂ prism, or a biotite reflection polarizer, to the modulator oriented with its principal axes at π/4 to the polarization plane.

The modulator [15] consists of a quartz piezoelectric transducer cemented to a CaF₂ optical element in which a periodic linear birefringence is induced at some 50 kHz. The peak and trough birefringence is adjusted to quarter-wave or half-wave retardation at the frequency of interest by control of the power-level delivered to the transducer drive. After leaving the modulator the left- and right-circularly polarized radiation periodic at 50 kHz, or the orthogonal linear components at 100 kHz in the case of half-wave modulation, pass through the sample to the detector, which ideally is a solar-blind photomultiplier equipped with a VUV transmitting window, although a silica window coated with sodium salicylate provides a satisfactory alternative.

The photomultiplier signal contains a d.c. and an a.c. component which are separately processed, the latter through a phase-sensitive lock-in amplifier taking a reference signal from the modulator. Where the g-factor is small, as is generally the case in fluid-phase studies, the CD is given by the ratio of the rectified a.c. signal to the d.c. signal. The d.c. signal is maintained at a constant level by a feedback automatic gain control on the EHT supply to the photomultiplier, so that the CD is represented by the amplified a.c. signal. A photomultiplier signal ratio a.c./d.c. of ~ 10⁻⁵ is required to detect a g-factor of the same order, and a minimum of 10¹⁵ photons are needed to measure such a ratio, so that source intensity and stability are major limitations in VUCD studies [16].

3. Applications. — The major applications of CD investigations are to stereochemical and to spectroscopic problems. The absolute stereochemical configuration of a chiral molecule, namely the particular left- or right-handed mirror-image structural form, may be determined non-empirically by CD spectroscopy, and also the preferred conformation in the secondary structure of a flexible chiral molecule of known primary configuration. The excited electronic states of the chromophore in a chiral molecule are characterized by the CD spectrum, as are those of achiral molecules by their Magnetic Circular Dichroism (MCD) spectrum, where the magnetic field oriented along the propagation direction of the radiation provides a quasi-chirality through the mirror of time-reversal antisymmetry.

Both of the primary applications are shared and complemented by LD spectroscopy. While LD studies in themselves provide no information as to absolute configuration, they give directly the polarization directions of the transition moments in a chromophore, and a knowledge of those moment-directions is prerequisite for an analysis of the CD spectrum and derivation of the stereochemical configuration of a chiral molecule containing that chromophore.

A number of simple but important chromophores display significant light absorption only in the VUV region, notably saturated organic molecules, including those containing the lighter heteroatoms, and non-conjugated unsaturated systems. In this set the amide group of peptides and proteins, and the alcohol group of sugars and polysaccharides, together with other chromophores of biochemical importance, are of particular interest. The impetus to the recent development of VUCD instrumentation derives as much in fact from the biophysical field as from chemical spectroscopy where the simple unsaturated chromophores are of fundamental concern. Recent developments in each of these main fields are briefly surveyed in the following sections.

4. Chemical spectroscopy. — The particular aims of VUCD and VULD studies in chemical spectroscopy are the characterization of the electronic states connected by the transitions prescribed by current quantum theory, the evaluation of the various mechanisms proposed for the origin of optical activity, and the determination of molecular structures. Most of the small VUV chromophores have secondary elements of symmetry, one or more rotation-reflection symmetry axes, and they are not in themselves chiral. The addition of substituent groups to the chromophore to remove the secondary symmetry elements and form a chiral molecule confers a rotational strength, measured by the CD band area, upon each electronic transition of the chromophore. The sign
and the magnitude of the induced rotational strength is sensitively-dependent upon the spatial disposition of the substituent group or groups relative to the chromophore, giving CD spectroscopy its potential in stereochemical studies, and raising the coupled problems of the characterization of the electronic transition investigated and the particular electronic origin of the rotational strength associated with that transition.

Optical activity was ascribed in classical electromagnetc theory to the displacement of electronic charge through a helical path in a chiral molecule on the absorption of radiation [17]. In quantum mechanical terms this description transforms into the requirement that a given electronic transition connecting the ground state \( \psi_0 \) with an excited state \( \psi_e \) of a polyatomic molecule has a collinear electric dipole \( \mu_{oe} \) and magnetic dipole \( m_{oe} \) transition moment [18]. The rotational strength of an electronic transition is represented by the scalar product of the two moments,

\[
R_{\text{th}} = \text{Im} \left\{ \langle 0 | \hat{\mu} | n \rangle \langle n | \hat{m} | 0 \rangle \right\}
\]

where \( \text{Im} \) signifies that the imaginary part is to be taken in order to give a real rotational strength, on account of the pure-imaginary character of the magnetic moment \( m_{oe} \) using real state functions.

In a molecule with one or more rotation-reflection axes of symmetry the electric and the magnetic dipole moment of a given electronic transition are either mutually orthogonal or the one or the other or both of the two moments are zero. In a chiral molecule the electric and magnetic moment of a particular transition have parallel components in one stereoisomer, representing a positive rotational strength and a classical right-handed helical charge displacement, while the corresponding components are antiparallel in the mirror-image enantiomer, the rotational strength then being negative and the analogue of the classical left-handed helical charge displacement.

Groups which are chromophoric only at higher frequencies in the VUV region, such as alkyl groups, when substituted into chromophores with secondary symmetry elements, like the olefin or the carbonyl chromophore, generally produce only minor changes in the electronic absorption spectrum at lower frequencies, even though the substitution produces a chiral molecule. From this observation two models for the electronic origin of optical activity arose at an early stage, both based on the independent-systems assumption that the charge-distributions of the substituent and of the chromophore are non-overlapping, the major interaction between them being the mutual Coulombic potential.

The group-polarization [19] or dynamic-coupling [20] model was a direct quantum-mechanical development of the classical polarizability and coupled-oscillator theories of optical activity. In the model the Coulombic field of the leading electric moment of the chromophore transition, dipole, quadrupole, or higher multipole, correlates the orientation of the electric dipole moment induced in the substituent group by the radiation field. The induced dipole, proportional to the group-polarizability at the transition frequency, forms a scalar product either with the magnetic dipole moment of the chromophore transition, or with the equivalent cross-product of the electric dipole transition moment and the vector directed along the line of centres between the chromophore and substituent group, to give a non-vanishing rotational strength [19, 20].

In the alternative static-field model [21], which owed much of its inspiration to earlier and contemporary developments in the crystal-field theory of transition-metal and lanthanide ions, a zero-order magnetic-dipole transition acquires a first-order electric dipole moment, borrowed from another transition of the symmetric chromophore, under the perturbing Coulombic field of the ground-state charge distribution of the substituent. Equally a zero-order electric dipole transition obtains a first-order magnetic dipole moment by the same mechanism, and it is a consequence of the static-field theory that a coupled-pair of transitions in a symmetric chromophore, one electric-dipole and the other magnetic dipole allowed, have rotational strengths of equal magnitude and opposite sign in a chirally substituted derivative of the chromophore [22].

5. Individual chromophores. — In the case of the C\(_{2v}\) carbonyl chromophore the extension of CD spectroscopy to the VUV region permits an evaluation of the relation expected from the static-field theory between a coupled pair of transitions in a symmetric chromophore. Since the time of the classical CD studies, the 300 nm absorption of chiral ketones has been of central importance in both experimental and theoretical investigations of optical activity. It was the subject of the first stereochemical sector rule relating the disposition of the substituent group in the molecular environment of the chromophore to the sign of the Cotton effect induced by the group, the well-known octant rule [23], and those Cotton effects were early interpreted by means of the static-field model [24], with subsequent refinements [25, 26]. The analysis ascribes the rotational strength of the 300 nm carbonyl absorption of a chiral ketone to the mixing of the zero-order magnetic dipole transition of a non-bonding electron from the 2p\(_x\) orbital of the oxygen atom to the antibonding 3d\(_{py}\) orbital of the carbonyl group, \( n_x \rightarrow \pi^*_{es} \), with the electric-dipole allowed Rydberg transition of the oxygen atom, \( n_y \rightarrow 3d_{yz} \), at higher energy [25, 26].

The main example considered [24, 25], (S)-(+-)-3-methylcyclopentanone (I), was the first chiral molecule studied by VUCD spectroscopy [8], the spectrum subsequently being remeasured and extended to higher frequencies [11, 12, 27]. The quartz and VUCD
FIG. 2. — The vapour-phase quartz and VUV absorption (lower curve) and CD spectrum (upper curve) of (S)-(+) 3-methylcyclopentanone (I) (adapted from references [8], [11] and [12]).

The signs of the CD bands near 195 nm of a series of conformationally-labile open-chain chiral olefins [33], conformationally-flexible olefins of the terpene and steroid series [14], e.g. (--)-a-pinene (III), and ethylene itself in a magnetic field [34]. The salient features of the VUCD spectra of chiral olefins are a couplet of oppositely-signed major CD bands with comparable areas in the 160-200 nm region which are preceded in a number of vapour-phase spectra by sharper but weaker CD bands near 220 nm (Fig. 3).

In the corresponding solution CD spectra, the sharp bands are broadened and shift to the blue, or disappear (Fig. 3), indicating that these bands arise from a Rydberg transition, generally taken to be the n, → π* transition at 300 nm and of the Rydberg n, → 3d transition near 165 nm [28] are both positive, indicating that the mixing of the two transitions under the static field of the methyl-substituent cannot be primarily responsible for either of the CD bands associated with these transitions.

The static field mechanism may well apply, however, to the mixing of the transitions near 195 and 165 nm which have rotational strengths of opposite sign and comparable magnitude (Fig. 2). The 195 nm band system has been assigned to the n, → 3s Rydberg transition overlying the valence shell excitation, n, → σCO, since the absorption persists in the condensed phase, although with a loss of some intensity and vibrational structure and a shift to the blue [28]. The electric dipole moment of the 195 nm band system is known to be directed in the plane of the carbonyl chromophore perpendicular to the carbonyl bond axis, i.e. the y-axis of molecule (I), from a comparison of the single-crystal VUV spectrum of heptadecanone (C₈H₁₇COC₈H₁₇) with that of the corresponding melt [29]. This polarization with the n, → 3s and the n, → σCO assignment [28] and it implies that the latter excitation has additionally an x-polarized magnetic dipole moment which, in conjunction with the collinear electric moment of the n, → 3d, Rydberg transition, accounts for the oppositely-signed CD bands of comparable area observed near 195 and 165 nm in the VUCD spectrum of (I) (Fig. 2) by the static-field or alternative mixing mechanisms.

The signs of the CD bands near 195 nm of a series of steroidal ketones in hexane solution have been fitted to a stereoechemical quadrant rule [30]. The sign follows that of the product XY of the coordinates of the substituent group in the Cartesian frame of the chromophore, e.g. that of molecule (I). The signs of the 195 and the 300 nm Cotton effects are generally the same for substituents placed in the + Z hemisphere of the chromophore coordinate frame, i.e. in the four rear octants of the -- XYZ octant rule for the 300 nm carbonyl CD bands [23], but a number of chiral cyclopentanones are exceptional [30], e.g. the molecule (I) which gives CD bands of opposite sign at 195 and 300 nm (Fig. 2).

Between the major negative and positive CD bands near 195 and 165 nm, respectively, in the VUCD spectrum of (S)-(+) 3-methylcyclopentanone (I), lie weak CD bands associated with the relatively low-intensity absorption band system originating at 178 nm (Fig. 2). This band system has been assigned to the n, → 3p Rydberg transition [28]. Below 160 nm a negative and two positive CD bands of moderate intensity are observed in association with rising absorption of high intensity (Fig. 2). The provenance of these bands is as yet uncertain, but the valence-state promotion πCO → π*CO is presumed to lie in this region [28].

As only a limited region of the ethylenic spectrum is accessible with quartz UV instruments, particular attention has been devoted to the VUCD spectroscopy of chiral olefins recently [11, 14, 31-34]. The alkenes studied include (R)-(--) 3-methylcyclopentene (II) [31, 32], in which the olefin chromophore is substantially distorted from planarity, a series of conformationally-labile open-chain chiral olefins [33], conformationally-flexible olefins of the terpene and steroid series [14], e.g. (--)-a-pinene (III), and ethylene itself in a magnetic field [34]. The salient features of the VUCD spectra of chiral olefins are a couplet of oppositely-signed major CD bands with comparable areas in the 160-200 nm region which are preceded in a number of vapour-phase spectra by sharper but weaker CD bands near 220 nm (Fig. 3).

In the corresponding solution CD spectra, the sharp bands are broadened and shift to the blue, or disappear (Fig. 3), indicating that these bands arise from a Rydberg transition, generally taken to be the π, → 3s excitation [28], where π, is the bonding MO formed by the π-overlap of the 2p, AOs of the trigonal carbon atoms in the chromophore coordinate frame of (II) and (III). A couplet of oppositely-signed CD bands in the spectrum of a monochromophoric chiral molecule is characteristic of the mixing of two transitions close in energy, one electric the other magnetic dipole allowed in the zero order. The π, → π*, 1A1g → 1B1u, transition of polysubstituted olefins, with a z-polarized electric dipole moment directed along the C=C bond
Each of these excitations when mixed with the \( \pi_x \rightarrow \pi_x^* \) transitions, either by the static-field or the group-polarization mechanism or by the torsional distortion of the chromophore, gives a stereochemical octant rule, but opposite signs are allocated in the two cases [14]. The rule relates the sign of the product \( XYZ \) of the coordinates of the substituent in the Cartesian frame of the olefin chromophore to the sign of the lower and of the higher energy band of the major CD couplet. While many cyclic chiral alkenes follow the octant rule based on the choice of \( \pi_x \rightarrow \pi_x^* \) as the significant magnetic-dipole promotion, a large number of exocyclic chiral olefins conform to the oppositely-signed octant rule based on the \( \pi_x \rightarrow \pi_x^* \) choice. A few chiral exocyclic alkylidene derivatives, with the effective substituent groups located solely in the symmetry planes of the olefin chromophore, cannot be accommodated to either type of octant rule.

The assignment of the major CD couplet observed in the VUCD spectra of chiral olefins to the mixing of zero-order electric dipole and magnetic dipole allowed transitions of the olefin chromophore implies that the latter transition acquires an appreciable absorption intensity in olefin derivatives of low symmetry and an electric dipole polarization identical to that of the donor \( \pi_x \rightarrow \pi_x^* \) transition. Discrete absorption bands of comparable intensity are associated with the members of the oppositely-signed CD couplet in the VUCD spectra of the majority, but not all [33], chiral olefins (Fig. 3). Both of the absorption bands are \( z \)-polarized, along the direction of the \( \text{C} = \text{C} \) bond, as is shown by the polarized single-crystal VUV spectrum [36] of bicyclohexylidene (IV).

The effect of a positively charged ammonium substituent upon the CD spectrum of a chiral olefin is similar to that of a correspondingly-substituted neutral alkyl group, suggesting that the static-field mechanism for the mixing of an electric with a magnetic dipole transition in a symmetric chromophore does not make a major contribution to the optical activity of chiral alkenes [14]. Both the static-field and the group-polarization model for optical activity are of limited application to CD spectra confined largely to the VUV region, however, as even the relatively inert alkyl substituents become chromophoric in this region, and coupled-chromophore treatments become more appropriate. The first VUCD band of the steroid alkane, \( 5 \alpha \)-cholestan, lies at 175 nm [14], for example, and that of the branched-chain alkane, \(( - )-(3S : 5S)-2,2,3,5\text{-tetramethylheptane}, at 148 \text{ nm} \) [37]. Moreover the steric distortions introduced by substitution are so severe in a number of chiral olefins, e.g. \(( R )-( - )\text{-trans-}
cyclooctene (II), that the molecule can no longer be considered as a symmetric chromophore in a chiral molecular environment, the type of case for which the two models were designed, and it becomes an inherently disymmetric chromophore, a class generally treated by MO methods [38].

The VUCD spectra of derivatives of the fundamental aromatic chromophore, benzene, have been reported, notably that of (S)+(−)-1-methylindan [39], (S)-(−)-2-phenylbutane [40], and that of the parent nucleus and of toluene in a magnetic field [41]. The spectra show CD features associated with the absorption bands due to transitions from the 1A1g ground state to the 1B2g, 1B1g, and 1E1g excited states of the benzene π-manifold, lying at 271, 218, and 188 nm, respectively, in 1-methylindan, but an additional pair of CD bands, one negative and the other positive, at 198 and 194 nm in 1-methylindan and at 191 and 187 nm in 2-phenylbutane, suggest a contribution from a transition to an E2g state in this region [39, 40]. The rotational strengths of (S)+(−)-1-methylindan calculated by the static field method are inadequate in themselves to account for the VUCD spectrum of the molecule, but the spectrum is satisfactorily explained when the static field terms are augmented by the coupled-chromophore contributions to the rotational strengths, calculated from the VUV absorption data for the alkanes [39]. The MCD spectrum of benzene in the 170-190 nm region remains enigmatic, but that of toluene in the same region gives the magnetic moment of the 1E1g state a value of −0.09 Bohr magneton compared with a calculated value of −0.14 β [41].

The VUCD spectrum of (−)-(1S : 28)-trans-dimethylcyclopropane has been measured, together with MCD of cyclopropane [42]. The first CD band of trans-1,2-dimethylcyclopropane lies at 190 nm and has a relatively large g-factor (2 × 10−3), suggesting that it has a magnetic-dipole origin. The transition is characterized as 1A1 → 1A2 in the D3h group of cyclopropane. The higher-energy CD bands at 177 and 160 nm have smaller g-factors, and they are assumed to be the analogues of the electric dipole transitions at 158 and 145 nm, respectively, in the parent molecule, both characterized as 1A1 → 1E′ from the MCD spectrum [42].

The MCD spectrum of acetylene [43] places the origin of the second band system 1Σ* → 1B0 at 185 nm, as the first system 1Σ* → 1A0, is found to give no MCD absorption. The MCD of the third system consists of a progression of four A-terms with a vibrational spacing of 1 850 cm−1, originating at 152 nm. The A-terms unambiguously confirm the πa character of the excited state and support the assignment of the third system as the first member of a Rydberg series, πa → 3s.

6. Biopolymers and their chromophores. — The particular aims of VUCD and VULD studies in the biophysical field are an understanding of the primary and secondary structure of biopolymers and of the optical properties of both the polymer and its monomeric units. Generally the detailed spectroscopic properties of the monomer chromophore are taken as a basis for evaluating the properties of model structures of the polymer, a method first adopted by Moffitt [44] in an analysis of the optical properties of the polypeptide α-helix. Moffitt employed the frequencies, polarization-directions, and oscillator strengths of the electronic transitions of the amide chromophore, taken from the VULD spectrum [45] of a single-crystal of myristamide (CH3(CH2)14CONH2) and from earlier VUV spectra of amide vapours [46], to calculate the dispersion transform of the CD spectrum expected for a helical array of amide chromophores (Fig. 4). From the treatment, in which the polymer rotational strengths were derived from the Coulombic coupling of the non-coplanar monomer transition dipoles, Moffitt [44] concluded correctly, but with subsequent reservations [47], that polypeptides derived from the natural L-aminoacids form a right-handed α-helix.

The stereochemical reservations were shown to be unfounded in later studies and Moffitt’s conclusions have been placed on a more secure theoretical foundation [48], while the extension of CD spectroscopy to the VUV region has given a more direct experimental access to the calculated rotational strengths than is afforded by optical rotatory dispersion measurements over the quartz UV and visible region. Recent investigations of peptide systems and their units include the single-crystal VULD spectrum of the cyclic amide dimer, diktetopiperazine [49] (CH3CONH)2, down to 160 nm and, over the same range, the VUCD spectra of five representative L-amino acids, measured as their N-alkyl derivatives in buffered water-acetonitrile mixtures or in hexafluoro-2-propanol as solvent [50]. The spectra of the L-aminoacids when compared with the expected CD, calculated by the group-polarization independent-systems model [19, 48] for a range of group-dispositions, affords the conformation of the carboxylate ion chromophore relative to the charged ammonium group and the alkyl groups in the zwitterionic form of the molecule [50].

Films of polypeptides cast from concentrated solution on to CaF₂ discs transmit down to 130 nm. The polypeptide chains become statistically oriented along the shear-direction if the film is stroked during the evaporation of the solvent. The VULD spectra of oriented films of poly-γ-ethyl-L-glutamate [51] and of poly-L-alanine [52] have been determined, together with the VUCD of isotropic films of two conformations of poly-L-proline [53, 54] and of a series of oligopeptides derived from four L-aminoacids [55, 56]. A comparison of the experimental with the calculated VUCD indicates the presence in the film of a substantial fraction of the β-conformation with both parallel and antiparallel chains [55, 56].
The VUCD spectrum of aqueous solutions of poly-L-glutamic acid in both the α-helix and the random-coil conformation have been measured, together with that of the γ-methyl derivative in hexafluoro-2-propanol as far as 140 nm [57]. The VUCD spectrum of helical PLGA shows, in addition to the \( n \rightarrow n^* \) amide band at 225 nm and the parallel and perpendicularly-coupled amide \( \pi \rightarrow n^* \) exciton modes at 210 and 190 nm, respectively, a new CD shoulder at 175 nm on the side of the 190 nm band (Fig. 4). The new VUCD band is assigned to an \( n \rightarrow \sigma^* \) amide transition [57]. A new parallel-polarized VULD band near 160 nm in the corresponding oriented-film spectrum is also assigned to this excitation or to the second \( \pi \rightarrow n^* \) amide transition [51].

Studies of the stereochemical and optical properties of the sugar units in the polysaccharides and the polynucleotides are dependent upon a spectroscopic understanding of the alcohol chromophore. To this end the VUCD of (S)-(−)-2-butanol \((\text{C}_2\text{H}_4\text{CH(OH)}\text{CH}_3)\) in the vapour phase has been determined as far as 135 nm and compared with the rotational strengths calculated by the group-polarization independent-systems' method for three principal conformations [58]. The calculation for the sterically-preferred conformation of 2-butanol provides good agreement with the experimental VUCD of the first three transitions, based upon the assignment of these to an electronic promotion from the \( 2p \) lone-pair of the oxygen atom to the \( \sigma_{\text{OH}}, \sigma_{\text{CO}} \) and \( 3s_0 \) orbitals, sequentially to higher energy [58]. The vapour-phase VUCD of the first two transitions of the stereochemically less-labile alcohol, (−)-borneol, has been similarly analysed [59].

The sugars contain not only the primary and secondary alcohol chromophore but also the acetal and the hemiacetal group. The VUV absorption of these groups has been measured, together with that of the ether linkage [60], and the results have been employed, on the assumption that the individual chromophore contributions are additive, to analyse the VUCD spectra of a range of aldo- and keto-pyranose anomers and of the methylaldopyranosides [61]. The measurements refer to aqueous solution and extend to 165 nm. From comparisons between the spectra, it is concluded that a pyranose and the corresponding methyl pyranoside have similar conformation in aqueous solution, and that the first CD band, 180-185 nm, arises from the ring-oxygen chromophore, and the second in the pyranosides, ~175 nm, from the methoxy group [61].

Analogues of these two bands appear in the VUCD spectrum of a film cast from aqueous solution of iota-carrageenan, a polysaccharide composed of alternating units of \( \beta\)-D-galactose-4-sulphate and 3,6-anhydro-\( \alpha\)-D-galactose-2-sulphate [62]. The CD bands of iota-carrageenan are substantially more intense [62] than those of the monomeric analogues, methyl-\( \alpha\)- and methyl-\( \beta\)-galactopyranoside [61], suggesting that

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**Fig. 4.** - The polypeptide α-helix; (a) the orientation of the \( \pi \rightarrow \pi^* \) transition moment of the amide chromophore, (b) the parallel coupling-mode of the individual amide moments in the polypeptide α-helix, (c) one of the corresponding perpendicularly-polarized coupling modes, and (d) the unpolarized absorbance spectrum (AB) and linear dichroism (LD), expressed as the transmittance ratio \((T_a - T_i)/(T_i + T_i)\) of an oriented film of poly-γ-ethyl-L-glutamate, and the circular dichroism spectrum (CD) of poly-γ-methyl-L-glutamate in hexafluoro-2-propanol solution (adapted from references [51] and [57]).
the sugar units are helically arrayed in the polysaccharide film.

The sugar units of DNA may make a contribution to the VUCD of this biopolymer in aqueous solution, as the new CD bands detected in the VUV region [63] lie close to those reported for the monosaccharides [61]. A contraindication is that the new VUCD bands of DNA are more sensitive to the particular bacterial or animal source of the biopolymer, i.e. to the particular purine and pyrimidine base-pair composition, than are the CD bands in the quartz UV region [63]. The VULD spectra of oriented films of DNA and of the double-stranded helical complex of polynucleotide with polynucleotide can be measured down to 150 nm [51], but the LD spectra of single crystals of the purine and pyrimidine nucleic acid bases are confined as yet to the quartz UV region [64]. The polarization-directions and the frequencies, including the VUV region, of the purine and pyrimidine bases have been calculated by all-valence-electron methods [65], and adequate information is now available for an interpretation of the optical properties of DNA and the polynucleotides in the VUV region.

References

[64] Single-crystal LD studies of the pyrimidine and purine nucleic acid bases are listed in the following reference [65].