

AN ABSTRACT OF THE THESIS OF

Richard Leroy Bowman for the degree of Doctor of Philosophy
in Biochemistry and Biophysics presented on August 22, 1978

Title: INTERPRETING THE CIRCULAR DICHROISM OF CYCLIC
DIMERS OF AMINO ACIDS

Abstract approved: Redacted for Privacy
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Independent systems theory has been used to interpret the circular dichroism (CD) spectra in the vacuum uv of three cyclic dimers of amino acids. First, the theory for rotational strengths is developed in terms of degenerate and nondegenerate group functions. All terms to first order in perturbation theory are kept. The theory is then used to calculate the CD due to the $n\pi_-$, $\pi_0\pi_-$, $n\sigma^*$, $\pi_0\sigma^*$ and $\pi_+\pi_-$ transitions on the amide groups. The $n\pi_-$ and $\pi_0\pi_-$ are assigned to the three long wavelength bands in L-prolyl-L-proline diketopiperazine (PPDKP). In the L-alanyl-glycine diketopiperazine (AGDKP) and L-alanyl-L-alanine diketopiperazine (AADKP), the first two bands are assigned to $\pi_0\pi_-$.

The intense bands below 180 nm in all three molecules cannot be explained by the transitions on the amide groups. Thus, a study of $\sigma\sigma^*$ transitions is carried out using alkane compounds as models for the diketopiperazines. Using degenerate perturbation theory, the energies and rotational strengths for these alkane compounds are

calculated. The resulting CD curves allow the assignment of the 140 nm and 160 nm bands in PPDKP and the 140 nm band in AGDKP and AADKP to $\sigma\sigma^*$ transitions. Through the interaction of the $\pi_0\pi_-$ transition with the 180 nm $\sigma\sigma^*$ transitions in PPDKP the intense band at 180 nm is assigned to $\sigma\sigma^*$.

The explicit interaction of the various $\sigma\sigma^*$ transitions with the $\pi_0\pi_-$ transition provides a nonconservative part to the $\pi_0\pi_-$ CD curve of correct sign and magnitude for the three molecules. The polarizability approximation gives the wrong sign to this part in the case of AGDKP and AADKP.

Interpreting the Circular Dichroism of Cyclic
Dimers of Amino Acids

by

Richard Leroy Bowman

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Doctor of Philosophy

Completed August 1978

Commencement June 1979

APPROVED:

Redacted for Privacy

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Date thesis is presented August 22, 1978

Typed by Clover Redfern for Richard Leroy Bowman

This thesis is dedicated to Elsie, my wife, and to Todd,
Jonathan, and Jennifer, our children, for their support and under-
standing during these years of my graduate studies.

ACKNOWLEDGEMENTS

I am indebted to a number of persons for making this thesis possible. The research could not have been undertaken nor carried out except for the direction and support given by my major professor, Dr. W. Curtis Johnson, Jr. He provided information, inspiration, challenges and affirmation when I needed them most. Also, I would like to thank Dr. Patricia Snyder, Dr. Önder Pamuk and Dr. Warren Innskeep for many helpful discussions. Special thanks goes to my wife, Elsie, for her willing typing of the various rough drafts of the manuscript.

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INTERPRETING THE CIRCULAR DICHROISM OF CYCLIC DIMERS OF AMINO ACIDS

I. INTRODUCTION

The optical absorption phenomena, normal absorption and circular dichroism (CD) spectroscopy, are sensitive to the conformation of a molecule. While CD can only be measured for optically active compounds, CD spectra can have positive and negative bands whose magnitude and position aids in the assignment of separate molecular transitions.

This study is an examination of the CD spectra of some cyclic dimers of glycine, alanine and proline. These cyclic dimers of amino acids, or diketopiperazines, are excellent models for the amino acid-amino acid interactions in proteins. Since CD is sensitive to near neighbor monomer interactions, diketopiperazines are especially useful models for protein secondary structure.

The conformation of diketopiperazines has been under investigation for some time. Crystallography,¹⁻⁴ nuclear magnetic resonance,⁵⁻⁷ CD and optical rotatory dispersion,⁸⁻¹⁴ conformational energy calculations¹⁵⁻¹⁹ and molecular orbital calculations^{20, 21} are some of the techniques used. These have shown that the various diketopiperazines assume a variety of conformations even though the rigidity of the amide groups restricts the number of allowed conformations.

Previous theoretical studies of electronic absorption and CD of diketopiperazines in solution have had to rely on spectra that did not go below 185 nm. Except for the absorption and CD bands above 240 nm that are due to the $n\pi^*$ and $\pi\pi^*$ ring transitions of tyrosine, tryptophan and phenolalanine, these spectra only give bands due to the $n\pi^*$ and the first $\pi\pi^*$ transition centered on the amide group.

Presented here are the CD spectra, from 240-135 nm, of L-alanyl-L-glycine diketopiperazine (AGDKP), L-alanyl-L-alanine diketopiperazine (AADKP) and L-prolyl-L-proline diketopiperazine (PPDKP). New bands are observed in each case for the 185-135 nm region. This supplies new information for conformational analysis.

Our calculations accurately account for the CD bands due to $n\pi^*$ and the first $\pi\pi^*$ couplet and allow assignment of the new bands to various $\sigma\sigma^*$ transitions. The predicted conformation for the rigid PPDKP is the same as that found in the crystal. However, AG- and AADKP are predicted to assume a folding in solution that is opposite to that found in the crystal.

The spectra are presented in Section II along with the equations necessary for comparison of the experimental spectra and theoretical rotational strengths. The complete equations for calculation of rotational strengths from the independent systems theory are developed in Section III. Section IV gives the results of this theory applied to the molecular transitions centered on the amide group. The assignable

transitions by this approach are the $\pi\pi^*$ and first $\pi\pi^*$ couplet.

Transitions of the amide group cannot account for the new, short wavelength transitions.

To explain the remaining CD bands, we calculated the rotational strengths and transition energies due to the interaction of $\sigma\sigma^*$ exciton states for model hydrocarbon compounds. These results allow the assignment of the bands between 180 and 135 nm to $\sigma\sigma^*$ transitions. They also predict the existence of $\sigma\sigma^*$ CD bands below 135 nm.

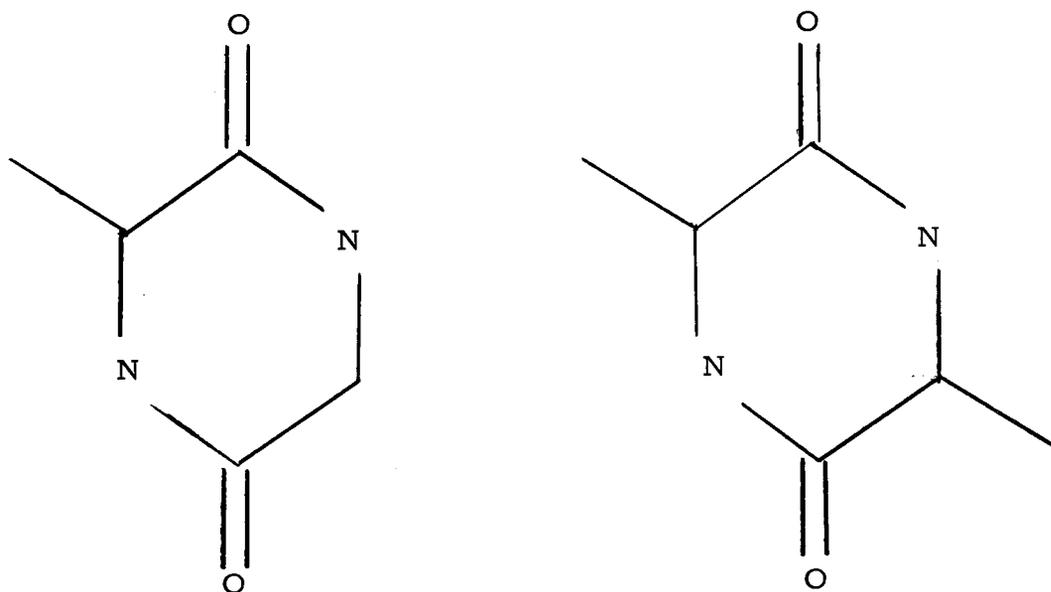
II. EXPERIMENTAL SPECTRA

A. The Compounds and their Spectra

Three cyclic dimers of amino acids, AGDKP, AADKP and PPDKP, have been examined by using absorption and CD spectroscopy in the vacuum ultraviolet region of the energy spectrum. These spectra were taken some time ago by M. Kellerman and W. C. Johnson. They remained unpublished until they could be adequately interpreted. The compounds were purchased from Cyclo Chemical, Los Angeles, CA.

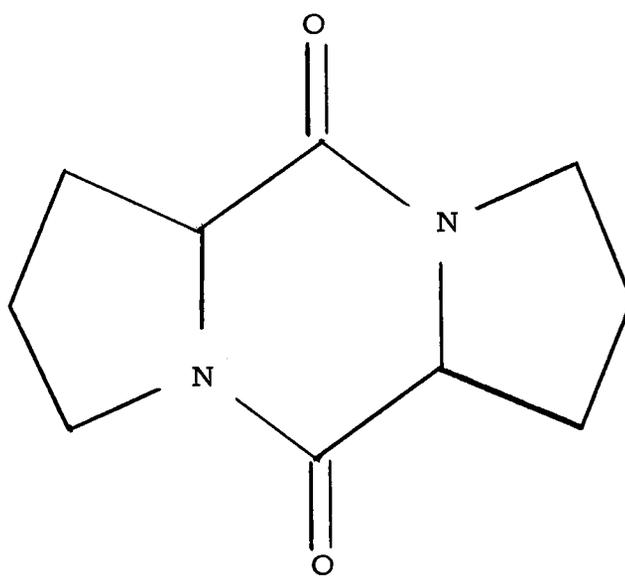
Figure 1 shows the chemical structures of the three compounds. The two amide groups are planar and rigid due to the lone pair of nitrogen (in a 2p-type orbital) conjugating into the π -structure of the carbonyl group. PPDKP has a relatively rigid conformation and thus provides a good model to which the theory developed in the next section can be applied. However, AGDKP and AADKP can assume various folded conformations. A folding of the planes of the amide groups about a line connecting the two alpha carbons, so that the $C^{\alpha} - C^{\beta}$ bonds rotate between axial and equatorial positions, is the only conformational variable. Part of this research then involved a search for the conformation preferred in solution.

The diketopiperazines were dissolved in water, and measurements were made to 175 nm using a standard cylindrical quartz cell with a nominal pathlength of 0.05 nm. Water can be used as a solvent down to 165 nm in extremely thin cells, but then its absorbance



AGDKP

AADKP



PPDKP

Figure 1. Chemical structures for AGDKP, AADKP and PPDKP.

becomes too great. Since a more transparent solvent would be used to extend the measurements, water was used only to get the position and magnitude of the first $\pi\pi^*$ couplet.

Spectrograde hexafluoroisopropanol (HFIP) was used as a solvent to complement the data taken with water and to extend useful measurements to 135 nm. HFIP dissolves the diketopiperazines and is very similar to water as a solvent except that it is transparent to 165 nm in the 0.05 mm cells. Measurements below 165 nm were made using a sandwich type cell made of two polished CaF_2 windows. These measurements were checked by comparing the long wavelength data with that for the standard quartz cell. PPDKP was also dissolved in acetonitrile (MeCN) and measurements were made to 160 nm.

All measurements were made on a vacuum uv CD spectrometer constructed by W.C. Johnson.²² The spectrometer was calibrated using a value of $\epsilon_L - \epsilon_R = 2.20$ at 290.5 nm for d-10-camphorsulfonic acid in water.

The spectra of the three compounds are shown in Figures 2, 3 and 4. The absorption spectrum given at the bottom of each figure shows one main band at 185 nm for AG- and AADKP and 190 nm for PPDKP. This is generally assigned to the molecular transition due to the first $\pi\pi^*$ transition of the amide groups. It is essentially a degenerate transition and appears only as a single band in the absorption spectra.

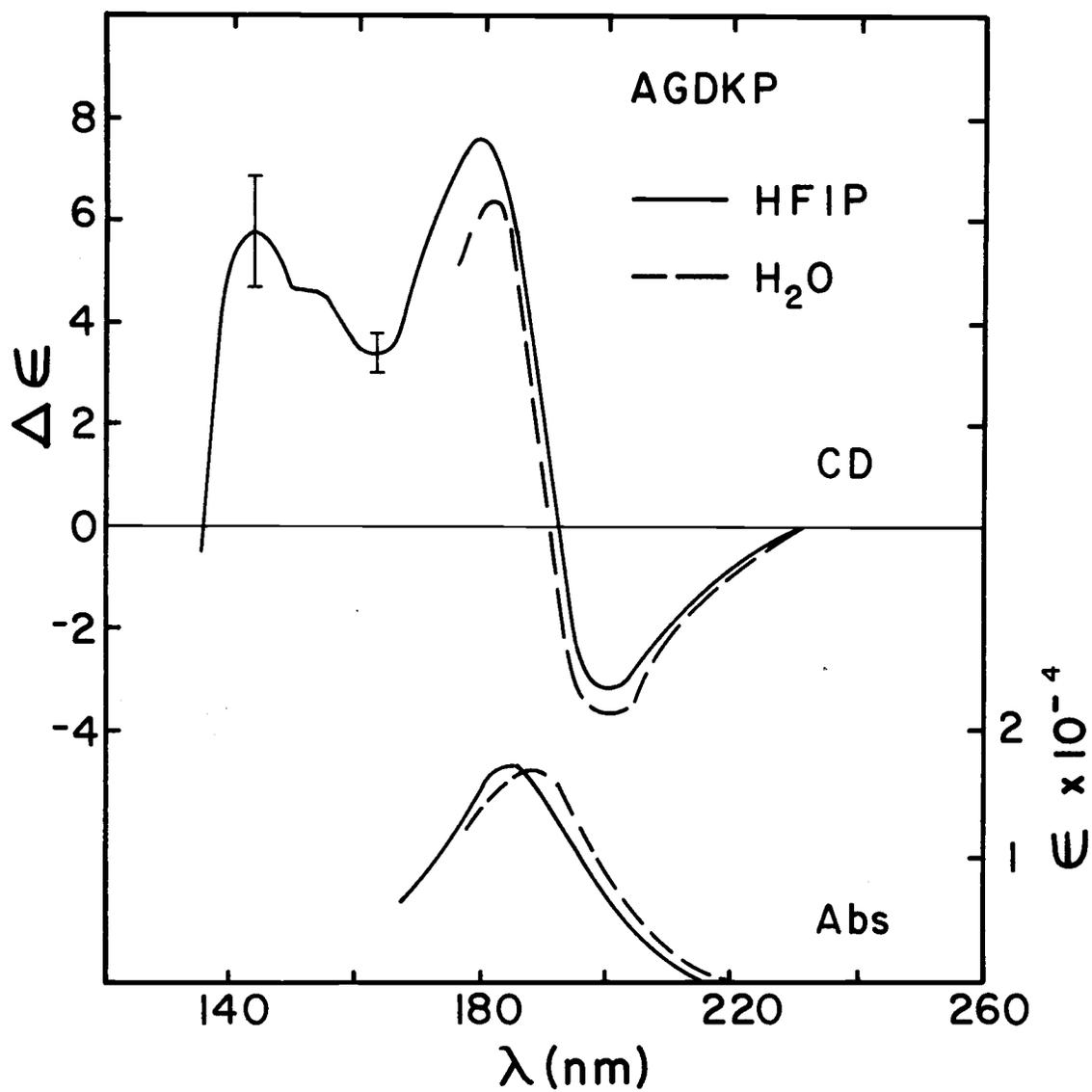


Figure 2. CD and absorption of AGDKP.

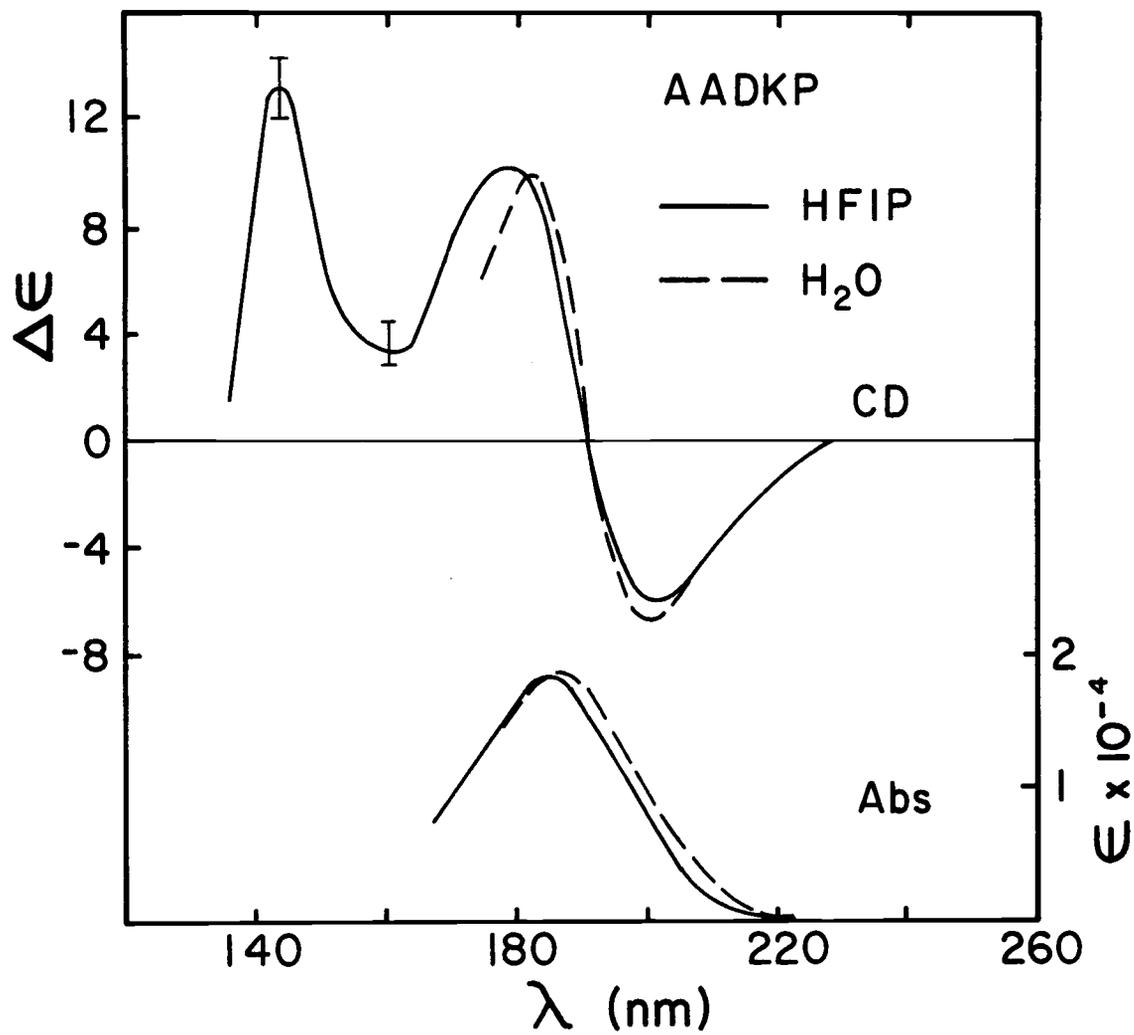


Figure 3. CD and absorption of AADKP.

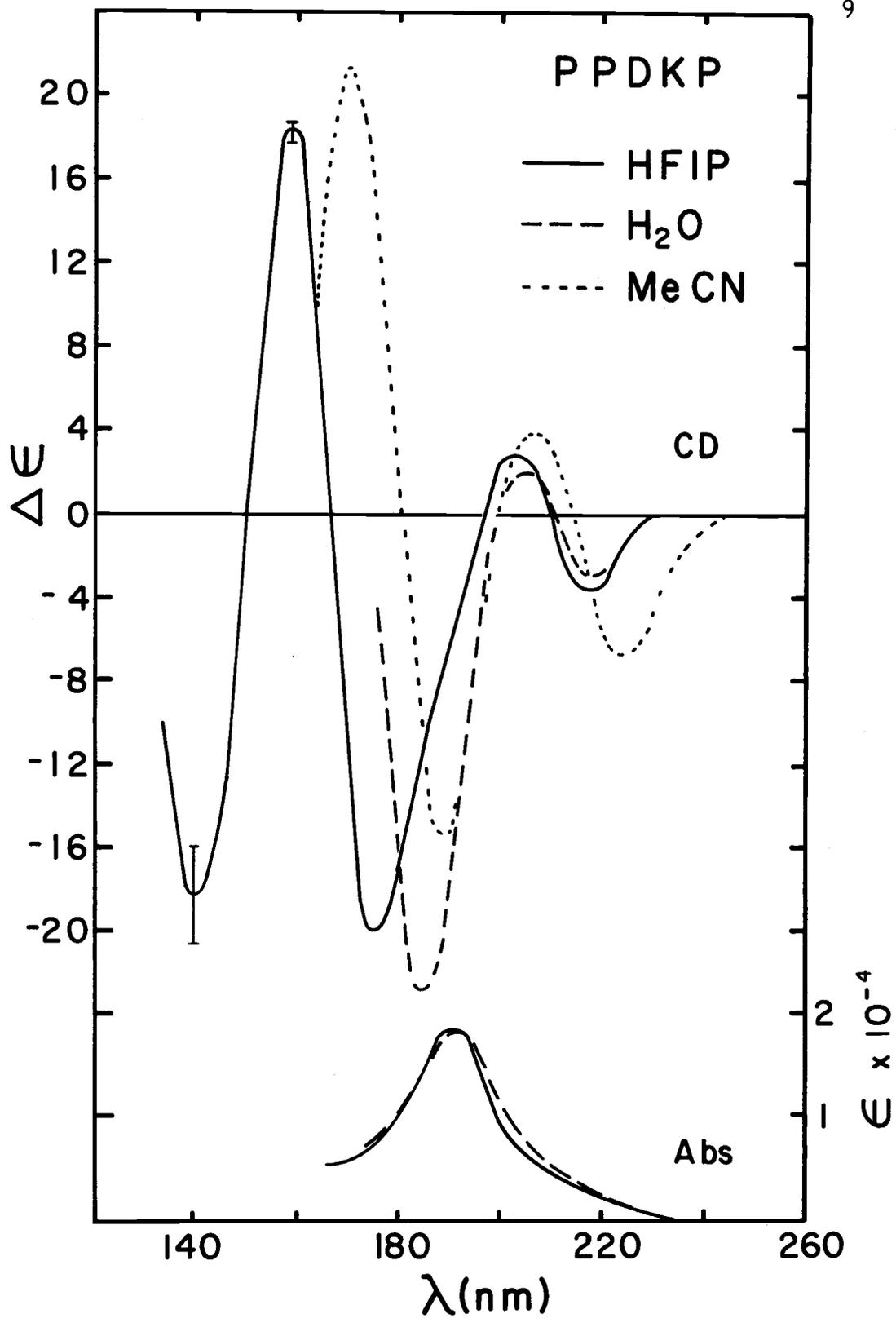


Figure 4. CD and absorption of PPDKP.

The literature indicates a molecular transition due to the $n\pi^*$ transition of the amide groups should occur to the red of the $\pi\pi^*$ band.²³⁻²⁵ Comparison of the three absorption spectra indicates only a pronounced shoulder in the PPDKP spectrum. However, $n\pi^*$ transitions are very sensitive to substituent and solvent effects.²⁵

The CD spectra of AG- and AADKP shows a couplet of bands of opposite sign centered about 185 nm. These are assigned to the first degenerate $\pi\pi^*$ transition of the amide groups. The long wavelength band is negative. The main remaining feature is a positive band at about 140 nm for both compounds. In addition, AGDKP shows a distinctive bump on the long wavelength side of the 140 nm band.

The PPDKP CD spectrum shows many more bands. Just as in the absorption spectrum, the $n\pi^*$ transition of the amide groups appears as the first band. The next two bands are the $\pi\pi^*$ couplet where the long wavelength band is positive (opposite of that for AG- and AADKP) and the short wavelength band appears as a long wavelength shoulder on a second large negative band centered at 180 nm. A positive and a negative band with $|\Delta\epsilon| \approx 18$ occur at 160 nm and 140 nm, respectively.

B. The Relationship Between Experimental Spectra
and Theoretical Calculations

The actual observable of absorption spectroscopy is the absorbance, A , defined by

$$A = -\log \frac{I}{I_0} \quad (1)$$

where I_0 is the intensity of the incoming light and I is the intensity of the transmitted light. However, the absorbance of a particular compound is proportional to its concentration, c , and the pathlength the light travels through the solution, l , through a constant peculiar to the molecule called its molar absorption coefficient. This proportionality constant, $\epsilon(\lambda)$, is a function of the wavelength of the incident light. According to the Lambert-Beer law

$$A(\lambda) = \epsilon(\lambda)cl \quad (2)$$

where ϵ is in units of liters per mole-centimeter, c is in moles per liter and l is in centimeters.

For optically active compounds there exists different absorption coefficients for left- and right-circularly polarized light. Since the Lambert-Beer law holds for both types of light,

$$A_L - A_R = (\epsilon_L - \epsilon_R)cl = \Delta\epsilon cl \quad (3)$$

This property is called circular dichroism (CD), and the sign of $\Delta\epsilon$ is defined as above by convention. This is usually a very small quantity. For example, the diketopiperazines have $\epsilon \approx 20,000$, and $|\Delta\epsilon| < 20$ for the first $\pi\pi^*$ transition.

The theoretical quantities that are calculated are not ϵ and $\Delta\epsilon$ but the dipole strength, D , and the rotational strength, R . The area under an electronic absorption band is a measure of the probability of that transition and is proportional to the dipole strength. In cgs units, the dipole strength is²⁶

$$D = \frac{3hc}{8\pi^3 L} 10^3 \ln 10 \int_0^\infty \frac{\epsilon(\lambda)}{\lambda} d\lambda \quad (4)$$

where h is Planck's constant, c is the velocity of light, L is Avogadro's number and λ is the wavelength of the incident light.

The probability of observing a CD band is similarly proportional to the rotational strength,²⁷ R , where

$$R = \frac{3hc}{32\pi^3 L} 10^3 \ln 10 \int_0^\infty \frac{\Delta\epsilon(\lambda)}{\lambda} d\lambda \quad (5)$$

For an isolated band, comparison of the experimental rotational strength given by Eq. (5) and the theoretical rotational strength calculated from the equations developed in the next section is straightforward. However, in practice rotational strengths derived from a

spectrum that has many overlapping bands will not be readily comparable to a series of theoretical rotational strengths. For example, two bands of opposite sign that occur close to each other will tend to cancel and the experimental rotational strengths calculated from the resulting CD curve will be much smaller than the actual rotational strengths for each of the transitions involved. Thus, a way must be found to generate a $\Delta\epsilon$ versus λ curve for each theoretical rotational strength so that these curves can then be added together to produce a theoretical spectrum.

Moffitt and Moscowitz²⁷ observed that a CD band and its associated absorption band will usually be identical in shape. For an allowed transition, its CD and absorption bands will be centered at the same energy while the center of a CD band for a forbidden transition may be shifted from that of the associated absorption band. Assuming identical shapes for both curves, Eqs. (4) and (5) can be combined. Solving for $\Delta\epsilon$ gives

$$\Delta\epsilon(\lambda) = 4\left(\frac{\epsilon(\lambda)}{D}\right)R \quad (6)$$

The quantity $4\epsilon(\lambda)/D$ can be viewed as a normalized shape factor. If all CD bands for a molecule are assumed to have the same shape, then only one absorption band needs to be known for that molecule.

These are the assumptions we have used in determining the shapes and sizes of the CD bands calculated in the following sections.

The rotational strength for a particular molecular transition is calculated, the dipole strength and ϵ values are taken from the spectrum and Eq. (6) is then evaluated.

Recalling that $d\lambda/\lambda = d \ln \lambda$, Eq. (4) can be written as

$$D = \frac{3hc \cdot 10^3 (\ln 10)}{8\pi^3 L} \int_0^{\infty} \epsilon(\lambda) d \ln \lambda \quad (7)$$

To find an experimental dipole strength, ϵ can be plotted versus $\ln \lambda$ on graph paper and the squares under the curve counted to perform the integration.

Alternatively, an analytical form for the band shape can be substituted for $\epsilon(\lambda)$, and the integration carried out. We chose to approximate the experimental absorption band by a curve that is Gaussian with respect to wavelength. Tinoco²⁸ gives the equation for such a Gaussian curve as

$$\epsilon = \epsilon_{\max} \exp[-(\lambda - \lambda_{\max})^2 / \theta_{\lambda}^2] \quad (8)$$

where ϵ_{\max} and λ_{\max} are the values of ϵ and λ at the point the absorption band reaches its peak value. θ_{λ} is a parameter that is proportional to the width of the band at half-height.

Let the width at half-height, Γ , be

$$\Gamma = 2(\lambda_{1/2} - \lambda_{\max}) \quad (9)$$

where $\lambda_{1/2}$ is the wavelength, greater than λ_{\max} , for $\epsilon = \epsilon_{\max}/2$. Equation (7) then becomes

$$\epsilon_{\max}/2 = \epsilon_{\max} \exp[-\Gamma^2/(4\theta_{\lambda}^2)].$$

Dividing by ϵ_{\max} and taking the natural logarithm of both sides gives

$$\ln(1/2) = -\Gamma^2/(4\theta_{\lambda}^2)$$

Therefore

$$\theta_{\lambda}^2 = \Gamma^2/(4 \ln 2). \quad (10)$$

Equation (7) can finally be stated as

$$\epsilon = \epsilon_{\max} \exp[(-2.7726(\lambda - \lambda_{\max})^2/\Gamma^2)] \quad (11)$$

All the parameters in the right-hand side of Eq. (11) are easily obtainable from experiment.

Substituting Eq. (8) into Eq. (4) gives

$$D = C\epsilon_{\max} \int_0^{\infty} \frac{1}{\lambda} \exp[-(\lambda - \lambda_{\max})^2/\theta_{\lambda}^2] d\lambda \quad (12)$$

where C is a constant

$$C = \frac{3hc \cdot 10^3 (\ln 10)}{8\pi^3 L}$$

For all practical purposes, absorption bands are finite and cover a narrow range of wavelength values. Tinoco expresses this constraint as $\theta_\lambda \ll \lambda_{\max}$. With this fact, the integral in Eq. (12) can be approximated as

$$\begin{aligned} & \int_0^\infty \frac{1}{\lambda} \exp[-(\lambda - \lambda_{\max})^2 / \theta_\lambda^2] d\lambda \\ &= \frac{1}{\lambda_{\max}} \int_0^\infty \exp[-(\lambda - \lambda_{\max})^2 / \theta_\lambda^2] d\lambda. \end{aligned}$$

Mathematically, it does not matter where the band is situated along the λ -axis since it is a finite band. The integral on the right above can be simplified by centering the integrand at zero and integrating from $-\lambda_{\max}$ to ∞ . But the band is essentially zero at $-\lambda_{\max}$, and so the integration can be from $-\infty$ to ∞ . The integral in Eq. (12) reduces to

$$\frac{1}{\lambda_{\max}} \int_{-\infty}^{\infty} \exp(-\lambda^2 / \theta_\lambda^2) d\lambda.$$

The integrand is symmetric about zero. From integral tables

$$\int_0^\infty \exp(-a^2 x^2) dx = (\pi)^{1/2} / 2a.$$

From the above integral $a = 1/\theta_\lambda$.

The final approximate form for the dipole strength is

$$D = C \frac{\epsilon_{\max}}{\lambda_{\max}} (\pi)^{1/2} \theta_{\lambda} \quad (13)$$

The actual value of the constant factor C can be calculated by using the appropriate cgs units.

$$\begin{aligned} C &= \frac{3 hc 10^3 \ln 10}{8\pi^3 L} = \frac{3 hc 10^3 \ln 10}{4\pi^2 L} \\ &= \frac{3(1.054 \times 10^{-27} \text{ erg}\cdot\text{sec})(2.998 \times 10^{10} \text{ cm/sec})(10^3 \text{ cm}^3/\text{cm mole})(2.303)}{4\pi^2 (6.022 \times 10^{23} / \text{mole})} \\ &= 9.183 \times 10^{-39} [\text{erg}\cdot\text{cm}^3] \end{aligned}$$

The dipole strength involves electrons in motion, so

1 erg = 1 esu²/cm. Therefore

$$D = (1.628 \times 10^{-38}) \frac{\epsilon_{\max}}{\lambda_{\max}} \theta_{\lambda} [\text{esu}^2 \text{ cm}^2] \quad (14)$$

By definition 1 Debye = 10^{-18} esu·cm, and D becomes

$$D = (1.628 \times 10^{-2}) \frac{\epsilon_{\max}}{\lambda_{\max}} \theta_{\lambda} [\text{Debye}^2] \quad (15)$$

The electronic charge (e) is 4.803×10^{-10} esu and the atomic distance unit is $a_0 = 0.52917\text{\AA}$. These allow conversions to $e^2 \text{\AA}^2$ and

$e^2 a_0^2$ (or atomic units).

$$D = (7.057 \times 10^{-4}) \frac{\epsilon_{\max}}{\lambda_{\max}} \theta_{\lambda} [e^2 \text{ \AA}^2] \quad (16)$$

$$D = (2.520 \times 10^{-3}) \frac{\epsilon_{\max}}{\lambda_{\max}} \theta_{\lambda} [e^2 a_0^2] \quad (17)$$

Equations (14) to (17) illustrate the four different systems of units used in this field. Table I lists the various conversion factors I have calculated to facilitate comparisons between results with different units. The unit for rotational strength, that is associated with Debye² for the dipole strength, is the Debye-magneton. The Bohr magneton is defined by

$$\beta_e = \frac{e\hbar}{2mc} = 9.273 \times 10^{-21} [\text{erg/gauss}] \quad (18)$$

In basic units, an erg/gauss is an esu·cm. Therefore, one Debye-magneton = 9.273×10^{-39} esu² cm².

The appropriate equation from Eq. (14) to (17) can be used to calculate the dipole strength for the Gaussian curve used to generate the ϵ values. These values can then be used in Eq. (6) to obtain $\Delta\epsilon$ values.

The absorption spectra of all three diketopiperazines have a $\epsilon_{\max} = 1.8 \times 10^4$. Since the $n\pi^*$ shoulder of the $\pi\pi^*$ band is further to

Table I. Unit conversion factors.

	$\text{esu}^2 \text{cm}^2$	Debye ²	Debye-magneton	$e^2 \text{Å}^2$	$e^2 a_0^2$
A. Dipole strengths and rotational strengths					
1 $\text{esu}^2 \text{cm}^2$	= 1	1×10^{36}	1.078×10^{38}	4.335×10^{34}	1.548×10^{35}
1 Debye ²	= 1×10^{-36}	1	---	4.335×10^{-2}	1.548×10^{-1}
1 Debye-magneton	= 9.273×10^{-39}	---	1	4.020×10^{-4}	1.435×10^{-3}
1 $e^2 \text{Å}^2$	= 2.307×10^{-35}	2.307×10^1	2.488×10^3	1	3.571×10^0
1 $e^2 a_0^2$	= 6.460×10^{-36}	6.460×10^0	6.967×10^2	2.800×10^{-1}	1
	esu·cm	Debye	Bohr magneton	e·Å	e·a ₀
B. Dipole moments					
1 esu·cm	= 1	1×10^{18}	1.078×10^{20}	2.082×10^{17}	3.934×10^{17}
1 Debye	= 1×10^{-18}	1	---	2.082×10^{-1}	3.934×10^{-1}
1 Bohr magneton	= 9.273×10^{-21}	---	1	1.931×10^{-3}	3.649×10^{-3}
1 e·Å	= 4.803×10^{-18}	4.803×10^0	5.179×10^2	1	1.890×10^0
1 e·a ₀	= 2.542×10^{-18}	2.542×10^0	2.740×10^2	5.292×10^{-1}	1

the red in PPDKP than AG- or AADKP, the spectrum of PPDKP was used to measure the width at half-height. From the curve, Γ is 20 nm. Equation (10) becomes

$$\theta_{\lambda}^2 = 20^2 / 2.7726 = 144.3 \text{ nm}^2$$

Substitution of these values into Eq. (11) gives the analytical equation for a Gaussian band for AG- and AADKP.

$$\epsilon = 1.8 \times 10^4 \exp[-(\lambda - 185)^2 / 144.3]$$

Table II is a list of the ϵ values for the first $\pi\pi^*$ transition (185 nm) in AG- and AADKP in steps of 5 nm.

Table II. Data for a Gaussian absorption band.

λ [nm]	ϵ
215	0.00
210	0.02
205	0.11
200	0.38
195	0.90
190	1.51
185	1.80
180	1.51
175	0.90
170	0.38
165	0.11
160	0.02
155	0.00

Note: The band is centered at 185 nm for AG- and AADKP. For PPDKP each point is shifted by +5 nm.

From Eq. (16), the dipole strength for this data is

$$D = \frac{(7.057 \times 10^{-4})(1.8 \times 10^4)(144.3)^{1/2}}{185}$$

$$D = 0.825 [e^2 \text{ \AA}^2] \quad (20a)$$

or

$$D = 2.94 [e^2 a_0^2] \quad (20b)$$

The values listed in Table II can be used to give shape to CD bands at other wavelengths, but the wavelength interval between data points must be adjusted so that the dipole strength remains constant. An examination of Eq. (13) indicates that the ratio $\theta_\lambda / \lambda_{\max}$ must be constant to keep the dipole strength constant. From the definition of θ_λ , the ratio to be kept constant is really Γ / λ_{\max} . For the data of Table II

$$\frac{\Gamma}{\lambda_{\max}} = \frac{20}{185} = 0.108$$

Therefore, the width at half-height of a transition at an arbitrary wavelength is given by

$$\Gamma = 0.108 \lambda_{\max} \quad (21)$$

Then the wavelength interval between data points, $\Delta \lambda$, in nm is

$$\Delta\lambda = \left(\frac{\Gamma}{20}\right)5. \quad (22)$$

A λ_{max} of 190 nm for the first $\pi\pi^*$ transition in PPDKP is close to 185 nm found in AG- and AADKP, so a data interval of 5 nm is used for all three molecules for the first $\pi\pi^*$ couplet. For the other transitions, Eqs. (21) and (22) are used to define the data intervals.

III. ROTATIONAL STRENGTHS THEORY FOR AMIDE TRANSITIONS

A. General Theory

If the wavelength of light is long with respect to the size of the molecule under consideration, then the rotational strength for a transition from molecular state 0 to state A is²⁹

$$R_{0A} = \text{Im} \langle 0 | \vec{\mu} | A \rangle \cdot \langle A | \vec{m} | 0 \rangle \quad (23)$$

where $\langle 0 | \vec{\mu} | A \rangle$ is the electric transition dipole moment from 0 to A and $\langle A | \vec{m} | 0 \rangle$ is the magnetic transition dipole moment from A to 0 .^{1/}

The problem of finding R_{0A} reduces to finding the molecular electric and magnetic transition moments. To begin we need to find the molecular wavefunctions, $|0\rangle$ and $|A\rangle$, that are then operated on by the operators $\vec{\mu}$ and \vec{m} . One way of finding these is the independent systems approach.³⁰ This method assumes that the molecule can be thought of as a number of independent groups interacting through coulombic forces with no electron exchange.

The general case for a molecule with n groups will be examined. Each group has several excited states in addition to the

^{1/} I use the same order of wavefunctions and operator as the literature in the field uses. However, it is the reverse order to the usual physics Dirac notation which would be $\langle A | \vec{\mu} | 0 \rangle$ and $\langle 0 | \vec{m} | A \rangle$.

ground state 0. The excited states of each group will be indexed by the letters a, b and c. The total Hamiltonian for the molecule is

$$H = H^0 + V = \sum_{i=1}^n h_i + \sum_{i=1}^n \sum_{j>i}^n v_{ij} \quad (24)$$

which has been separated into H^0 , a sum of the unperturbed group Hamiltonians, and V , a sum of the interaction potentials between states on group i and states on group j .

The group eigenfunctions are assumed known and are the solutions to the unperturbed group Hamiltonian, h_i . These solutions also give the isolated group energies, ϵ_i . The ground state functions are $|10\rangle$, $|20\rangle$, etc. The excited state functions are represented by $|1a\rangle$, $|2a\rangle$, etc. By taking products of these functions we can generate a basis set of wavefunctions for the molecule. This is the same as the zeroth order perturbation set. In the following all summations are from 1 to n except as specifically noted.

$$|0\rangle = |10\ 20\ \dots\ n0\rangle \quad (25)$$

and the molecular energy in terms of group energies is

$$E_0 = \sum_i \epsilon_{i0} \quad (26)$$

The singly-excited wavefunctions are identified as

$$|ia) = |10\ 20\ \dots ia\ \dots n0) \quad (27)$$

with energy

$$E_{ia} = \epsilon_{ia} + \sum_{j \neq i} \epsilon_{j0} \quad (28)$$

The doubly-excited wavefunctions belong to the type

$$|iajb) = |10\ \dots ia\ \dots jb\ \dots n0) \quad (29)$$

with energy

$$E_{iajb} = \epsilon_{ia} + \epsilon_{jb} + \sum_{\substack{k \neq i \\ k \neq j}} \epsilon_{k0} \quad (30)$$

To indicate clearly what group excited state contributes to each zero-order molecular excited wavefunction, I have labelled the molecular functions with the lower case letters used for the excited group functions.

The molecular functions $|0\rangle$ and $|A\rangle$ can now be expanded as a linear combination of the basis functions.

$$|A\rangle = C_0^A |0\rangle + \sum_i \sum_a C_{ia}^A |ia\rangle + \sum_i \sum_{j \neq i} \sum_a \sum_b C_{iajb}^A |iajb\rangle \quad (31)$$

Equation (31) is an approximate expansion for $|A\rangle$ since the expansion was truncated after doubly excited basis functions. However, to first order, as described below, the higher terms will not contribute to $\bar{\mu}$ and \bar{m} .

The molecular operators $\vec{\mu}$ and \vec{m} are sums of group operators, $\vec{\mu}_i$ and \vec{m}_i . In turn, the group operators are sums of one-electron operators. Since the eigenfunctions of a given group are orthogonal, the only contribution to a molecular operator will be the group operator corresponding to the electron which undergoes the transition. Only group transitions involving a single electron will be considered.

The electric dipole transition moment in this expansion is

$$\begin{aligned}
\langle 0 | \vec{\mu} | A \rangle = & C_0^0 C_0^A \langle 0 | \vec{\mu} | 0 \rangle + \sum_i \sum_a C_0^0 C_{ia}^A \langle 0 | \vec{\mu} | ia \rangle \\
& + \sum_i \sum_{j \neq i} \sum_a \sum_b C_0^0 C_{iajb}^A \langle 0 | \vec{\mu} | iajb \rangle \\
& + \sum_i \sum_a C_{ia}^0 C_0^A \langle ia | \vec{\mu} | 0 \rangle + \sum_i \sum_j \sum_a \sum_b C_{ia}^0 C_{jb}^A \langle ia | \vec{\mu} | jb \rangle \\
& + \sum_i \sum_j \sum_{k \neq j} \sum_a \sum_b \sum_c C_{ia}^0 C_{jbkc}^A \langle ia | \vec{\mu} | jbkc \rangle \\
& + \sum_i \sum_{j \neq i} \sum_a \sum_b C_{iajb}^0 C_0^A \langle iajb | \vec{\mu} | 0 \rangle \\
& + \sum_i \sum_{j \neq i} \sum_k \sum_a \sum_b \sum_c C_{iajb}^0 C_{kc}^A \langle iajb | \vec{\mu} | kc \rangle \\
& + \sum_i \sum_{j \neq i} \sum_k \sum_{l \neq k} \sum_a \sum_b \sum_c \sum_d C_{iajb}^0 C_{kcld}^A \langle iajb | \vec{\mu} | kcld \rangle
\end{aligned} \tag{32}$$

In a perturbation theory treatment, the coefficients C_{ia}^0 and C_{iajb}^0 would represent the first order corrections to the molecular ground state wavefunction, and C_0^A and C_{iajb}^A would represent the first order corrections to the molecular excited state wavefunction. Therefore to keep Eq. (32) correct to first order, we can drop all terms involving products of two first order correction coefficients. The dropped terms are 4, 6, 7, and 9. The C_{ia}^A coefficients may represent either zeroth order or first order corrections, so they are all retained at this point.

Keeping in mind that the group eigenfunctions are orthonormal, we can simplify the terms in Eq. (32) by using the one-electron operators. A change in notation is also introduced to shorten the equation: $\vec{\mu}_{i00}$ is the ground state electric dipole moment for the isolated group i , and $\vec{\mu}_{i0a}$ is the electric dipole transition moment of the isolated group for transition $0a$. The following equations spell out these ideas.

$$\begin{aligned} \langle 0 | \vec{\mu} | 0 \rangle &= \langle 10 \ 20 \dots n0 | \sum_i \vec{\mu}_i | 10 \ 20 \dots n0 \rangle \\ &= \sum_i \vec{\mu}_{i00} \end{aligned} \quad (33a)$$

$$\begin{aligned} \langle 0 | \vec{\mu} | ia \rangle &= \langle 10 \dots n0 | \sum_j \vec{\mu}_j | 10 \dots ia \dots n0 \rangle \\ &= \vec{\mu}_{i0a} \end{aligned} \quad (33b)$$

For $i \neq j$,

$$(0|\vec{\mu}|iajb) = 0 \quad (33c)$$

$$(ia|\vec{\mu}|jb) = 0 \quad (33d)$$

Also $\vec{\mu}_{i0a} = \vec{\mu}_{ia0}$.

Additionally, some of the summations can be simplified although they do not vanish. For $i = j$

$$\sum_i \sum_a \sum_b C_{ia}^0 C_{ib}^A (ia|\vec{\mu}|ib) = \sum_i \sum_a C_{ia}^0 C_{ia}^A (\vec{\mu}_{iaa} + \sum_{k \neq i} \vec{\mu}_{k00}) + \sum_{b \neq a} C_{ia}^0 C_{ib}^A \vec{\mu}_{iab} \quad (34a)$$

Also

$$\sum_i \sum_{j \neq i} \sum_k \sum_a \sum_b \sum_c C_{iajb}^0 C_{kc}^A (iajb|\vec{\mu}|kc) = \sum_i \sum_{j \neq i} \sum_a \sum_b C_{iajb}^0 C_{ia}^A \vec{\mu}_{j0b} \quad (34b)$$

Using Eqs. (33) and (34) the electric transition moment, Eq. (32), can now be written to first order as

$$\begin{aligned} \langle 0|\vec{\mu}|A\rangle &= C_0^0 C_0^A \sum_i \vec{\mu}_{i00} + C_0^0 \sum_i \sum_a C_{ia}^A \vec{\mu}_{i0a} \\ &+ \sum_i \sum_a C_{ia}^0 C_{ia}^A (\vec{\mu}_{iaa} + \sum_{k \neq i} \vec{\mu}_{k00}) + \sum_{b \neq a} C_{ia}^0 C_{ib}^A \vec{\mu}_{iab} \\ &+ \sum_i \sum_{j \neq i} \sum_a \sum_b C_{iajb}^0 C_{ia}^A \vec{\mu}_{j0b} \end{aligned} \quad (35)$$

For the magnetic dipole transition moment $\langle A | \vec{m} | 0 \rangle$ an equation similar to Eq. (32) can be written. In this case the order of the wavefunctions about the operator \vec{m} is important since $\langle A | \vec{m} | 0 \rangle = -\langle 0 | \vec{m} | A \rangle$. The same terms are identically zero, too, since they were dropped either because the operator was a sum of one-electron operators or due to keeping only first order correction terms.

The explicit form of the magnetic transition moment operator is^{2/}

$$\vec{m} = \sum_j [\vec{m}_j - (\pi i / c) \nu_j \vec{R}_j \times \vec{\mu}_j] \quad (36)$$

where \vec{m}_j is the operator for the intrinsic magnetic transition moment of the isolated group, and $(\pi i / c) \nu_j \vec{R}_j \times \vec{\mu}_j$ is the contribution to the magnetic transition moment of the molecule due to the choice of origin for the coordinate system of the molecule. \vec{R}_j is the position vector of the center of the group transition charges, ν_j is the frequency of the transition, c is the velocity of light and $i = (-1)^{1/2}$.

In general there is no intrinsic magnetic dipole moment in the ground state of the isolated group. These terms drop out of the

^{2/}See Section III E for a derivation.

equation for \vec{m} corresponding to Eq. (13). The final equation to first order is

$$\begin{aligned}
\langle A | \vec{m} | 0 \rangle = & C_0^0 \sum_i \sum_a C_{ia}^A \vec{m}_{ia0} + \sum_i \sum_a \sum_{b \neq a} C_{ia}^0 C_{ib}^A \vec{m}_{iba} \\
& + \sum_i \sum_{j \neq i} \sum_a \sum_b C_{iajb}^0 C_{ia}^A \vec{m}_{j0b} \\
& + (\pi i / c) C_0^0 \sum_i \sum_a C_{ia}^A \nu_{i0a} \vec{R}_i^{0a} \times \vec{\mu}_{i0a} \\
& + \sum_i \sum_a \sum_{b \neq a} C_{ia}^0 C_{ib}^A \nu_{iab} \vec{R}_i^{ab} \times \vec{\mu}_{iab} \\
& - \sum_i \sum_{j \neq i} \sum_a \sum_b C_{iajb}^0 C_{ia}^A \nu_{j0b} \vec{R}_j^{0b} \times \vec{\mu}_{j0b} \tag{37}
\end{aligned}$$

where $\nu_{i0a} = E_{ia} - E_0$ and the identity $\nu_{ia0} = -\nu_{i0a}$ was used in the above equation. Also a superscript was used on \vec{R}_i to indicate for which transition a particular center of transition charge is given. In general, for $a \neq b$, $\vec{R}_i^{0a} \neq \vec{R}_i^{0b}$.

Using Eqs. (37) and (35) in Eq. (23) the rotational strength for the molecular transition 0 to A can be expanded to first order in terms of group quantities.

$$\begin{aligned}
R_{0A} = \text{Im} & \left[C_0^{0^2} C_0^A \sum_i \sum_j \sum_a C_{ja}^A \vec{\mu}_{i0a} \cdot \vec{m}_{ja0} \right. \\
& + C_0^{0^2} \sum_i \sum_j \sum_a \sum_b C_{ia}^A C_{jb}^A \vec{\mu}_{i0a} \cdot \vec{m}_{jb0} \\
& + C_0^0 \sum_i \sum_j \sum_a \sum_b \sum_{c \neq b} C_{ia}^A C_{jb}^0 C_{jc}^A \vec{\mu}_{i0a} \cdot \vec{m}_{jcb} \\
& + C_0^0 \sum_i \sum_j \sum_{k \neq j} \sum_a \sum_b \sum_c C_{ia}^A C_{jb, kc}^0 C_{jb}^A \vec{\mu}_{i0a} \cdot \vec{m}_{k0c} \\
& + C_0^0 \sum_i \sum_j \sum_a \sum_b C_{ia}^0 C_{ia}^A C_{jb}^A (\vec{\mu}_{iaa} + \sum_{k \neq i} \vec{\mu}_{k00}) \cdot \vec{m}_{jb0} \\
& + C_0^0 \sum_i \sum_j \sum_a \sum_{b \neq a} \sum_c C_{ia}^0 C_{ib}^A C_{jc}^A \vec{\mu}_{iab} \cdot \vec{m}_{jc0} \\
& \left. + C_0^0 \sum_i \sum_{j \neq i} \sum_k \sum_a \sum_b \sum_c C_{ia, jb}^0 C_{ia}^A C_{kc}^A \vec{\mu}_{j0b} \cdot \vec{m}_{kc0} \right] \\
& + (\pi/c) \left[C_0^{0^2} C_0^A \sum_i \sum_j \sum_a C_{ja}^A \nu_{i0a} \vec{\mu}_{i00} \cdot \vec{R}_j^{0a} \times \vec{\mu}_{j0a} \right. \\
& + C_0^{0^2} \sum_i \sum_j \sum_a \sum_b C_{ia}^A C_{jb}^A \nu_{j0b} \vec{\mu}_{i0a} \cdot \vec{R}_j^{0b} \times \vec{\mu}_{j0b} \\
& + C_0^0 \sum_i \sum_j \sum_a \sum_b \sum_{c \neq b} C_{ia}^A C_{jb}^0 C_{jc}^A \nu_{jbc} \vec{\mu}_{i0a} \cdot \vec{R}_j^{bc} \times \vec{\mu}_{jbc} \\
& \left. - C_0^0 \sum_i \sum_j \sum_{k \neq j} \sum_a \sum_b \sum_c C_{ia}^A C_{jb, kc}^0 C_{jb}^A \nu_{k0c} \vec{\mu}_{i0a} \cdot \vec{R}_k^{0c} \times \vec{\mu}_{k0c} \right] +
\end{aligned}$$

$$\begin{aligned}
& + C_0^0 \sum_i \sum_j \sum_a \sum_b C_{ia}^0 C_{ia}^A C_{jb}^A \nu_{j0b} (\vec{\mu}_{iaa} + \sum_{k \neq i} \vec{\mu}_{k00}) \cdot \vec{R}_j^{0b} \times \vec{\mu}_{j0b} \\
& + C_0^0 \sum_i \sum_j \sum_a \sum_{b \neq a} \sum_c C_{ia}^0 C_{ib}^A C_{jc}^A \nu_{j0c} \vec{\mu}_{iab} \cdot \vec{R}_j^{0c} \times \vec{\mu}_{j0c} \\
& + C_0^0 \sum_i \sum_{j \neq i} \sum_k \sum_a \sum_b \sum_c C_{ia;jb}^0 C_{ia}^A C_{kc}^A \nu_{k0c} \vec{\mu}_{j0b} \cdot \vec{R}_k^{0c} \times \vec{\mu}_{k0c} \quad \Big] \quad (38)
\end{aligned}$$

Equation (38) is the general equation for all of the CD terms we calculated. The problem becomes one of evaluating the various coefficients. Johnson and Tinoco³¹ follow a similar derivation, but their equations have many fewer terms because of their neglect of static fields and intrinsic magnetic moments of the groups.

B. Coefficients from Nondegenerate Perturbation Theory

Generally, experimental spectra exist only for the energy region where the low lying transitions occur. Small molecules usually have only one group undergoing transitions in this region. Such a group is called a chromophore. If the low lying transitions are well separated, then first order nondegenerate perturbation theory³² can be used to find the coefficients.

Recall that the total Hamiltonian for a molecule with n groups is

$$H = H^0 + V = \sum_i h_i + \sum_i \sum_{j>i} V_{ij} \quad (24)$$

where V_{ij} is the coulombic potential energy operator between the electrons of group i and the electrons of group j . The interactions between electrons on the same group are not considered explicitly since these form part of the Hamiltonian operator, h_i , for the isolated group.

In general, the first order perturbation wavefunction $|m\rangle$, where m can be the ground state or an excited state, will be given by

$$|m\rangle = |m\rangle - \sum_{m' \neq m} \frac{\langle m'|V|m\rangle}{E_{m'} - E_m} |m'\rangle \quad (39)$$

The right-hand side of Eq. (39) involves only zeroth order wavefunctions and energies.

Equation (31) is the variational form for a molecular wavefunction written as a linear combination of basis functions. The result is general and nothing is specified about the size of particular coefficients. However, when nondegenerate perturbation theory is used to define the coefficients, the molecular wavefunction $|ia\rangle$ is identified as the zeroth order wavefunction corresponding to the first order wavefunction $|A\rangle$. Other excited state wavefunctions for the chromophore are identified as $|ib\rangle$ while all excited state

wavefunctions on the other groups are identified as $|jb\rangle$.

Now the wavefunctions for the ground and excited states of the molecule to first order in perturbation theory can be written using the basis functions of Eqs. (25), (27) and (29).

$$\begin{aligned}
 |0\rangle = & |0\rangle - \frac{(ia|V|0)}{E_{ia} - E_0} |ia\rangle - \sum_{b \neq a} \frac{(ib|V|0)}{E_{ib} - E_0} |ib\rangle \\
 & - \sum_{j \neq i} \sum_{b \neq a} \frac{(jb|V|0)}{E_{jb} - E_0} |jb\rangle - \sum_{j \neq i} \sum_{b \neq a} \frac{(iajb|V|0)}{E_{iajb} - E_0} |iajb\rangle
 \end{aligned} \tag{40a}$$

$$\begin{aligned}
 |A\rangle = & - \frac{(0|V|ia)}{E_0 - E_{ia}} |0\rangle + |ia\rangle - \sum_{b \neq a} \frac{(ib|V|ia)}{E_{ib} - E_{ia}} |ib\rangle \\
 & - \sum_{j \neq i} \sum_{b \neq a} \frac{(jb|V|ia)}{E_{jb} - E_{ia}} |jb\rangle
 \end{aligned} \tag{40b}$$

Only the doubly excited wavefunctions that contribute to the rotational strength to first order are explicitly listed.

Comparison of Eq. (40) with Eq. (31) gives the coefficients when nondegenerate perturbation theory is applicable. The coefficients for basis functions corresponding to the ground state and doubly excited states are straight forward. However, the redefinition of the indices in this section gives rise to three distinct classes of coefficients for the basis functions corresponding to the singly excited states. The sums in Eq. (38) are non-specific, assuming all values for i, j, k ,

a, b and c that are allowed. Whenever the values for the pairs i, a or j, b or k, c in the summations of Eq. (38) are equal to that of the particular $|ia\rangle$ associated with $|A\rangle$, then the coefficient is specified by C_{ia}^0 or C_{ia}^A . Similarly, C_{ib}^0 and C_{ib}^A are used when the summations correspond to $|ib\rangle$, and C_{jb}^0 and C_{jb}^A are used when the summations correspond to $|jb\rangle$.

The coefficients in Eq. (38) can now be identified.

$$C_0^0 = 1$$

$$\begin{aligned} C_{ia}^0 &= -(ia|V|0)/(E_{ia}-E_0) \\ &= -\sum_{j \neq i} (ia|j0|V|j0|0)/(E_{ia}-E_0) \\ &= -\sum_{j \neq i} v_{i0a;j00}/h\nu_{i0a} \end{aligned}$$

$$\begin{aligned} C_{ib}^0 &= -(ib|V|0)/(E_{ib}-E_0) \\ &= -\sum_{j \neq i} v_{i0b;j00}/h\nu_{i0b} \end{aligned}$$

$$\begin{aligned} C_{jb}^0 &= -(jb|V|0)/(E_{jb}-E_0) \\ &= -\sum_{k \neq j} v_{j0b;k00}/h\nu_{j0b} \end{aligned}$$

$$\begin{aligned}
C_{ia, jb}^0 &= -(iajb|V|0)/(E_{iajb}-E_0) \\
&= -V_{i0a; j0b}/h(\nu_{j0b}+\nu_{i0a}) \\
C_0^A &= -(0|V|ia)/(E_0-E_{ia}) \\
&= -C_{ia}^0 = \sum_{j \neq i} V_{i0a; j00}/h\nu_{i0a}
\end{aligned}$$

$$C_{ia}^A = 1$$

$$\begin{aligned}
C_{ib}^A &= -(ib|V|ia)/(E_{ib}-E_{ia}) \\
&= -\sum_{j \neq i} V_{iab; j00}/h(\nu_{i0b}-\nu_{i0a})
\end{aligned}$$

$$\begin{aligned}
C_{jb}^A &= -(jb|V|ia)/(E_{jb}-E_{ia}) \\
&= -V_{i0a; j0b}/h(\nu_{j0b}-\nu_{i0a})
\end{aligned}$$

From Eq. (38), the rotational strength, correct to first order in nondegenerate perturbation theory, is

$$\begin{aligned}
R_{0A} = \text{Im} & \left[\sum_{j \neq i} \frac{V_{i0a; j00}(\vec{\mu}_{i00} + \sum_{k \neq i} \vec{\mu}_{k00}) \cdot \vec{m}_{ia0}}{h\nu_{i0a}} + \vec{\mu}_{i0a} \cdot \vec{m}_{ia0} \right. \\
& \left. - \sum_{j \neq i} \sum_{b \neq a} \frac{V_{iab; j00}(\vec{\mu}_{i0a} \cdot \vec{m}_{ib0} + \vec{\mu}_{i0b} \cdot \vec{m}_{ia0})}{h(\nu_{i0b} - \nu_{i0a})} \right]
\end{aligned}$$

$$\begin{aligned}
& - \sum_{j \neq i} \sum_{b \neq a} \frac{V_{i0a; j0b} (\vec{\mu}_{i0a} \cdot \vec{m}_{jb0} + \vec{\mu}_{j0b} \cdot \vec{m}_{ia0})}{h(\nu_{j0b} - \nu_{i0a})} \\
& - \sum_{j \neq i} \sum_{b \neq a} \frac{V_{i0b; j00} \vec{\mu}_{i0a} \cdot \vec{m}_{iab}}{h\nu_{i0b}} - \sum_{j \neq i} \sum_{b \neq a} \frac{V_{i0a; j0b} \vec{\mu}_{i0a} \cdot \vec{m}_{j0b}}{h(\nu_{j0b} + \nu_{i0a})} \\
& - \sum_{j \neq i} \frac{V_{i0a; j00} (\vec{\mu}_{iaa} + \sum_{k \neq i} \vec{\mu}_{k00}) \cdot \vec{m}_{ia0}}{h\nu_{i0a}} \\
& - \left[\sum_{j \neq i} \sum_{b \neq a} \frac{V_{i0b; j00} \vec{\mu}_{iab} \cdot \vec{m}_{ia0}}{h\nu_{i0b}} - \sum_{j \neq i} \sum_{b \neq a} \frac{V_{i0a; j0b} \vec{\mu}_{j0b} \cdot \vec{m}_{ia0}}{h(\nu_{j0b} + \nu_{i0a})} \right] \\
& - \left(\frac{\pi}{C} \right) \left[\sum_{j \neq i} \sum_{b \neq a} \frac{V_{i0a; j0b} (\vec{\mu}_{i0a} \cdot \vec{R}_j^{0b} \times \vec{\mu}_{j0b} \nu_{j0b} + \vec{\mu}_{j0b} \cdot \vec{R}_i^{0a} \times \vec{\mu}_{i0a} \nu_{i0a})}{h(\nu_{j0b} - \nu_{i0a})} \right. \\
& - \sum_{j \neq i} \sum_{b \neq a} \frac{V_{i0a; j0b} \vec{\mu}_{i0a} \cdot \vec{R}_j^{0b} \times \vec{\mu}_{j0b} \nu_{j0b}}{h(\nu_{j0b} + \nu_{i0a})} \\
& \left. + \sum_{j \neq i} \sum_{b \neq a} \frac{V_{i0a; j0b} \vec{\mu}_{j0b} \cdot \vec{R}_i^{0a} \times \vec{\mu}_{i0a} \nu_{i0a}}{h(\nu_{j0b} + \nu_{i0a})} \right]
\end{aligned}$$

All interactions between electric dipole transition moments on the same monomer are zero. Therefore such terms as

$\vec{\mu}_{i0a} \cdot \vec{R}_i^{0b} \times \vec{\mu}_{i0b}$ do not appear. Also to make R_{0A} correct to first order in perturbation coefficients, all terms in h^2 and higher were dropped. Note that the summation over $k \neq i$ for the $\vec{\mu}_{k00} \cdot \vec{m}_{ia0}$

quantities in terms 1 and 7 appear with opposite sign and cancel.

This equation can be dressed up a bit by multiplying the numerator and denominator of the terms containing $V_{i0a; j0b}$ by the appropriate sum or difference $(\nu_{j0b} \pm \nu_{i0a})$ and collecting the terms. The vector identities $\vec{A} \cdot \vec{B} \times \vec{C} = -\vec{B} \cdot \vec{A} \times \vec{C}$ and $\vec{A} \cdot \vec{B} \times \vec{C} = -\vec{A} \cdot \vec{C} \times \vec{B}$ must also be used. The final result is

$$\begin{aligned}
 R_{0A} = & \text{Im} \vec{\mu}_{i0a} \cdot \vec{m}_{ia0} - 2 \sum_{j \neq i} \sum_{b \neq a} \text{Im} \frac{V_{i0a; j0b} (\vec{\mu}_{i0a} \cdot \vec{m}_{jb0} \nu_{i0a} + \vec{\mu}_{j0b} \cdot \vec{m}_{ia0} \nu_{j0b})}{h(\nu_{j0b}^2 - \nu_{i0a}^2)} \\
 & - \sum_{j \neq i} \sum_{b \neq a} \text{Im} \frac{V_{iab; j00} (\vec{\mu}_{i0a} \cdot \vec{m}_{ib0} + \vec{\mu}_{i0b} \cdot \vec{m}_{ia0})}{h(\nu_{i0b} - \nu_{i0a})} \\
 & - \sum_{j \neq i} \sum_{b \neq a} \text{Im} \frac{V_{i0b; j00} (\vec{\mu}_{i0a} \cdot \vec{m}_{iab} + \vec{\mu}_{iab} \cdot \vec{m}_{ia0})}{h \nu_{i0b}} \\
 & - \sum_{j \neq i} \sum_{b \neq a} \text{Im} \frac{V_{i0a; j00} (\vec{\mu}_{iaa} - \vec{\mu}_{i00}) \cdot \vec{m}_{ia0}}{h \nu_{i0a}} \\
 & - \left(\frac{2\pi}{c} \right) \sum_{j \neq i} \sum_{b \neq a} \frac{V_{i0a; j0b} \nu_{i0a} \nu_{j0b} (\vec{R}_j^{0b} - \vec{R}_i^{0a}) \cdot (\vec{\mu}_{j0b} \times \vec{\mu}_{i0a})}{h(\nu_{j0b}^2 - \nu_{i0a}^2)} \quad (41)
 \end{aligned}$$

Equation (41) is identical to Tinoco's³³ Eq. (IIIB-22) for the case where there is no summing over i , i.e. no degeneracy. This equation has been used successfully by Snyder and Johnson³⁴⁻³⁶ for several one chromophore molecules.

C. Coefficients from Degenerate Perturbation Theory

If any of the group energy levels within the spectral region of interest are degenerate, then for that energy there is not a unique eigenfunction solution to the unperturbed Hamiltonian, H^0 in Eq. (24). In fact, if the level is N -fold degenerate, then any linear combination of the N basis functions for that level will be a solution. In general these solutions can be written as

$$|aK\rangle = \sum_{i=1}^N c_{iaK} |ia\rangle \quad (42)$$

where K is a counter for the different possible solutions. At this point K is unbounded. The basis functions are numbered such that the first N are the degenerate ones.

First order degenerate perturbation theory³² can be used to solve the problem of degeneracy in zeroth order. It limits the number of K -states to an orthonormal set of N functions and specifies the c_{iaK} 's and the first order correction to the energy, E_K^1 , associated with each K -state.

The first order Hamiltonian is again Eq. (24).

$$H = H^0 + V = \sum_i h_i + \sum_i \sum_{j>i} v_{ij} \quad (24)$$

However, only the set of degenerate basis functions $|ia\rangle$, for $i = 1$ to N , is considered.

With this basis set, the eigenvalue problem can be stated as a series of N homogeneous equations. Each equation has the form

$$\sum_{i=1}^N [(ma|H|ia) - E(ma|ia)]c_{iaK} = 0 \quad (43)$$

where $m = 1$ to N . In each equation the c_{iaK} 's form a set of N unknowns with the coefficients being the quantity inside the square brackets. A nontrivial solution to Eq. (43) exists if the determinant of the coefficients is zero.

$$\begin{vmatrix} H_{11}^0 + V_{11} - ES_{11} & H_{12}^0 + V_{12} - ES_{12} & \dots & H_{1N}^0 + V_{1N} - ES_{1N} \\ H_{21}^0 + V_{21} - ES_{21} & H_{22}^0 + V_{22} - ES_{22} & \dots & H_{2N}^0 + V_{2N} - ES_{2N} \\ \vdots & \vdots & & \vdots \\ H_{N1}^0 + V_{N1} - ES_{N1} & H_{N2}^0 + V_{N2} - ES_{N2} & \dots & H_{NN}^0 + V_{NN} - ES_{NN} \end{vmatrix} = 0 \quad (44)$$

where $H_{ij}^0 = (ia|H^0|ja)$, $V_{ij} = (ia|V|ja)$ and $S_{ij} = (ia|ja)$.

The independent systems approach assumes no electron exchange between groups, so that the overlap integral $S_{ij} = 0$ for $i \neq j$. The perturbing operator $V_{ij} = 0$ for $i = j$ and the unperturbed Hamiltonian $H_{ij}^0 = 0$ for $i \neq j$. E can be written as a sum of the zeroth order energy and the first order correction

$$E = E^0 + E^1 \quad (45)$$

Since the system being considered is degenerate and the unperturbed energies occur only on the diagonal, the zeroth order components cancel.

The resulting determinant for the first order correction to the unperturbed energy is

$$\begin{vmatrix} -E^1 & (1a|V|2a) & \dots & (1a|V|Na) \\ (2a|V|1a) & -E^1 & \dots & (2a|V|Na) \\ \vdots & \vdots & & \vdots \\ (Na|V|1a) & (Na|V|2a) & \dots & -E^1 \end{vmatrix} = 0 \quad (46)$$

where V_{ij} is written in bracket form again for the sake of clarity.

After the roots to Eq. (46) are found, they can be used in Eq. (43), one at a time, to determine the N sets of coefficients, one set for each E_K^1 .

The resulting $|aK\rangle$'s are orthogonal and may be normalized.

Therefore the wavefunction coefficients satisfy the following

$$\sum_{i=1}^N c_{iaK}^* c_{iaK} = 1 \quad (47a)$$

$$\sum_{k=1}^N c_{iaK}^* c_{jaK} = 0, \quad \text{for } i \neq j. \quad (47b)$$

In the following all the c_{iaK} 's are assumed real. This orthonormal set of zeroth order functions is sometimes referred to as the "correct" zeroth order functions as compared with the original set of basis functions for the degenerate level.

Generally, the zeroth order energy is taken from experiment. Then the first order corrections to this energy found by solving Eq. (46) are substituted into Eq. (45) giving a set of new energies. This calculation may or may not have removed the energy degeneracy. If it has not, then for all practical purposes the molecular states will be spectrally degenerate.

Now that an orthonormal set of wavefunctions and associated energies have been calculated, what are the rotational strengths associated with these wavefunctions and situated at the new energies? The problem becomes one of evaluating the coefficients in Eq. (38). The transition considered will be from the ground state $|0\rangle$ of the molecule to one of the excited states $|AK\rangle$ of the molecule that is degenerate in zeroth order. The first order wavefunctions from degenerate perturbation theory analogous to Eq. (40) can be written

$$\begin{aligned}
 |0\rangle = & |0\rangle - \sum_{i=1}^N \frac{(ia|V|0)}{E_{ia} - E_0} |ia\rangle - \sum_{i=1}^N \sum_{b \neq a} \frac{(ib|V|0)}{E_{ib} - E_0} |ib\rangle \\
 & - \sum_{j > N} \sum_{b \neq a} \frac{(jb|V|0)}{E_{jb} - E_0} |jb\rangle - \sum_{i=1}^N \sum_{j > N} \sum_{b \neq a} \frac{(iajb|V|0)}{E_{iajb} - E_0} |iajb\rangle \quad (48a)
 \end{aligned}$$

$$\begin{aligned}
|AK\rangle = & - \sum_{i=1}^N c_{iaK} \frac{(0|V|ia)}{E_0 - E_{ia}} |0\rangle + \sum_{i=1}^N c_{iaK} |ia\rangle \\
& - \sum_{i=1}^N \sum_{b \neq a} c_{iaK} \frac{(ib|V|ia)}{E_{jb} - E_{ia}} |ib\rangle - \sum_{i=1}^N \sum_{j>N} \sum_{b \neq a} c_{iaK} \frac{(jb|V|ia)}{E_{jb} - E_{ia}} |jb\rangle
\end{aligned} \tag{48b}$$

As in Eq. (40), only the doubly excited states that contribute to the first order rotational strength are explicitly listed in Eq. (48). The energies in the denominator are all zeroth order energies. Each $|AK\rangle$ is the first order wavefunction corresponding to a particular zeroth order wavefunction $|aK\rangle$ where, as defined by Eq. (42), each $|aK\rangle$ is a sum of basis functions identified by $|ia\rangle$. All other basis functions are identified by $|ib\rangle$ or $|jb\rangle$.

Comparison of Eq. (48) with Eq. (31) gives the coefficients when degenerate perturbation theory is applicable. The coefficients for the ground state and doubly excited state basis functions are straight forward. However, the above redefinition of indices gives rise to three distinct classes of coefficients for the basis functions corresponding to the singly excited states. These are identified as was done in Section III B except that now there is a set of $|ia\rangle$'s corresponding to $|AK\rangle$ instead of one $|ia\rangle$ corresponding to $|A\rangle$.

$$C_0^0 = 1$$

$$\begin{aligned} C_{ia}^0 &= -(ia|V|0)/(E_{ia}-E_0) \\ &= -\sum_{j \neq i} (ia|j0|V|j0|0)/(E_{ia}-E_0) \\ &= -\sum_{j \neq i} V_{i0a;j00}/h\nu_{i0a} \end{aligned}$$

$$C_{ib}^0 = -\sum_{j \neq i} V_{i0b;j00}/h\nu_{i0b}$$

$$C_{jb}^0 = -\sum_{k \neq j} V_{j0b;k00}/h\nu_{j0b}$$

$$\begin{aligned} C_{ia;jb}^0 &= -(iajb|V|0)/(E_{iajb}-E_0) \\ &= -V_{i0a;j0b}/h(\nu_{j0b} + \nu_{i0a}) \end{aligned}$$

$$\begin{aligned} C_0^A &= -c_{iaK}(0|V|ia)/(E_0-E_{ia}) \\ &= c_{iaK} \sum_{j \neq i} V_{i0a;j00}/h\nu_{i0a} \end{aligned}$$

$$C_{ia}^A = c_{iaK}$$

$$\begin{aligned} C_{ib}^A &= -c_{iaK}(ib|V|ia)/(E_{ib}-E_{ia}) \\ &= -c_{iaK} \sum_{j \neq i} V_{iab;j00}/h(\nu_{i0b} - \nu_{i0a}) \end{aligned}$$

$$\begin{aligned}
 C_{jb}^A &= -c_{iaK} (jb|V|ia) / (E_{jb} - E_{ia}) \\
 &= -c_{iaK} V_{i0a; j0b} / h(\nu_{j0b} - \nu_{i0a})
 \end{aligned}$$

When these coefficients are substituted into Eq. (38) and only the terms correct to first order are kept, then each remaining term has a factor of $c_{iaK} c_{jaK}$.

The rotational strength for the transition 0 to AK separates naturally into two parts.

$$R_{0AK} = R_{0AK}^{nd} + R_{0AK}^d \quad (49)$$

R_{0AK}^{nd} contains the terms with factors $c_{iaK} c_{iaK}$ that are related to the nondegenerate Eq. (41). R_{0AK}^d contains the "crossterms" with factors $c_{iaK} c_{jaK}$ for $i \neq j$ that exist due to the degeneracy in the basis functions $|ia\rangle$, and terms such as $\vec{\mu}_{i0a} \cdot \vec{R}_j^{0a} \times \vec{\mu}_{j0a}$ which are zero when $i = j$.

By comparing these coefficient equations with those for the nondegenerate case, it can be seen that

$$R_{0AK}^{nd} = \sum_{i=1}^N (c_{iaK}^2 R_{0A}^{nd}) \quad (50)$$

where R_{0A}^{nd} is the rotational strength, Eq. (41), from the nondegenerate case and is a function of i .

The explicit form of R_{0AK}^d is

$$\begin{aligned}
R_{0AK}^d = & \operatorname{Im} \sum_i \sum_{j \neq i}^N c_{iaK} c_{jaK} \left[\sum_{k \neq i} \frac{V_{i0a; k00}^{\vec{\mu}_{i00} \cdot \vec{m}_{ja0}}}{h^{\nu_{i0a}}} + \vec{\mu}_{i0a} \cdot \vec{m}_{ja0} \right. \\
& - \sum_{k \neq j} \sum_{b \neq a} \frac{V_{jab; k00}^{\vec{\mu}_{i0a} \cdot \vec{m}_{jb0} + \vec{\mu}_{j0b} \cdot \vec{m}_{ia0}}}{h^{\nu_{j0b} - \nu_{j0a}}} \\
& - \sum_{k \neq j} \sum_{b \neq a} \frac{V_{j0a; k0b}^{\vec{\mu}_{i0a} \cdot \vec{m}_{kb0} + \vec{\mu}_{k0b} \cdot \vec{m}_{ia0}}}{h^{\nu_{k0b} - \nu_{j0a}}} \\
& - \sum_{k \neq j} \sum_{b \neq a} \frac{V_{j0b; k00}^{\vec{\mu}_{i0a} \cdot \vec{m}_{jab}}}{h^{\nu_{j0b}}} - \sum_{k \neq j} \sum_{b \neq a} \frac{V_{j0a; k0b}^{\vec{\mu}_{i0a} \cdot \vec{m}_{k0b}}}{h^{\nu_{k0b} + \nu_{i0a}}} \\
& - \sum_{k \neq i} \frac{V_{i0a; k00}^{\vec{\mu}_{iaa} \cdot \vec{m}_{ja0}}}{h^{\nu_{i0a}}} - \sum_{k \neq j} \sum_{b \neq a} \frac{V_{j0b; k00}^{\vec{\mu}_{jab} \cdot \vec{m}_{ia0}}}{h^{\nu_{j0b}}} \\
& \left. - \sum_{k \neq j} \sum_{b \neq a} \frac{V_{j0a; k0b}^{\vec{\mu}_{k0b} \cdot \vec{m}_{ia0}}}{h^{\nu_{k0b} + \nu_{j0a}}} \right] \\
& + \left(\frac{\pi}{c} \right) \sum_i \sum_{j \neq i}^N c_{iaK} c_{jaK} \left[\sum_{k \neq i} \frac{V_{i0a; k00}^{\vec{\mu}_{i00} \cdot \vec{R}_j^{0a}}}{h} x^{\vec{\mu}_{j0a}} \right. \\
& + \vec{\mu}_{i0a} \cdot \vec{R}_j^{0a} x^{\vec{\mu}_{j0a} \nu_{i0a}} \\
& \left. - \sum_{k \neq j} \sum_{b \neq a} \frac{V_{jab; k00}^{\vec{\mu}_{i0a} \cdot \vec{R}_j^{0b}}}{h^{\nu_{j0b} - \nu_{j0a}}} x^{\vec{\mu}_{j0b} \nu_{j0b}} + \vec{\mu}_{j0b} \cdot \vec{R}_i^{0a} x^{\vec{\mu}_{i0a} \nu_{i0a}} \right]
\end{aligned}$$

$$\begin{aligned}
& - \sum_{\substack{k \neq j \\ k \neq i}} \sum_{b \neq a} \frac{V_{j0a; k0b} (\vec{\mu}_{i0a} \cdot \vec{R}_k^{0b} \times \vec{\mu}_{k0b} \nu_{k0b} + \vec{\mu}_{k0b} \cdot \vec{R}_i^{0a} \times \vec{\mu}_{i0a} \nu_{i0a})}{h(\nu_{k0b} - \nu_{j0a})} \\
& - \sum_{\substack{k \neq j \\ k \neq i}} \sum_{b \neq a} \frac{V_{j0b; k00} \vec{\mu}_{i0a} \cdot \vec{R}_j^{ab} \times \vec{\mu}_{jab} \nu_{jab}}{h \nu_{j0b}} \\
& + \sum_{\substack{k \neq j \\ k \neq i}} \sum_{b \neq a} \frac{V_{j0a; k0b} \vec{\mu}_{i0a} \cdot \vec{R}_k^{0b} \times \vec{\mu}_{k0b} \nu_{k0b}}{h(\nu_{k0b} + \nu_{j0a})} \\
& - \sum_{k \neq i} \frac{V_{i0a; k00} \vec{\mu}_{iaa} \cdot \vec{R}_j^{0a} \times \vec{\mu}_{j0a}}{h} \\
& - \sum_{\substack{k \neq j \\ k \neq i}} \sum_{b \neq a} \frac{V_{j0b; k00} \vec{\mu}_{jab} \cdot \vec{R}_i^{0a} \times \vec{\mu}_{i0a} \nu_{i0a}}{h \nu_{j0b}} \\
& - \sum_{\substack{k \neq j \\ k \neq i}} \sum_{b \neq a} \left[\frac{V_{i0a; k0b} \vec{\mu}_{k0b} \cdot \vec{R}_i^{0a} \times \vec{\mu}_{i0a} \nu_{i0a}}{h(\nu_{k0b} + \nu_{j0a})} \right]
\end{aligned}$$

Collecting terms as was done for Eq. (41) produces the following equation, where the identity $\nu_{i0a} = \nu_{j0a}$ has been used.

$$\begin{aligned}
R_{0AK}^d = & \sum_i \sum_{j \neq i}^N c_{iaK} c_{jaK} \left[\text{Im} \vec{\mu}_{i0a} \cdot \vec{m}_{ja0} \right. \\
& - 2 \sum_{k \neq j} \sum_{b \neq a} \text{Im} \frac{V_{j0a; k0b} (\vec{\mu}_{i0a} \cdot \vec{m}_{k0b} \nu_{i0a} + \vec{\mu}_{k0b} \cdot \vec{m}_{i0a} \nu_{k0b})}{h(\nu_{k0b}^2 - \nu_{i0a}^2)} \\
& - \sum_{k \neq j} \sum_{b \neq a} \text{Im} \frac{V_{jab; k00} (\vec{\mu}_{i0a} \cdot \vec{m}_{j0b} + \vec{\mu}_{j0b} \cdot \vec{m}_{i0a})}{h(\nu_{j0b} - \nu_{j0a})} \\
& - \sum_{k \neq j} \sum_{b \neq a} \text{Im} \frac{V_{j0b; k00} (\vec{\mu}_{i0a} \cdot \vec{m}_{jab} + \vec{\mu}_{jab} \cdot \vec{m}_{i0a})}{h \nu_{j0b}} \\
& \left. - \sum_{k \neq i} \text{Im} \frac{V_{i0a; k00} (\vec{\mu}_{iaa} - \vec{\mu}_{i00}) \cdot \vec{m}_{ja0}}{h \nu_{i0a}} \right] \\
& + \left(\frac{\pi}{c} \right) \sum_i \sum_{j \neq i}^N c_{iaK} c_{jaK} \left[\vec{\mu}_{i0a} \cdot \vec{R}_j^{0a} \times \vec{\mu}_{j0a} \nu_{i0a} \right. \\
& - 2 \sum_{k \neq j} \sum_{b \neq a} \sum_{k \neq i} \frac{V_{j0a; k0b} \nu_{i0a} \nu_{k0b} (\vec{R}_k^{0b} - \vec{R}_i^{0a}) \cdot (\vec{\mu}_{k0b} \times \vec{\mu}_{i0a})}{h(\nu_{k0b}^2 - \nu_{i0a}^2)} \\
& - \sum_{k \neq j} \sum_{b \neq a} \frac{V_{jab; k00} (\vec{\mu}_{i0a} \cdot \vec{R}_j^{0b} \times \vec{\mu}_{j0b} \nu_{j0b} + \vec{\mu}_{j0b} \cdot \vec{R}_i^{0a} \times \vec{\mu}_{i0a} \nu_{i0a})}{h(\nu_{j0b} - \nu_{i0a})} \\
& + \sum_{k \neq j} \sum_{b \neq a} \frac{V_{j0b; k00} (\vec{\mu}_{i0a} \cdot \vec{R}_j^{ab} \times \vec{\mu}_{jab} \nu_{jab} - \vec{\mu}_{jab} \cdot \vec{R}_i^{0a} \times \vec{\mu}_{i0a} \nu_{i0a})}{h \nu_{j0b}} \\
& \left. - \sum_{k \neq i} \frac{V_{i0a; k00} (\vec{\mu}_{iaa} - \vec{\mu}_{i00}) \cdot \vec{R}_j^{0a} \times \vec{\mu}_{j0a}}{h} \right] \tag{51}
\end{aligned}$$

This result can be re-written in compact form.

$$R_{0AK}^d = \sum_i^N \sum_{j \neq i} (c_{iaK} c_{jaK} R'_{0A}) \quad (52)$$

where R'_{0A} represents the quantities within the square brackets above and is a function of i and j .

Equations (50) and (52) substituted into Eq. (45) define the total rotational strength for a transition $0AK$ where AK is one member of a zeroth order degenerate transition.

$$R_{0AK} = \sum_i^N (c_{iaK}^2 R_{0A}) + \sum_i^N \sum_{j \neq i} (c_{iaK} c_{jaK} R'_{0A}) \quad (53)$$

The first order energy correction may or may not remove all of the degeneracy. If the degeneracies are removed, then CD bands of rotational strengths, R_{0AK} , are placed at discrete energies.

Tinoco³³ does not have the second term of Eq. (50) in his Eq. (III B-22). He sums over K and, using the results of Eq. (47b), retains only the first term in Eq. (53). This gives correct results for the manifold of K -states taken as a whole. However, if any features of a spectrum are due to distinct $0AK$ transitions, these will be obliterated by summing over K .

An examination of Eq. (51) reveals that the first $\vec{\mu} \cdot \vec{m}$ and $\vec{\mu} \cdot \vec{R} \times \vec{\mu}$ terms are the zeroth order interactions between degenerate groups. The rest of the terms are first order corrections. Since there is a zeroth order interaction term, many authors³⁷⁻³⁹ consider only this contribution to R_{0AK}^d .

D. Application to the Amide Transitions in Diketopiperazines

A diketopiperazine molecule, two amino acid monomers combined into a six-numbered ring, contains two planar amide groups. If only the amide transitions are considered, then the molecule can be divided into amide group 1, amide group 2 and each remaining bond in the molecule as the other groups. Since there are two amide groups, each transition investigated will be doubly degenerate, and the results of Section C from first order degenerate perturbation theory will be used.

The appropriate equation for the rotational strength R_{0AK} is Eq. (53). If a group (such as the amide group) has a plane of symmetry, then it can have no intrinsic optical activity. In this case, $\vec{\mu}_{i0a} \cdot \vec{m}_{ia0} = 0$. This allows R_{0AK}^{nd} to separate neatly into two parts. One is the interaction of $\vec{\mu}_{i0a}$ with other group electric and magnetic transition moments, and the other is the interaction of \vec{m}_{i0a} with other group electric and magnetic transition moments.

The rotational strength for an electrically allowed transition is

$$R_{0AK}^{\text{nd}}(\text{elec}) = \sum_{i=1}^N c_{iaK}^2 \left[-\left(\frac{2\pi}{c}\right) \sum_{j \neq i} \sum_{b \neq a} \frac{V_{i0a; j0b} \nu_{i0a} \nu_{j0b} (\vec{R}_j^{0b} - \vec{R}_i^{0a}) (\vec{\mu}_{j0b} \times \vec{\mu}_{i0a})}{h(\nu_{j0b}^2 - \nu_{i0a}^2)} \right] \quad (54a)$$

$$-2 \sum_{j \neq i} \sum_{b \neq a} \frac{\text{Im } V_{i0a; j0b} \nu_{i0a} (\vec{\mu}_{i0a} \cdot \vec{m}_{j0b})}{h(\nu_{j0b}^2 - \nu_{i0a}^2)} \quad (54b)$$

$$- \sum_{j \neq i} \sum_{b \neq a} \frac{\text{Im } V_{iab; j00} (\vec{\mu}_{i0a} \cdot \vec{m}_{ib0})}{h(\nu_{i0b} - \nu_{i0a})} \quad (54c)$$

$$- \sum_{j \neq i} \sum_{b \neq a} \frac{\text{Im } V_{i0b; j00} (\vec{\mu}_{i0a} \cdot \vec{m}_{iab})}{h \nu_{i0b}} \quad (54d)$$

The rotational strength for a magnetically allowed transition is

$$R_{0AK}^{\text{nd}}(\text{mag}) = \sum_{i=1}^N c_{iaK}^2 \left[-2 \sum_{j \neq i} \sum_{a \neq b} \frac{\text{Im } V_{i0a; j0b} \nu_{j0b} (\vec{\mu}_{j0b} \cdot \vec{m}_{ia0})}{h(\nu_{j0b}^2 - \nu_{i0a}^2)} \right] \quad (55a)$$

$$- \sum_{j \neq i} \sum_{b \neq a} \frac{\text{Im } V_{iab; j00} (\vec{\mu}_{i0b} \cdot \vec{m}_{ia0})}{h(\nu_{i0b} - \nu_{i0a})} \quad (55b)$$

$$- \sum_{j \neq i} \sum_{b \neq a} \frac{\text{Im } V_{i0b; j00} (\vec{\mu}_{iab} \cdot \vec{m}_{ia0})}{h \nu_{i0b}} \quad (55c)$$

$$- \sum_{j \neq i} \frac{\text{Im } V_{i0a; j00} (\vec{\mu}_{iaa} \cdot \vec{\mu}_{i00}) \cdot \vec{m}_{ia0}}{h \nu_{i0a}} \quad (55d)$$

These equations require explicit values for the electric and magnetic transition moments. These parameters are available for the $n\pi^*$, $\pi\pi^*$, $n\sigma^*$ and $\pi\sigma^*$ amide transitions. Two approaches exist for treating other transitions. Schellman and coworkers⁴⁰ interact only those transitions for which explicit data is available. The experimental rotational strengths are subjected to the criteria that $\sum_m R_m / \sum_m |R_m|$ be less than 0.1, where m counts the transitions considered, as a check on the reasonableness of making this approximation. As they noted, this is not a sufficient condition to insure the negligible influence from higher transitions on a particular lower energy transition since they could interact such that the contributions when summed over all the experimental bands sum to zero.

Another solution is to treat the other transitions through the use of polarizabilities.⁴¹ This has been the direction taken by Tinoco, Johnson and Synder.^{31, 34-36, 42} The polarizability approximation averages together all of the electric dipole transition moments for a particular group. Therefore it can only be applied to the terms of Eq. (54a) and Eq. (55a) since they involve $\vec{\mu}_{j0b}$ interacting with $\vec{\mu}_{i0a}$ and \vec{m}_{ia0} , respectively. In the dipole approximation,

$$V_{i0a; j0b} = \vec{\mu}_{i0a} \cdot \vec{T}_{ij} \cdot \vec{\mu}_{j0b} \quad (56)$$

where

$$\vec{T}_{ij} = \frac{1-3\hat{e}_{ij}\hat{e}_{ij}}{|\vec{R}_{ij}|^3}$$

and \hat{e}_{ij} is the unit vector in the direction of $\vec{R}_{ij} = \vec{R}_j^{0b} - \vec{R}_i^{0a}$. \vec{T} is the tensor operator specifying the interaction between $\vec{\mu}_{i0a}$ and $\vec{\mu}_{j0b}$. The polarizability tensor for group j is

$$\vec{\alpha}_j(\nu) = 2 \sum_b \frac{\nu_{j0b} \vec{\mu}_{j0b} \vec{\mu}_{j0b}}{h(\nu_{j0b}^2 - \nu^2)} \quad (57)$$

The values used in the polarizability tensor must be corrected for any group transitions that were examined explicitly. Two types of polarizabilities are commonly used: group (or atomic) and bond polarizabilities. We will use bond polarizabilities.

Substituting these relationships into term (54a) gives this term in the polarizability approximation

$$\left(\frac{\pi}{c}\right) \sum_{i \neq j} \sum_{a \neq b} c_{ia}^2 \nu_{i0a} \vec{E}_{i0a}^j \cdot \vec{\alpha}_j \times \vec{\mu}_{i0a} \cdot \vec{R}_{ij} \quad (54a')$$

where the field at group j due to the transition $i0a$ is

$$\vec{E}_{i0a}^j = -\vec{\mu}_{i0a} \cdot \vec{T}_{ij} \quad (58)$$

Substitution into term (55a) gives this term in the polarizability approximation

$$\sum_i \sum_{j \neq i} c_{iaK}^2 \vec{E}_{i0a}^j \cdot \vec{\alpha}_j \cdot \vec{m}_{ia0} \quad (55a')$$

Equations (56) and (58) are definitions using the dipole approximation. An alternate approach is to use the monopoles^{3/} approximation. Each group is divided into regions, and monopole charges are placed at the center of the transition electron cloud for that region. This approximates the interaction energy between transitions better than the dipole approximation because it describes the actual transition electron cloud more accurately.⁴³

\vec{E}_{i0a}^j and $V_{i0a; j0b}$, at the level of the monopole approximation, are

$$\vec{E}_{i0a}^j = \sum_s \frac{\rho_s^{i0a}}{r_{sj}^3} \vec{r}_{sj} \quad (59)$$

and

^{3/}I prefer to call this the "monopoles" approximation instead of the "monopole" approximation. The dipole approximation means there is one dipole at each group. The monopole approximation would logically imply there is one monopole per group. However, if there was only one monopole per group, it would be zero since the groups are neutral. In fact, several monopoles per group replace the one group dipole moment. Therefore I call it the "monopoles" approximation.

$$V_{i0a;j0b} = \sum_s \sum_t \frac{\rho_s^{i0a} \rho_t^{j0b}}{r_{st}} \quad (60)$$

where ρ_s^{i0a} is the monopole of region s for the transition $0a$ of group i , \vec{r}_{sj} is the vector distance from region s of group i to the center of group j , and r_{st} is the distance between region s of group i and the region t of group j . All of our calculations will use the monopoles approximation.

R_{0AK}^d does not separate so neatly into two parts. Since $\vec{\mu}_{i0a}$ and \vec{m}_{ja0} refer to the same degenerate transition on different groups, the scalar product of these is not necessarily zero. However Eq. (51) can be separated into three parts. The first gives the interaction between $\vec{\mu}_{i0a}$ and \vec{m}_{ja0} .

$$R_{0AK}^d(\text{elec-mag}) = \sum_i \sum_{j \neq i} c_{iaK} c_{jaK} \text{Im} \vec{\mu}_{i0a} \cdot \vec{m}_{ja0} \quad (61)$$

The interactions between $\vec{\mu}_{i0a}$ and other electric and magnetic transition moments is

$$R_{0AK}^d(\text{elec}) = \sum_i \sum_{j \neq i} c_{iaK} c_{jaK} \left[-2 \sum_{k \neq j} \sum_{b \neq a} \text{Im} \frac{V_{j0a;k00} \vec{\mu}_{i0a} \cdot \vec{m}_{kb0} \nu_{i0a}}{h(\nu_{k0b}^2 - \nu_{i0a}^2)} \right] \quad (62a)$$

$$- \sum_{k \neq j} \sum_{b \neq a} \text{Im} \frac{V_{jab;k00} \vec{\mu}_{i0a} \cdot \vec{m}_{jb0}}{h(\nu_{j0b} - \nu_{j0a})} \quad (62b)$$

$$- \sum_{k \neq j} \sum_{b \neq a} \text{Im} \left[\frac{V_{j0b; k00} \vec{\mu}_{i0a} \cdot \vec{m}_{jab}}{h \nu_{j0b}} \right] \quad (62c)$$

$$+ \left(\frac{\pi}{c} \right) \sum_i \sum_{j \neq i} c_{ia} K^c_{ja} K \left[\vec{\mu}_{i0a} \cdot \vec{R}_j^{0a} \times \vec{\mu}_{j0a} \nu_{j0a} \right] \quad (62d)$$

$$- 2 \sum_{k \neq j} \sum_{b \neq a} \sum_{k \neq i} \frac{V_{j0a; k0b} \nu_{i0a} \nu_{k0b} (\vec{R}_k^{0b} - \vec{R}_i^{0a}) \cdot (\vec{\mu}_{k0b} \times \vec{\mu}_{i0a})}{h(\nu_{k0b}^2 - \nu_{i0a}^2)} \quad (62e)$$

$$- \sum_{k \neq j} \sum_{b \neq a} \frac{V_{jab; k00} (\vec{\mu}_{i0a} \cdot \vec{R}_j^{0b} \times \vec{\mu}_{j0b} \nu_{j0b} + \vec{\mu}_{j0b} \cdot \vec{R}_i^{0a} \times \vec{\mu}_{i0a} \nu_{i0a})}{h(\nu_{j0b} - \nu_{i0a})} \quad (62f)$$

$$+ \sum_{k \neq j} \sum_{b \neq a} \frac{V_{j0b; k00} (\vec{\mu}_{i0a} \cdot \vec{R}_j^{ab} \times \vec{\mu}_{jab} \nu_{jab} - \vec{\mu}_{jab} \cdot \vec{R}_i^{0a} \times \vec{\mu}_{i0a} \nu_{i0a})}{h \nu_{j0b}} \quad (62g)$$

$$- \sum_{k \neq i} \left[\frac{V_{i0a; k00} (\vec{\mu}_{iaa} \cdot \vec{\mu}_{i00}) \cdot \vec{R}_j^{0a} \times \vec{\mu}_{j0a}}{h} \right] \quad (62h)$$

The interactions between \vec{m}_{ia0} or \vec{m}_{ja0} and other electric and magnetic transition moments is

$$R_{0AK}^d(\text{mag}) = \sum_i \sum_{j \neq i} c_{ia} K^c_{ja} K \left[-2 \sum_{k \neq j} \sum_{b \neq a} \text{Im} \frac{V_{j0a; k0b} \vec{\mu}_{k0b} \cdot \vec{m}_{ia0} \nu_{k0b}}{h(\nu_{k0b}^2 - \nu_{ia0}^2)} \right] \quad (63a)$$

$$- \sum_{k \neq j} \sum_{b \neq a} \text{Im} \frac{V_{jab; k00} \vec{\mu}_{j0b} \cdot \vec{m}_{ia0}}{h(\nu_{j0b} - \nu_{j0a})} \quad (63b)$$

$$- \sum_{k \neq j} \sum_{b \neq a} \text{Im} \frac{V_{j0b; k00}^{\vec{\mu}_{jab}, \vec{m}_{ia0}}}{h\nu_{j0b}} \quad (63c)$$

$$- \sum_{k \neq i} \text{Im} \frac{V_{i0a; k00}^{(\vec{\mu}_{iaa}, -\vec{\mu}_{i00}), \vec{m}_{ja0}}}{h\nu_{i0a}} \quad (63d)$$

Again it should be noted that terms (61) and (62d) are the zeroth order interaction terms. All other terms are first order corrections. Only the zeroth order interactions will be calculated for the diketopiperazines. If the first order terms are considered, then the polarizability approximation may be applied to the terms of Eq. (62e) and (63a)..

Before these equations can be applied to diketopiperazines, the coefficients, c_{iaK} , and the first order corrections to the degenerate energy need to be found.

The eigenvalue problem can be stated in two homogenous equations.

$$-E^1 c_{1aK} + V_{10a; 20a} c_{2aK} = 0 \quad (64a)$$

$$V_{10a; 20a} c_{1aK} - E^1 c_{2aK} = 0 \quad (64b)$$

where $K = 1$ or 2 . The determinant of the coefficients of the c 's in Eq. (64) is

$$\begin{vmatrix} -E^1 & V_{10a;20a} \\ V_{10a;20a} & -E^1 \end{vmatrix} = 0$$

and has the roots

$$E_1^1 = V_{10a;20a} \quad \text{and} \quad E_2^1 = -V_{10a;20a}. \quad (65)$$

Substituting E_1^1 into either Eq. (64a) or (64b) gives $c_{1a1} = c_{2a1}$.

Similarly, substituting E_2^1 into Eq. (64a) or (64b) gives

$$c_{1a2} = -c_{2a2}.$$

Applying the normalization condition removes the remaining indeterminacy in the coefficients. The final result is

$$\begin{aligned} c_{1a1} = c_{2a1} &= (2)^{-1/2} \\ c_{1a2} = -c_{2a2} &= (2)^{-1/2} \end{aligned} \quad (66)$$

Therefore, the zeroth order contributions to R_{0AK}^d for a dimer with no intrinsic group CD are³⁷⁻³⁹

$$R_{0A1,2}^d = \mp \frac{\pi \nu_{10a}}{2c} [(\vec{R}_2^{0a} - \vec{R}_1^{0a}) (\vec{\mu}_{10a} \times \vec{\mu}_{20a})] \quad (67)$$

These contributions occur at energies

$$E_{1,2} = E_{0a} \pm V_{10a;20a} \quad (68)$$

E. Molecular Origin, Group Centers and Origin Dependency

The rotational strength for a particular molecular transition is an observable. Therefore, the calculated rotational strength should be independent of the choice of origin for the coordinate system of the molecule. The origin dependency of the theoretical rotational strength with molecular wavefunctions is discussed first. Various equivalent forms for the rotational strength exist if exact wavefunctions are used. The use of approximate wavefunctions leads to the choice of the length form for the electric transition moment and the linear momentum.

With this discussion as background, the rotational strength in terms of group functions is examined for origin dependency. Criteria are developed for evaluating the quantities in the equations developed in Section III D such that they are independent of choice of molecular origin. With group functions, the rotational strength does depend on the choice of group origins. The choice of a group origin as the center of transition charge is discussed in the last subsection.

1. Molecular Wavefunctions and Origin Dependency

The investigation of the origin dependency of the theoretical rotational strength begins with the initial definition of R_{0A} .

$$R_{0A} = \text{Im} \langle 0 | \vec{\mu} | A \rangle \cdot \langle A | \vec{m} | 0 \rangle \quad (23)$$

The magnetic transition moment for the molecule can be written as

$$\langle A | \vec{m} | 0 \rangle = \frac{e}{2mc} \langle A | \vec{r} \times \vec{p} | 0 \rangle \quad (69)$$

where e and m are the charge and mass, respectively, of an electron, c is the velocity of light, \vec{r} is the vector operator for the position of the electron undergoing transition and \vec{p} is the vector operator for the linear momentum of the electron. The electric transition moment for the molecule can be written in the dipole length form as

$$\langle 0 | \vec{\mu} | A \rangle = e \langle 0 | \vec{r} | A \rangle. \quad (70)$$

With these definitions the rotational strength is

$$R_{0A} = \frac{e^2}{2mc} \text{Im} \langle 0 | \vec{r} | A \rangle \cdot \langle A | \vec{r} \times \vec{p} | 0 \rangle. \quad (71)$$

No approximations have been made in going from Eq. (23) to Eq. (71); Eq. (71) is simply a redefinition of Eq. (23) so that the problem of origin dependency can be more readily examined.

If the origin in Eq. (71) is moved to a new position that is the vector distance \vec{R} away from the old origin, then \vec{r} becomes $\vec{R} + \vec{r}$. The linear momentum is independent of the choice of origin since

$$\vec{p} = -i\hbar\vec{\nabla} \quad (72)$$

where \hbar is the reduced Planck's constant and $\vec{\nabla}$ in Cartesian coordinates is $\hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z}$. Therefore, the scalar product in Eq. (71) becomes⁴⁴

$$\langle 0 | \vec{R} + \vec{r} | A \rangle \cdot \langle A | (\vec{R} + \vec{r}) \times \vec{p} | 0 \rangle = \vec{R} \langle 0 | A \rangle \cdot \vec{R} \times \langle A | \vec{p} | 0 \rangle \quad (73a)$$

$$+ \vec{R} \langle 0 | A \rangle \cdot \langle A | \vec{r} \times \vec{p} | 0 \rangle \quad (73b)$$

$$+ \langle 0 | \vec{r} | A \rangle \cdot \vec{R} \times \langle A | \vec{p} | 0 \rangle \quad (73c)$$

$$+ \langle 0 | \vec{r} | A \rangle \cdot \langle A | \vec{r} \times \vec{p} | 0 \rangle \quad (73d)$$

Terms (73a) and (73b) are zero due to the orthogonality of the molecular wavefunctions.

If exact wavefunctions are used, term (73c) is also zero. To prove this the commutator of the position and Hamiltonian operators is used.

$$[H, \vec{r}] = H \vec{r} - \vec{r} H = -\frac{i\hbar}{m} \vec{p} \quad (74)$$

This is an operator relationship and holds for any wavefunction, exact or approximate. If exact wavefunctions are used, then $|0\rangle$ and $|A\rangle$ are eigenfunctions of H

$$H|0\rangle = E_0|0\rangle$$

$$H|A\rangle = E_A|A\rangle$$

Approximate wavefunctions are not eigenfunctions of H and the above relationships do not hold. For exact wavefunctions

$$\begin{aligned} \langle A | \vec{p} | 0 \rangle &= -\frac{m}{i\hbar} \langle A | H \vec{r} - \vec{r} H | 0 \rangle \\ &= \frac{im}{\hbar} [\langle A | H \vec{r} | 0 \rangle - \langle A | \vec{r} H | 0 \rangle] \\ &= \frac{im}{\hbar} [\langle A | H \vec{r} | 0 \rangle - E_0 \langle A | \vec{r} | 0 \rangle] \end{aligned}$$

Since H is Hermitian

$$\langle A | H | \vec{r} | 0 \rangle = \langle \vec{r} | 0 | H | A \rangle^* = E_A \langle A | \vec{r} | 0 \rangle$$

Therefore,

$$\langle A | \vec{p} | 0 \rangle = \frac{im}{\hbar} (E_A - E_0) \langle A | \vec{r} | 0 \rangle \quad (75)$$

LaPaglia and Sinanoglu⁴⁵ refer to Eq. (75) as the off-diagonal hypervirial theorem. They also cite the books by Bethe and Salpeter⁴⁶ and Slater⁴⁷ as sources. My derivation parallels that done by Levine³² for the on-diagonal hypervirial theorem.

Equation (75) is an identity for exact wavefunctions. Therefore, $\langle A | \vec{p} | 0 \rangle$ is parallel to $\langle 0 | \vec{r} | A \rangle$ and the triple product in term (73c) is zero.⁴⁴ However, since approximate wavefunctions are not eigenfunctions of H , $\langle A | \vec{p} | 0 \rangle$ and $\langle 0 | \vec{r} | A \rangle$ are not simply proportional and thus not parallel except for certain cases determined

by symmetry.⁴⁸ As Moscowitz points out, using approximate wavefunctions can lead to a large origin dependency.

Moscowitz used the electric transition moment in the dipole velocity form, so that the term similar to (73c) is zero.^{44, 49} Using the dipole velocity form in Eq. (23) gives the rotational strength as

$$R_{0A} = \frac{1}{2c} \left(\frac{e\hbar}{m} \right)^2 (E_A - E_0)^{-1} \text{Im} \langle 0 | \vec{\nabla} | A \rangle \cdot \langle A | \vec{r} \times \vec{p} | 0 \rangle \quad (76)$$

With a change in origin, the scalar product in Eq. (76) becomes

$$\langle 0 | \vec{\nabla} | A \rangle \cdot \langle A | (\vec{R} + \vec{r}) \times \vec{p} | 0 \rangle = \langle 0 | \vec{\nabla} | A \rangle \cdot \vec{R} \times \langle A | \vec{p} | 0 \rangle \quad (77a)$$

$$+ \langle 0 | \vec{\nabla} | A \rangle \cdot \langle A | \vec{r} \times \vec{p} | 0 \rangle \quad (77b)$$

The linear momentum operator is $\vec{p} = i\hbar\vec{\nabla}$, and thus $\langle 0 | \vec{\nabla} | A \rangle$ is parallel to $\langle A | \vec{p} | 0 \rangle$ and the triple product of term (77a) is zero even for approximate wavefunctions. Thus, the rotation strength in the form of Eq. (76) is independent of the choice of molecular origin regardless of the wavefunctions used. However, Harris⁵⁰ has shown that when the dipole velocity form is used with Hartree-Fock wavefunctions, the sum rule for rotational strengths is violated.

The solution we use is to write both $\vec{\mu}$ and \vec{p} in the dipole length form. However, putting Eq. (23) in this form is not trivial. The magnetic transition moment, as defined by Eq. (69), has the integral $\langle A | \vec{r} \times \vec{p} | 0 \rangle$ where the operator is a cross product. The

identity given by Eq. (75) which puts $\langle A | \vec{p} | 0 \rangle$ in length form is an integral equation and not an operator equation. Therefore, it cannot be directly substituted into the definition for the magnetic transition moment. We can, however, easily make this substitution after expanding the molecular wavefunctions in terms of group functions. This method was used in arriving at Eq. (38).

Then instead of evaluating $\langle 0 | \vec{\mu} | A \rangle \cdot \langle A | \vec{m} | 0 \rangle$, terms such as

$$(0 | \vec{\mu}_i | a) \cdot \{ (a | \vec{m}_j | 0) + \frac{e}{2mc} [\vec{R}_j^{0a} \times (a | \vec{p}_j | 0)] \} \quad (78)$$

are evaluated, where all the quantities are group quantities which have been previously defined. Since the group functions are eigenfunctions of the group operators, the identity of Eq. (75) can be used to write term (78) as

$$\begin{aligned} & (0 | \vec{\mu}_i | a) \cdot \{ (a | \vec{m}_j | 0) + \frac{ie}{2c\hbar} (E_a - E_0) [\vec{R}_j^{0a} \times (a | \vec{p}_j | 0)] \} \\ & = (0 | \vec{\mu}_i | a) \cdot \{ (a | \vec{m}_j | 0) + \frac{\pi i}{c} \nu_{0a} \vec{R}_j^{0a} \times (a | \vec{p}_j | 0) \} \end{aligned} \quad (79)$$

Thus, there are two types of terms in Eq. (38). Using the compact notation introduced in Section III A, these terms are (a) $\vec{\mu}_{i0a} \cdot \vec{m}_{jb0}$ and (b) $\vec{\mu}_{i0a} \cdot \vec{R}_j^{0b} \times \vec{\mu}_{j0b}$. Each of these will be examined for origin dependency in the next subsection. In arriving at Eq. (38), the wavefunctions for each group were assumed to be

eigenfunctions and thus orthogonal, just as the molecular functions were assumed to be orthogonal to eliminate terms (73a) and (73b).

If the group quantities are not evaluated consistent with the orthogonality condition for the approximate wavefunctions used in the computation, then the rotational strength will be origin dependent. This will also be examined for approximate group functions in the next subsection.

2. Group Functions and Origin Dependency

Terms of type (a) are clearly independent of origin. The group magnetic moments, \vec{m}_{jb0} , are intrinsic moments (they cannot be made zero) and have an "intrinsic" group center from which they are computed. In our calculations they come from $(2p_x | \vec{m} | 2p_y)$ on one atom. Therefore they are always evaluated as atomic integrals at the nuclear center. With this choice of center, \vec{m}_{jb0} is independent of molecular origin. Due to the orthogonality of the group functions, $\vec{\mu}_{i0a}$ is also independent of the choice of molecular origin. Under a change in origin, $(0 | \vec{r} | a)$ becomes

$$(0 | \vec{R} + \vec{r} | a) = \vec{R}(0 | a) + (0 | \vec{r} | a) = (0 | \vec{r} | a) \quad (80)$$

Thus, $\vec{\mu}_{i0a} \cdot \vec{m}_{jb0}$ is independent of molecular origin.

Terms of type (b), $\vec{\mu}_{i0a} \cdot \vec{R}_j^{0b} \times \vec{\mu}_{j0b}$ in Eq. (38), occur in the final equations for the rotational strength in Section III D as terms

(54a) and (62d, e, f, g and h). In arriving at term (54a), the corresponding terms in Eq. (38) were taken by pairs and added.

$$\vec{\mu}_{i0a} \cdot \vec{R}_j^{0b} \times \vec{\mu}_{j0b} + \vec{\mu}_{j0b} \cdot \vec{R}_i^{0a} \times \vec{\mu}_{i0a} = (\vec{R}_j^{0b} - \vec{R}_i^{0a}) \cdot (\vec{\mu}_{j0b} \times \vec{\mu}_{i0a})$$

Since $\vec{R}_j^{0b} - \vec{R}_i^{0a}$ is a difference, any change in origin will be subtracted out. The cross product $\vec{\mu}_{j0b} \times \vec{\mu}_{i0a}$ is independent of molecular origin because each $\vec{\mu}$ is independent of origin. Therefore term (54a) is independent of choice of origin. Term (62d) can be treated the same way. Equation (67) gives the result for the dimer, and it is independent of origin. Term (62e) is handled identically to term (54a). To show that terms (62f), (62g) and (62h) are independent of molecular origin is much more complex. It will not be pursued here since we do not compute these terms for the diketopiperazines.

In the development of the equations for the rotational strength, the group functions are assumed orthogonal. In particular, the dipole length form of the electric transition moment, Eq. (70), is independent of the choice of origin only if the orthogonality condition is consistently applied. To illustrate the problem, the electric transition moment, $\vec{\mu}_{0a}$, for π -electrons will be derived.^{51, 52} The electric transition moment for a one-electron transition $0a$ is

$$\vec{\mu}_{0a} = e(2)^{1/2} (K|\vec{r}|L) \quad (81)$$

where e is the charge of an electron ($e = -1$ atomic units) and $|K\rangle$ and $|L\rangle$ are the one-electron basis functions involved in the group transition $0a$. The square root of two arises in the full deviation using Slater determinants where the singlet excited state is represented by the difference of two determinants.

In the LCAO (linear combination of atomic orbitals) approximation, the basis functions are

$$|K\rangle = \sum_i c_{iK} |i\rangle \quad \text{and} \quad |L\rangle = \sum_j c_{jL} |j\rangle .$$

These are then substituted into Eq. (52).

$$\vec{P}_{0a} = e(2)^{1/2} \sum_i c_{iK} c_{iL} (i|\vec{r}|i) + \sum_i \sum_{j \neq i} c_{iK} c_{jL} (i|\vec{r}|j) \quad (82)$$

Since the atomic $2p$ orbitals that form the π -system are symmetric about a plane, the first integral reduces to

$$(i|\vec{r}|i) = \vec{R}_i \quad (83)$$

where \vec{R}_i is the position vector for the center of atom i .

Evaluating the second integral in Eq. (82) is more difficult.

First the integral can be transformed by arbitrarily choosing atom i to be the center of a new coordinate system. This integral is then

$$\begin{aligned}
 (i|\vec{r}|j) &= (i|\vec{R}_i + \vec{r}_i|j) \\
 &= \vec{R}_i S_{ij} + (i|\vec{r}_i|j)
 \end{aligned}
 \tag{84}$$

where S_{ij} is the overlap integral and \vec{r}_i is the vector operator for the position of the electron in the new coordinate system. If \vec{z}_i points along a line between i and j , then for π -orbitals

$$\begin{aligned}
 (i|\vec{r}_i|j) &= (i|\vec{z}_i|j) \\
 &= \hat{e}_{ij}(i|z|j)
 \end{aligned}
 \tag{85}$$

where \hat{e}_{ij} is a unit vector pointing from center i to center j . Ehrens and Phillipson⁵³ have tabulated values for the integral on the right-hand side of Eq. (85) using Slater-type orbitals.

By substituting Eqs. (83) to (85) into Eq. (82), the electric transition moment is given by

$$\vec{\mu}_{0a} = e(2)^{1/2} \sum_i c_{iK} c_{iL} \vec{R}_i + \sum_i \sum_{j \neq i} c_{iK} c_{jL} [\vec{R}_i S_{ij} + \hat{e}_{ij}(i|z|j)] \tag{86}$$

Equation (59) appears to depend on the choice of origin through the quantity \vec{R}_i . However, it does not.

If the origin of the coordinate system is moved a vector distance \vec{R} , then each \vec{R}_i becomes $\vec{R}_i + \vec{R}$ and the electric transition moment, $\vec{\mu}'_{0a}$, in the new coordinate system is

$$\vec{\mu}'_{0a} = \vec{\mu}_{0a} + e(2)^{1/2} \vec{R} \left[\sum_i c_{iK} c_{iL} + \sum_i \sum_{j \neq i} c_{iK} c_{jL} S_{ij} \right] \quad (87)$$

The quantity in the brackets is just the LCAO orthogonality condition and is zero. Thus, $\vec{\mu}_{0a}$ is independent of origin.

We have found that some workers are inconsistent in applying the orthogonality condition. For example, various authors⁵⁴⁻⁵⁶ use or suggest using transition moments computed with overlap terms even though the wavefunctions are found by neglecting overlap. Thus, the first term in the brackets in Eq. (87) is zero, but the second is not and leads to origin dependent results for the electric transition moment.

If $\vec{\mu}_{0a}$ is evaluated consistently with respect to the level of approximation used in the MO calculation specifying the coefficients, then $\vec{\mu}_{0a}$ is independent of the choice of origin. In practice this means zero-differential-overlap (ZDO) calculations should only use the first term of Eq. (86) and not include any overlap terms. On the other hand, if the coefficients come from an ab initio calculation, then considering only the first term will produce an origin dependent transition moment.

Many workers have been concerned with the choice of operator (dipole length or dipole velocity) or the effect of including overlap or hybrid terms when using ZDO coefficients,^{45, 53, 56-61} but they have

not considered the criteria that the results be independent of the choice of origin. More work needs to be done in this whole area of transition moment calculations. For example, Bendazzoli, et al⁶² have used ab initio wavefunctions with the dipole length and dipole velocity operators for propylene sulfide. The resulting rotational strengths for the different operators are significantly different.

With the above restrictions, the equations for the rotational strength will not vary with a change in the origin of the molecular coordinate system. However, the equations do depend on another choice of origin, the origins within the groups, \vec{R}_i^{0a} .

3. Choice of Group Origin

The origin within a group, \vec{R}_i^{0a} , is the position for $\vec{\mu}_{i0a}$, so that it is crucial to evaluating $(\vec{R}_j^{0a} - \vec{R}_i^{0a}) \cdot (\vec{\mu}_{i0a} \times \vec{\mu}_{j0a})$ and similar quantities. The interaction energy, V , also depends on \vec{R}_i^{0a} when the dipole approximation is used.

Initially, V for the first $\pi\pi^*$ of the amide groups in the diketopiperazines was calculated by the dipole approximation. $\vec{R}^{\pi\pi^*}$ was placed at the center of the positive nuclear charge. The resulting rotational strengths from term (67) created a couplet of bands with opposite sign to that found in the experimental spectrum of PPDKP. By changing the origin to that outlined below, bands of the correct sign were calculated. So the choice of group origin may be critical.

particularly for asymmetric groups.

From classical electrostatics, multipole expansions in cases of net charge should be carried out at the center of total charge given by Eq. (88), particularly if the series is truncated after the monopole term.

$$\vec{R} = \sum_s |q_s| \vec{r}_s / \sum_s |q_s| \quad (88)$$

where q_s is the charge situated at position \vec{r}_s . Similarly we suggest that for neutral groups undergoing excitation the correct origin for a dipole transition moment is the center of absolute transition charge given by Eq. (89).

$$\vec{R}_i^{0a} = \sum_s |\rho_s^{i0a}| \vec{r}_s^{0a} / \sum_s |\rho_s^{i0a}| \quad (89)$$

where ρ_s^{i0a} is a transition monopole defined previously and \vec{r}_s^{0a} is the position vector for the monopole in the molecular coordinate system. Cech and Tinoco⁶³ have independently used this equation.

IV. CALCULATIONS FOR THE TRANSITIONS ON THE AMIDE GROUP

A. Introduction

The equations for the rotational strength that were developed in Section III D are applied to the molecular transitions centered on the amide groups. The quantities needed to calculate these different terms are discussed below. First, the molecular structures and atomic coordinates are given. Second, the energy of the various transitions, the electric transition moments and their positions within the amide group, the magnetic transition moments and the monopoles and their positions associated with the different transition moments are discussed. In addition, the polarizabilities of the other bonds in the molecular are needed to estimate the contributions of the $\sigma\sigma^*$ transitions to the transitions of the amide group.

The methods used to arrive at each of these quantities are presented, then the rotational strengths are calculated for each transition and are converted to CD bands. The peak $\Delta\epsilon$ values are given for the terms of Eq. (54), (55) and (67) in Section III D.

B. Coordinates

Figure 5 shows the position of the DKP ring atoms and the molecular coordinate system used in this study. Each amide group is

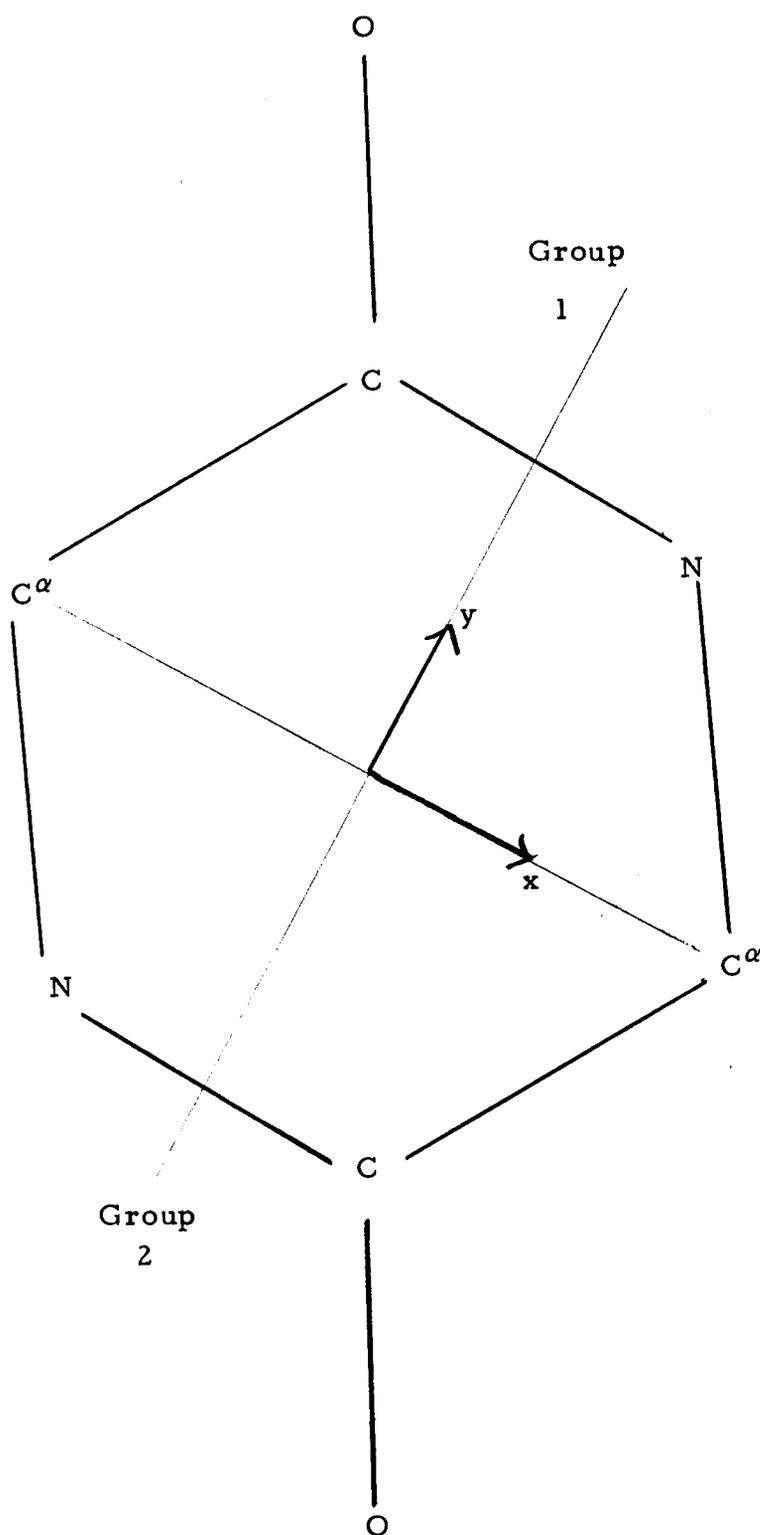


Figure 5a. Coordinate system for the diketopiperazine ring.

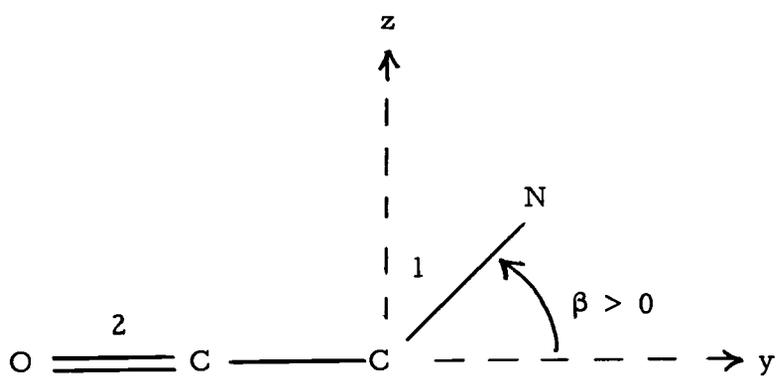


Figure 5b. The convention for the folding of amide group one with respect to amide group 2. The angle of folding, β , is positive in the positive z -direction.

assumed planar and rigid. Hooker's³⁶ nomenclature for the folding of the DKP ring is followed. The acute angle the plane of group one makes with the plane of group two, β , is positive for the folding of the plane of group one in the positive z-direction.

Table III contains the coordinates used for the atoms of the three compounds. Refer to Figure 1 for the corresponding chemical structures. All DKP coordinates in Table III are for the conformation in which the diketopiperazine ring is planar. For L-amino acids, the side groups come out of the plane in Figure 5. The computer program folds the molecule by the appropriate angle, β , before the calculations are carried out. AGDKP and AADKP can be folded by various amounts. However, PPDKP has a relatively fixed conformation ($\beta \approx 35$).³ The prolyl ring has an envelope conformation where C^β is out of the plane in the positive z-direction.³

C. Transitions of the Amide Group

What electronic transitions of the amide group occur in this region of the spectrum? To answer this, a look at the electronic structure of the amide group is needed. In the orbital picture, the wavefunctions for the valence electrons can be considered a product of orbital functions: a nonbonding n-orbital, a nonbonding n'-orbital, the π -orbitals, and the σ -orbitals.

Table III. Atomic coordinates.

Molecule /Atoms	(x, y, z) [\AA]
Diketopiperazine ring (planar)	
O(1)	(-1.24, 2.39, 0)
C(1)	(-0.66, 1.28, 0)
N(1)	(0.65, 1.21, 0)
H ^N (1)	(1.12, 2.10, 0)
C ^{α} (1)	(1.46, 0 , 0)
O(2)	(1.24, -2.39, 0)
C(2)	(0.66, -1.28, 0)
N(2)	(-0.65, -1.21, 0)
H ^N (2)	(-1.12, -2.10, 0)
C ^{α} (2)	(-1.46, 0 , 0)
AGDKP	
H ^{α} (1)	(2.09, 0 , -0.89)
H ^{α} (1)	(2.09, 0 , 0.89)
H ^{α} (2)	(-2.09, 0 , -0.89)
C ^{β} (2)	(-2.34, 0 , 1.26)
H ^{β} (2)	(-1.70, 0 , 2.15)
H ^{β} (2)	(-2.98, -0.89, 1.26)
H ^{β} (2)	(-2.98, 0.89, 1.26)
AADKP	
H ^{α} (1)	(2.09, 0 , -0.89)
C ^{β} (1)	(2.34, 0 , 1.26)
H ^{β} (1)	(1.70, 0 , 2.15)
H ^{β} (1)	(2.98, 0.89, 1.26)
H ^{β} (1)	(2.98, -0.89, 1.26)
H ^{α} (2)	(-2.09, 0 , -0.89)
C ^{β} (2)	(-2.34, 0 , 1.26)

Table III. Continued.

Molecule / Atoms	(x, y, z) [\AA]
AADKP (continued)	
H ^{β} (2)	(-1.70, 0, 2.15)
H ^{β} (2)	(-2.98, -0.89, 1.26)
H ^{β} (2)	(-2.98, 0.89, 1.26)
PPDKP (no H ^N on diketopiperazine ring)	
H ^{α} (1)	(2.09, -0.67, -0.59)
C ^{β} (1)	(2.79, 0.48, 0.52)
H ^{β} (1)	(2.87, 0.47, 1.61)
H ^{β} (1)	(3.61, -0.13, 0.14)
C ^{γ} (1)	(2.87, 1.86, 0)
H ^{γ} (1)	(3.52, 2.46, 0.64)
H ^{γ} (1)	(3.27, 1.86, -1.01)
C ^{δ} (1)	(1.48, 2.44, 0)
H ^{δ} (1)	(2.10, 2.50, 0.89)
H ^{δ} (1)	(2.10, 2.50, -0.89)
H ^{α} (2)	(-2.09, 0.67, -0.59)
C ^{β} (2)	(-2.79, -0.48, 0.52)
H ^{β} (2)	(-2.82, -0.47, 1.61)
H ^{β} (2)	(-3.61, 0.13, 0.14)
C ^{γ} (2)	(-2.87, -1.86, 0)
H ^{γ} (2)	(-3.52, -2.46, 0.64)
H ^{γ} (2)	(-3.27, -1.86, -1.01)
C ^{δ} (2)	(-1.48, -2.44, 0)
H ^{δ} (2)	(-2.10, -2.50, 0.89)
H ^{δ} (2)	(-2.10, -2.50, -0.89)

The n-orbital is assumed to be a 2p atomic orbital of oxygen lying in the amide plane and perpendicular to the C-O bond. The low energy n'-orbital on oxygen is mostly 2s and is not considered in our study. The lone pair of electrons on nitrogen are in a 2p atomic orbital perpendicular to the amide plane and thus conjugate into the π -structure of the carbonyl group. This arrangement produces three π levels with four electrons filling the lowest two levels. Since the π -structure of the amide group is isoelectronic to allyl anion, the π -wavefunctions are labelled as in allyl anion. Starting with the function representing the unfilled level, the three wavefunctions are π_- , π_0 and π_+ . The first $\pi\pi^*$ transition is then a $\pi_0\pi_-$ transition. We assume two directed and independent σ -orbitals. The first is a carbonyl σ -orbital, and the second is a C-N σ -orbital.

The five transitions we will study are $n\pi_-$, $\pi_0\pi_-$, $n\sigma^*$, $\pi_0\sigma^*$ and $\pi_+\pi_-$. From an examination of the absorption and CD curves in Figures 2-4 we can place the $\pi_0\pi_-$ transition at 185 nm and estimate the position of $n\pi_-$ at 210 nm. The myristamide ($C_{13}H_{27}CONH_2$) absorption⁶⁴ shows peaks at 190 and 166 nm. This second band is tentatively assigned to $n\sigma^*$. Peterson and Simpson then estimate $\pi_+\pi_-$ to be at 152 nm. We expected the $\pi_+\pi_-$ transition to produce a conservative CD couplet where the 140 band in AADKP is the low wavelength part. The crossover point of this couplet could be at about 153 nm in agreement with the Simpson estimation. The $\pi_0\sigma^*$

placement is much more uncertain and is arbitrarily placed at 150 nm. This will be discussed more fully in the section giving the $\pi_0\sigma^*$ results. The transitions and their wavelength assignments are listed in Table IV. The values given in Table IV for the transition moment vectors will be discussed under the appropriate sections.

To find the transition moments, numerous molecular orbital (MO) calculations of the amide π electrons and the π and σ electrons of formamide, a model compound for the peptide (amide) linkage between amino acids, were examined. These studies separate into three types: (1) semi-empirical π -electron calculations,^{23, 54, 65} (2) all valence electron calculations (e.g. CNDO)^{66, 67} and (3) ab initio calculations.⁶⁸⁻⁷³

The criteria used in finally selecting an MO calculation were: (1) Are the transition moment vectors given for $n\pi_-$, $\pi_0\pi_-$ and $\pi_+\pi_-$ or can they be readily calculated? and (2) How well does $\vec{\mu}_{\pi_0\pi_-}$ agree with that experimentally found for $\vec{\mu}_{\pi_0\pi_-}$ in myristamide?

Using these criteria we chose to use the π wavefunctions derived from Nagakura's work⁶⁵ by Schellman and Oriol.⁷⁴ The coefficients of the σ^* wavefunctions were found by neglecting overlap and treating oxygen, carbon and nitrogen as contributing equally. While this is a poor approximation, our results will show that a more sophisticated treatment is not worthwhile. The atomic orbitals are assumed to be sp^2 hybridized. The atomic orbitals and LCAO

Table IV. Amide transition properties.

Transition	Energy [nm]	\vec{R}_i^{0a} [Å]	$\vec{\mu}_{i0a}(x, y, z)$ [e·Å]	$\text{Im}(\vec{m}_{ia0})(x, y, z)$ [e·Å]
$n\pi_-$	210	---	0	$(3.38 \times 10^{-4}, -6.49 \times 10^{-4}, 0)$
$\pi_0\pi_-$	185	(-0.230, 1.667, 0)	(-0.752, 0.400, 0)	0
$n\sigma^*$	165	(-1.24, 2.39, 0)	(0.1716, 0.0898, 0)	(0, 0, 0.00112)
$\pi_0\sigma^*_{CO}$	(a)	(-1.137, 2.192, 0)	(0, 0, 0.0560)	$(-3.35 \times 10^{-4}, -1.94 \times 10^{-4}, 0)$
$\pi_0\sigma^*_{CN}$	(a)	(0.496, 1.218, 0)	(0, 0, 0.0646)	$(1.23 \times 10^{-4}, 6.98 \times 10^{-4}, 0)$
$\pi_+\pi_-$	153	(-0.602, 1.617, 0)	(-0.075, -0.430, 0)	0

(a) See the $\pi_0\sigma^*$ section.

coefficients for the n , π and σ wavefunctions are listed in Table V.

Most ab initio studies do not provide the transition moment directions we need or easy routes to their calculation. The most recently published ab initio study⁶⁸ is concerned mainly with the $\pi\pi_0$ and $\pi_0\pi_0$ results and gives no transition moment directions. The authors do survey and discuss the previous studies. Various ab initio studies⁶⁹⁻⁷¹ do help in suggesting which transitions have significant dipole strengths and what their order in energy might be.

D. Transition Moments, Monopoles and Polarizabilities

The electric dipole transition moments were evaluated using the dipole length operator neglecting all overlap terms, which is consistent with the wavefunctions. This leaves only one-center terms of type $\langle 2p_z | \vec{r} | 2p_z \rangle$ and $\langle 2s | \vec{r} | 2p_z \rangle$. The atomic orbitals are Slater-type functions. For simplicity in interpretation, the following equations are in atomic units (the charge on the electron = -1).

The first type of integral comes from $\pi\pi^*$ transitions and to be origin independent in the ZDO approximation is evaluated as

$$\langle (2p_z)_i | \vec{r} | (2p_z)_i \rangle = \vec{R}_i \quad (90)$$

Corresponding monopoles were found following Woody's suggestion.²³

Charges of

Table V. Amide wavefunction coefficients.

	$(2p_z)_O$	$(2p_z)_C$	$(2p_z)_N$	$(2p_n)_O$	$(2s)_O$	$(2p_\sigma)_O$	$(2p_\sigma)_C$	$(2s)_C$	$(2p_\sigma)_C$	$(2p_\sigma)_N$	$(2s)_N$
σ_{CO}^*	0	0	0	0	0.408	0.577	-0.577	-0.408	0	0	0
σ_{CN}^*	0	0	0	0	0	0	0	0.408	0.577	-0.577	-0.408
π_-	0.397	-0.839	0.373	0	0	0	0	0	0	0	0
n	0	0	0	1.000	0	0	0	0	0	0	0
π_0	-0.581	0.090	0.809	0	0	0	0	0	0	0	0
π_+	0.716	0.537	0.446	0	0	0	0	0	0	0	0

$$\rho_{i0a} = -(1/2)^{1/2} c_{ia} c_{i0} \quad (91)$$

were placed at points \vec{r}_i on either side of \vec{R}_i in the direction of $(2p_z)_i$. Vector \vec{r}_i is the average position vector in the half-space on one side of the nodal plane for the electron undergoing transition.

$$|\vec{r}_i| = \frac{15}{8} \frac{1}{\zeta_i} \quad (92)$$

where ζ_i is the Slater exponent for $(2p)$ and $(2s)$ of atom i .

For $n\sigma^*$ and $\pi\sigma^*$ transitions the second type of integral occurs.

It is evaluated as

$$\langle (2s)_i | \vec{r} | (2p_z)_i \rangle = (1/2)^{1/2} \frac{s}{2\zeta_i} \hat{k} \quad (93)$$

Corresponding monopole charges

$$\rho_{i0a} = \frac{6^{1/2}}{4} c_{ia} c_{i0} \quad (94)$$

are placed at \vec{r}_i on either side of \vec{R}_i in the direction of $(2p_z)_i$.

$$|\vec{r}_i| = \frac{5}{3} \frac{1}{\zeta_i} \quad (95)$$

These transitions also have a magnetic dipole transition moment that arises from terms of the type $\langle (2p_x)_i | \vec{m} | (2p_y)_i \rangle$ where

$\vec{m} = -(\frac{1}{2c})\vec{r} \times \vec{p}$. The solution of this integral is independent of the type of atom.

$$\langle (2p_x)_i | \vec{m} | (2p_y)_i \rangle = -i\beta \hat{k} \quad (96)$$

where β is the Bohr-magneton (1.931×10^{-3} eA) and $i = (-1)^{1/2}$.

In the formal development from Slater determinants, a factor of $2^{1/2}$ arises in finding \vec{m}_{i0a} just as it does for $\vec{\mu}_{i0a}$ in Section III E 2. However, it disappears in Eq. (96) for the following reasons. Vector \vec{m}_{i0a} really has non-zero x and y components. However, only the length of \vec{m}_{i0a} and one of its components can be found simultaneously, and \vec{m}_{i0a} precesses about the z -axis. However, for a large enough system of molecules, the x and y components of \vec{m}_{i0a} sum to zero when making macroscopic measurements. Therefore, \vec{m}_{i0a} is treated as only having a value along the z -axis, and the maximum projection of \vec{m}_{i0a} on the z -axis is $|\vec{m}_{i0a}|/2^{1/2}$.

Monopoles corresponding to the magnetic transition moment are found by dividing the space about the atomic center into quadrants in which the product $(2p_x)(2p_y)$ has constant sign.²⁴ Monopole charges³⁴

$$\rho_{i0a} = -c_{ia} c_{i0} (0.158) \quad (97)$$

are placed at \vec{r}_i from the atomic center and toward the center of each quadrant.

$$|\vec{r}_i| = \frac{15\pi}{2^{1/2} 16} \zeta_i \quad (98)$$

Each monopole is multiplied by the sign of $(2p_x)(2p_y)$ in that quadrant.

According to Slater's rules, $\zeta_i = Z^*/n$ where Z^* is the effective nuclear charge seen by the electron and n is the principal quantum number (two in this case). Woody²³ calculates some semi-empirical Z^* values which result in smaller ζ_i values. Table VI gives the monopole distances $|\vec{r}_i|$ for Slater Z^* values and the semi-empirical values given by Woody. The semi-empirical values give larger magnitudes to the rotational strength for magnetic transitions such as $n\pi_-$.³⁴ Since the $n\pi_-$ results are generally too low,^{23, 24, 74} the semi-empirical distances are used whenever possible.

The transition moments and monopoles outlined above are used to explicitly interact the $n\pi_-$, $\pi_0\pi_-$, $n\sigma^*$, $\pi_0\sigma^*$ and $\pi_+\pi_-$ transitions of the amide groups. The rotational strength for a particular transition is found by evaluating Eqs. (54), (55) and (67). Terms (54d), (55c) and (55d) have large denominators and are not calculated in the present study. The effect of the far uv $\sigma\sigma^*$ transitions of the σ structure of the

whole molecule is estimated by using polarizabilities and Eqs. (54a') and (55a').

Table VI. Monopole distances.

Transition	$ \vec{r}_i _S$ [A]	$ \vec{r}_i _{SE}$ [A]
$\pi\pi^*$ (electric monopoles)		
O ^a	0.5052	0.7737
C ^a	0.7072	1.0806
N ^a	0.5893	0.9813
$n\sigma^*$, $\pi\sigma^*$ (electric monopoles) ^b		
O	0.7326	
C	1.0256	
N	0.8548	
$n\pi^*$, $n\sigma^*$, $\pi\sigma^*$ (magnetic monopoles)		
O ^a	0.4843	0.8593
C	0.6782	1.1979
N	0.5651	0.9982

^aFrom R. W. Woody, J. Chem. Phys., 49, 4797.

^bThe semi-empirical values are based on (2p) → (2p) transitions. So only Slater values are given here.

The bond polarizabilities of LeFevre and co-workers⁷⁵ are used. C-N and N-H bonds are treated the same as C-C and C-H bonds, respectively, to a first approximation. These polarizabilities are corrected from 0kK to 54kK (the $\pi_0\pi_0$ transition energy) as outlined by Snyder, et al.³⁴ Table VII gives the appropriate values.

Table VII. Bond polarizabilities [A^3].

Bond	α_{\parallel} (0kK)	α_{\perp} (0kK)	α_{\parallel} (54kK)	α_{\perp} (54kK)
C-C, C-N	0.99	0.27	1.40	0.38
C-H, N-H	0.64	0.64	0.90	0.90

Note: $1\text{kK} = 10^3 \text{ cm}^{-1}$

E. Results and Discussion

1. $n\pi_{\perp}$

Hooker, et al¹² studied this transition in some detail both experimentally and theoretically. The position and magnitude of the $n\pi_{\perp}$ CD band is very solvent dependent. They found that AADKP in aqueous solution does not show a separate $n\pi_{\perp}$ CD band. However, in 100% dioxane a positive CD band of $\Delta\epsilon \approx 1$ appears at 235 nm. In aqueous solution PPDKP shows a negative CD band at 220 nm of $\Delta\epsilon \approx -3$. They found that in methanol or triethyl phosphate this band becomes even stronger, $\Delta\epsilon$ from -4.5 to -6.0.

Their computed $n\pi_{\perp}$ rotational strength for $\beta = 30^{\circ}$ (no data is given for $\beta = 35^{\circ}$) is -0.12 Debye-magneton (DM). With our assumed band shape, this translates to a $\Delta\epsilon = -4.2$ for PPDKP. For AADKP with $\beta = -10^{\circ}$ to -20° , their $n\pi_{\perp}$ rotational strength is between 0.10 and 0.13 DM or a $\Delta\epsilon$ between 3.5 and 4.6. These values are for separated CD bands. The actual peak value in a curve found by summing the $n\pi_{\perp}$ and $\pi_0\pi_{\perp}$ bands would be considerably less.

Our less sophisticated results presented in Table VIII give the correct sign for the first negative band in PPDKP but the magnitude is at least four times too small. For AADKP the results predict a small positive band which agrees qualitatively with the experimental spectrum in dioxane. The main contribution to the $n\pi_{-}$ CD comes from the polarizability term, i. e. the interaction with higher energy $\sigma\sigma^{*}$ transitions.

Table VIII. Results for the $n\pi_{-}$ band.

Interaction ^a	Interacting Transition	$\Delta \epsilon_{\max}$		
		β : -20°	-10°	35°
Dynamic field (55a)	$\pi_0 \pi_{-}$	-0.07	-0.04	0.13
	$n\sigma^{*}$	0	0	0
	$\pi_0 \sigma^{*}$	0	0	0
	$\pi_{+} \pi_{-}$	0.01	0	-0.01
Static field (55b)	$\pi_0 \pi_{-}$	0.04	0.02	-0.08
	$n\sigma^{*}$	0	0	0
	$\pi_0 \sigma^{*}$	0	0	0
	$\pi_{+} \pi_{-}$	0.01	0	-0.02
	Total $\Delta \epsilon \times 2^b$	-0.02	-0.04	0.04
Magnetic polarizability (55a')	AGDKP	0.3	0.3	
	AADKP	0.5	0.7	
	PPDKP			-0.8

^aThe number of the equation term giving the rotational strength is listed in parentheses.

^bThe amide transitions are doubly degenerate and therefore the factor of two is needed.

Hooker, et al have done an excellent job of studying the $n\pi_{-}$ transition. So, we have not pursued this transition further, particularly since as noted above, $n\pi_{-}$ results are generally too low.

2. $\pi_0\pi_{-}$

The portion of the CD spectra due to the $\pi_0\pi_{-}$ transition is the couplet of bands centered about the first absorption maximum at 185 nm for AG- and AADKP and 190 nm for PPDKP. The main feature of the couplet is the conservative parts with rotational strengths and split in energy given by Eqs. (67) and (68). The rotational strengths for the conservative bands were calculated, and a computer program then generated two bands with these rotational strengths, placed them at the energies defined by Eq. (68) and added the bands together. The result is the characteristic "differential-type" CD curve. Figure 6 is a plot of the sign and magnitude of the $\Delta\epsilon$ for the long wavelength band of the summed curve as a function of the angle of folding for the diketopiperazine ring, β .

The calculated magnitudes in Figure 6 and the observed magnitudes in Figures 2 and 3 place the folding for AG- and AADKP in the region of β equal to -10° to -20° . This agrees with the consistent force field study by Karplus and Lifson¹⁸ which shows a shallow minimum at $\beta = -20^{\circ}$. With a shallow minimum, the molecules are probably distributed over a span of β values,¹² but the CD would

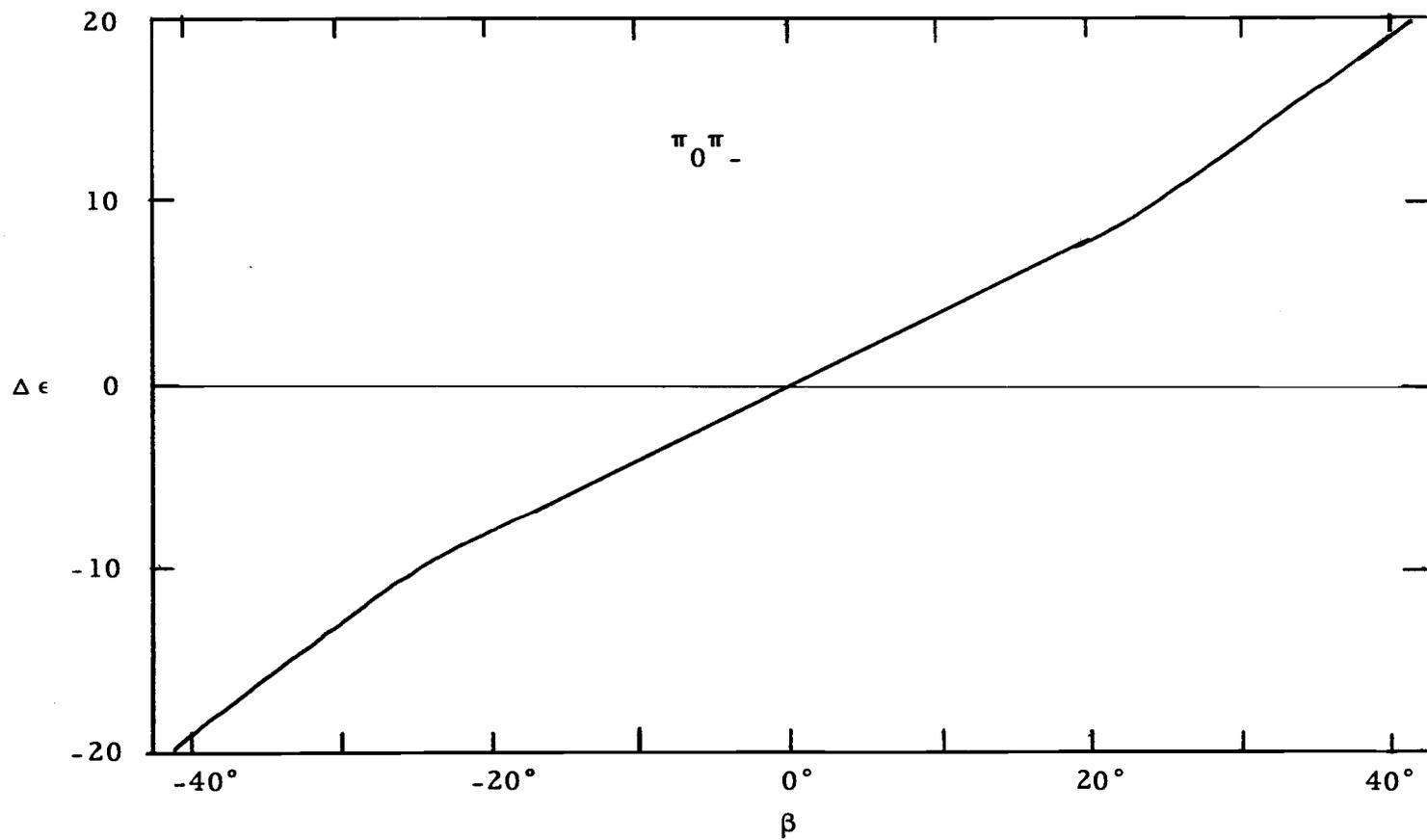


Figure 6. Maximum $\Delta\epsilon$ of the long wavelength band of the summed CD curve due to the conservative $\pi_0\pi_-$ interactions as a function of the folding of the diketo-piperazine ring.

remain close to that given for $\beta = -15^\circ$.

PPDKP, from an x-ray diffraction study of L-prolyl-L-leucine diketopiperazine,³ has a folding of $\beta \approx 35^\circ$. With this folding, the value calculated for $\Delta\epsilon$ is a bit too large. The first order corrections to the rotational strength, R_{0AK}^d , would adjust the theoretical $\Delta\epsilon$ value somewhat. However, even with the approximations in our theory, the fit to experiment is good.

Hooker, et al have examined this transition, too, in their study of AADKP and PPDKP. They calculated for $\beta = -20^\circ$ (AADKP) a long wavelength band with a rotational strength of -0.7 DM and a short wavelength band with a rotational strength of +0.57 DM. These are separate bands with a $\Delta\epsilon$ of -24.6 and 20.0, respectively, and a split in energy given by Eq. (68). The non-conservative terms have been added into each band already. By averaging the absolute magnitudes of the two bands, the conservative part is found to have $|\Delta\epsilon| = 22.3$ which agrees well with our calculation of $|\Delta\epsilon| = 23.0$ for the magnitude of the separate CD bands before they were summed.

The x-ray study of L-prolyl-L-leucine appeared after Hooker, et al completed their work. They have used a value of $\beta = 25^\circ$ gotten by geometrically constructing two cis peptides with prolyl rings. Thus they have only reported rotational strengths for β from -30° to $+30^\circ$. The long wavelength band at 30° has a rotational strength of 0.9 DM, and the short wavelength band has a value of

-0.78 DM. The $\Delta\epsilon$ values of 31.6 and -27.4 indicate that the conservative part has a $|\Delta\epsilon| = 29.5$ which compares well with our calculation of $|\Delta\epsilon| = 33.6$ for the separate bands before they were summed for $\beta = 30^\circ$. However, in our calculations we have used $\beta = 35^\circ$ as found by Karle.³

The value calculated by Hooker, et al for the non-conservative part of the CD curve is found by adding the $\Delta\epsilon$ values for the long and short wavelength bands. A $\Delta\epsilon = -4.6$ is found for AADKP, and a $\Delta\epsilon = 4.2$ is found for PPDKP ($\beta = 30^\circ$). These terms have opposite sign to that found by examining the spectra of AADKP and PPDKP. We have a similar problem in our results which is corrected by explicit calculation of $\sigma\sigma^*$ transitions interacting with $\pi_0\pi_-$.

Our final results for the $\pi_0\pi_-$ transition for all three molecules are presented in Table IX. Since $\pi_0\pi_-$ is only an electrically-allowed transition, the rotational strength of the non-conservative part is given by Eq. (54). The non-conservative contributions from explicitly interacting all of the amide group transitions are of right sign and magnitude to fit the spectra. The total $\Delta\epsilon$ results are 7.0 (-20°), 4.4 (-10°) and -14.6 (35°). The main contribution comes from the interaction specified by term (54a) between $\vec{\mu}_{\pi_0\pi_-}$ on one amide group and $\vec{\mu}_{\pi_+\pi_-}$ on the other amide group. However, inclusion of the electric polarizability destroys this fit in the case of AG- and AADKP.

Table IX. Results for the $\pi_0\pi_-$ band.

Interaction	Interacting Transition	$\Delta\epsilon_{\max}$		
		$\beta: -20^\circ$	-10°	35°
Degenerate exciton ^a (67)		-8.0	-4.0	16.4
Nondegenerate exciton (54a)	$n\sigma^*$	-0.3	-0.1	0.5
	$\pi_0\sigma^*$	-0.3	-0.1	0.4
	$\pi_+\pi_-$	2.7	1.8	-5.5
Dynamic field (54b)	$n\pi_-$	0.1	0	-0.1
	$n\sigma^*$	0.7	0.3	-1.5
	$\pi_0\sigma^*$	0.2	0.1	-0.3
Static field (54c)	$n\pi_-$	0	0	0.1
	$n\sigma^*$	-- ^b	-- ^b	-- ^b
	$\pi_0\sigma^*$	0.4	0.2	-0.9
	Total $\Delta\epsilon \times 2$	7.0	4.4	-14.6
Electric polarizability (54a')	AGDKP	-6.4	-4.8	
	AADKP	-7.9	-7.2	
	PPDKP			6.6

^aThe value for the $\Delta\epsilon_{\max}$ of the long wavelength band of the summed conservative curve.

^bThe interaction energy is identically zero.

The AG- and AADKP polarizability term ranges from a $\Delta\epsilon$ of -6.4 to -7.9 for $\beta = -20^\circ$ and -4.8 to -7.2 for $\beta = -10^\circ$. This cancels the results of the explicit interaction of transitions on the amide group and gives negative non-conservative bands. For PPDKP, a $\Delta\epsilon = 6.6$ from the polarizability term brings the total non-conservative contribution to $\Delta\epsilon = -8.0$ which agrees well with the

spectra. In Section V we will show that by considering the $\sigma\sigma^*$ transitions explicitly (instead of by a polarizability approximation) the fit to experiment is restored for AG- and AADKP.

3. $n\sigma^*$

The $n\sigma^*$ is both an electrically- and magnetically-allowed transition. Since the n-orbital is centered on oxygen, $n\sigma^*$ is within our approximations an atomic transition on oxygen. By comparing $|\vec{\mu}_{n\sigma^*}| = 0.194$ and $|\vec{m}_{n\sigma^*}| = 0.0011$ with $|\vec{\mu}_{\pi_0\pi_-}| = 0.852$ and $|\vec{m}_{n\pi_-}| = 0.0007$ (in units of $e\text{\AA}$) and the preceding results for the $\pi_0\pi_-$ and $n\pi_-$ transitions, it can be seen that there will be difficulty in attributing any of the large CD bands of PPDKP to $n\sigma^*$. The results listed in Table X bear this out. The total non-conservative CD of $\Delta\epsilon$ equal to -0.8 (-20°), -0.4 (-10°) and 1.6 (35°) for the explicit interaction of transitions on the amide group is negligible. The polarizability terms contribute more value but their total magnitude is $|\Delta\epsilon| \leq 3.5$. There is essentially no splitting due to $V_{1n\sigma^*; 2n\sigma^*}$ and so there is no conservative contribution.

4. $\pi_0\sigma^*$

Apart from doing a complete molecular orbital treatment, we can form two extreme pictures of the σ levels of the amide group. First we could assume that the C-O amide bond is shorter than the

Table X. Results for the $n\sigma^*$ band.

Interaction	Interacting Transition	$\Delta \epsilon_{\max}$		
		β : -20°	-10°	35°
Degenerate exciton (67)		0	0	0
Nondegenerate exciton (54a)	$\pi_0 \pi_-$	0.3	0.1	-0.5
	$\pi_0 \sigma^*$	0	0	0
	$\pi_+ \pi_-$	0.3	0.1	-0.6
Dynamic field (elec.) (54b)	$n\pi_-$	0	0	0
	$\pi_0 \sigma^*$	0	0	0
Static field (elec.) (54c)	$n\pi_-$	0	0	0
	$\pi_0 \sigma^*$	0	0	0
Dynamic field (mag.) (55a)	$\pi_0 \pi_-$	-0.7	-0.3	1.3
	$\pi_0 \sigma^*$	0	0.0	0
	$\pi_+ \pi_-$	-0.3	-0.1	0.6
Static field (mag.) (55b)	$\pi_0 \pi_-$	--	--	--
	$\pi_0 \sigma^*$	0	0	0
	$\pi_+ \pi_-$	--	--	--
	Total $\Delta \epsilon \times 2$	-0.8	-0.4	1.6
Electric polarizability (54a')	AGDKP	0.4	0.6	
	AADKP	1.2	1.2	
	PPDKP			1.2
Magnetic polarizability (55a')	AGDKP	-1.6	-2.0	
	AADKP	-3.9	-4.2	
	PPDKP			-4.7

C-N bond because the sigma level for C-O lies lower in the energy well than that for C-N. The order in energy for the σ levels is then σ_{CO} , σ_{CN} , σ_{CN}^* and σ_{CO}^* . Second, the σ^* levels may be nearly degenerate in energy. Then, to a first level of approximation σ_{CO}^* would interact with σ_{CN}^* and the two resulting wavefunctions would be $\sigma_{\pm}^* = \frac{1}{\sqrt{2}}(\sigma_{CO}^* \pm \sigma_{CN}^*)$. The resulting energy levels would be split in energy.

Either picture gives the same total rotational strength for the two $\pi_0\sigma^*$ transitions combined. The pictures differ in how it is divided out. In the first view $\pi_0\sigma_{CO}^*$ and $\pi_0\sigma_{CN}^*$ will give two separate bands of different rotational strengths not too far apart in energy. The second view divides the contributions from the two components equally between two separate but close bands.

With this in mind we calculated the $\pi_0\sigma_{CO}^*$ and $\pi_0\sigma_{CN}^*$ contributions separately. These results are presented in Table XI. For ease in calculation, both $\pi_0\sigma^*$ transitions were placed at 150 nm but 10 nm to the red of the $\pi_+\pi_-$ transition. Moving $\pi_0\sigma^*$ to 175 nm would only increase the appropriate contributions by a factor of four. Even then it would be very difficult to assign any band to $\pi_0\sigma^*$.

We included this transition in our study because an INDO calculation by Richardson and Pitts²⁰ indicated that $\pi_0\sigma^*$ transitions should play a role in the CD of various diketopiperazines. Our calculations do not bear this out in any way. Thus, we did not pursue a more

Table XI. Results for the $\pi_0\sigma^*$ band.

Interaction	Interacting Transition	$\Delta\epsilon_{\max}$					
		$\beta: -20^\circ$		-10°		35°	
		C-O	C-N	C-O	C-N	C-O	C-N
Degenerate exciton (67)		0	0	0	0	0	0
Nondegenerate exciton (54a)	$\pi_0\pi_-$	0	0.3	0	0.1	0	-0.4
	$n\sigma^*$	0	0	0	0	0	0
Dynamic field (elec.) (54b)	$\pi_+\pi_-$	0	0	0	0	0	0
	$n\pi_-$	0	0	0	0	0	0
Static field (elec.) (54c)	$n\pi_-$	-	-	-	-	-	-
	$n\sigma^*$	0	0	0	0	0	0
Dynamic field (mag.) (55a)	$\pi_0\pi_-$	0	-0.2	0	-0.1	0	0.3
	$n\sigma^*$	0	0	0	0	0	0
	$\pi_+\pi_-$	0	0.3	0	0.2	0	-0.5
Static field (mag.) (55b)	$\pi_0\pi_-$	-0.4	0	-0.2	0	0.9	0
	$n\sigma^*$	0	0	0	0	0	0
	$\pi_+\pi_-$	-	-	-	-	-	-
Total $\Delta\epsilon \times 2$		0		0		0.6	
Electric polarizability							
(54a')	AGDKP	0.1	0.3	0.0	0.5		
	AADKP	-0.1	0.4	-0.1	0.4		
	PPDKP					0.3	0.7
Magnetic polarizability							
(55a')	AGDKP	0	0	0	0		
	AADKP	0	0	0	0		
	PPDKP					0	0

sophisticated calculation for $\pi_0\sigma^*$.

5. $\pi_+\pi_-$

The results for $\pi_+\pi_-$ are listed in Table XII. Only for PPDKP is there any significant conservative CD curve and then only a $\Delta\epsilon = -3$ for the long wavelength band. The non-conservative contributions are larger but cannot explain the 140 nm band in AG- and AADKP or the three bands between 180 and 140 nm in PPDKP although the 160 band could presumably have a $\pi_+\pi_-$ component. Treating the non-conservative part as a polarizability is probably wrong because a number of $\sigma\sigma^*$ transitions occur in this region.

These results for $\pi_+\pi_-$ prompted a search for alternate solutions to the higher energy CD spectra of all three molecules. This led to the following study of $\sigma\sigma^*$ transitions. Although the $\pi_+\pi_-$ transition does contribute to the CD of diketopiperazines, it is overshadowed by large bands due to $\sigma\sigma^*$ transitions, and experimentally its effect is hard to evaluate.

Table XII. Results for the $\pi_+ \pi_-$ band.

Interaction	Interacting Transition	$\Delta \epsilon_{\max}$		
		β : -20°	-10°	35°
Degenerate exciton (67)		0.9	0.5	-3.0
Nondegenerate exciton (54a)	$\pi_0 \pi_-$	-2.7	-1.8	5.5
	$n\sigma^*$	-0.3	-0.1	0.6
	$\pi_0 \sigma^*$	-0.2	-0.1	0.3
Dynamic field (54b)	$n\pi_-$	0	0	0
	$n\sigma^*$	0.3	0.1	-0.6
	$\pi_0 \sigma^*$	-0.3	-0.2	0.5
Static field (54c)	$n\pi_-$	0	0	0
	$n\sigma^*$	-	-	-
	$\pi_0 \sigma^*$	-	-	-
	Total $\Delta \epsilon \times 2$	-6.4	-4.2	12.6
Electric polarizability (54a')	AGDKP	4.5	2.1	
	AADKP	3.5	1.4	
	PPDKP			-9.6

V. $\sigma \rightarrow \sigma^*$ TRANSITIONSA. Transition Energies and Rotational Strengths

Sigma-sigma* transitions were investigated since the amide transitions cannot explain the gross features of the CD spectra below 180 nm. The method of Raymond and Simpson,⁷⁶ as applied to alkanes, was used to find the transition energies and transition moments, and thus the rotational strengths for all of the $\sigma\sigma^*$ transitions of the diketopiperazines.

Following Simpson and Raymond, the independent systems approach is again used for the calculations. In their calculations, alkane compounds are divided so that each C-C sigma bond is a group. This division, at least qualitatively, allows the assumption of no electron exchange between groups. All C-C bonds are made equal in length, and the systems are then composed of groups that are degenerate with each other. The average effect of the C-H bonds are incorporated into the parameters for each group. First order degenerate perturbation theory can be used to give the first order corrections to the degenerate transition energy and the "correct" zeroth order wavefunctions.

The ground state wavefunction is

$$|0\rangle = |10\ 20 \dots N0\rangle. \quad (99)$$

The singly-excited basis functions for the molecule are identified as

$$|ia) = |10 \dots ia \dots N0). \quad (100)$$

The Hamiltonian operator is again Eq. (24)

$$H = H^0 + V = \sum_i h_i + \sum_i \sum_{j>i} v_{ij} \quad (24)$$

where h_i is the Hamiltonian operator for the isolated group and v_{ij} is the coulombic potential operator between different groups.

The correct zeroth order wavefunctions from first order perturbation theory are

$$|K) = \sum_i c_{iK} |ia) \quad (101)$$

With these definitions the eigenvalue problem can be stated as N homogeneous equations of form

$$\sum_{i=1}^N [(ma|H|ia) - E(ma|ia)] c_{iK} = 0 \quad (102)$$

where $m = 1$ to N . The determinant of the coefficients of the c_{iK} 's must be zero in order for a non-trivial solution to exist. The determinant has the form

$$\begin{vmatrix} \alpha - E & \beta_{12} & \cdots & \beta_{1n} \\ \beta_{21} & \alpha - E & \cdots & \beta_{2n} \\ \vdots & \vdots & & \vdots \\ \beta_{n1} & \beta_{n2} & \cdots & \alpha - E \end{vmatrix} = 0 \quad (103)$$

where $\alpha = (ia|H^0|ia)$ and $\beta_{ij} = (ia|V|ja)$. In the independent systems approach the overlap integral is zero except for the diagonal elements $(ia|ia)$ which equal one.

The molecular quantity β_{ij} can be rewritten in terms of group functions.

$$\begin{aligned} \beta_{ij} &= (ia|V|ja) \\ &= (10\dots ia\dots N0|V|10\dots ja\dots N0) \\ &= (ia\ j0|V|i0ja) \end{aligned}$$

So that β_{ij} can now be interpreted as a quantity expressing interaction between two groups.

Similarly the molecular quantity α can be rewritten as a group quantity.

$$\begin{aligned} \alpha &= (ia|H^0|ia) \\ &= (10\dots ia\dots N0|\sum_j h_j|10\dots ia\dots N0) \\ &= \epsilon_{ia} + \sum_{j \neq i} \epsilon_{j0} \\ &= (\epsilon_{ia} - \epsilon_{i0}) + \sum_j \epsilon_{j0} \end{aligned}$$

Since the system is degenerate in zeroth order, all ϵ_{ia} 's are equal. The zero point for potential energy is arbitrary. So, if ϵ_{j0} is chosen to be zero for all j , then α can be identified as the transition energy for the group transition $0a$. The particular choice for α does not effect the first order splittings in energy just the positioning of the center of the manifold of transitions.

In the independent systems approach β is the electrostatic interaction between two bond transitions. The phases of the bond excitations may be indicated by the direction an arrow points that depicts the transition moment. The sign of the interaction is then determinable by inspection: assuming tetrahedral angles, head-to-head implies $\beta > 0$ and head-to-tail implies $\beta < 0$.

Raymonda and Simpson measure the C-C bond transition moment to be $\vec{\mu}_{cc} = 0.435 \text{ e}\overset{\circ}{\text{A}}$. They suggest placing a point charge of $\pm 1e$ at $0.218 \overset{\circ}{\text{A}}$ from the center of the C-C bond. Then nearest-neighbor β_{ij} 's can be calculated by the monopole approximation. All other β 's are assumed zero.

From their calculation, Raymonda and Simpson assign $\alpha = 109.0\text{kK}$, which includes the average effect of the C-H bonds. By comparison with experiment they show that the lowest energy transition should occur at 63kK for cyclic compounds. The lowest transition energy for a six-membered ring, considering only C-C bonds by the above method, occurs at $\epsilon_0 = \alpha + 2\beta$. β calculated with monopoles

comes to -18.9kK for planar cyclic hexane (a model for the planar DKP ring). To match ϵ_0 with experiment we assign $\alpha = 100.8\text{kK}$ (8.2kK lower than Raymond and Simpson's value).

After Eq. (103) is solved for the first order transition energies, they can be substituted into Eq. (102), one at a time, to generate the c_{iK} 's associated with each transition energy.

One big advantage of doing an independent systems calculation is that the coefficients found above are also the coefficients specifying the contribution of each bond transition moment to the total transition moment for a given molecular transition. The electric transition moment is

$$\begin{aligned}
 \vec{\mu}_{0K} &= (0|\vec{\mu}|K) \\
 &= \sum_i c_{iK} (0|\vec{\mu}|ia) \\
 &= \sum_i c_{iK} (10\dots N0 | \sum_j \vec{\mu}_j | 10\dots ia\dots N0) \\
 &= \sum_i c_{iK} \vec{\mu}_i
 \end{aligned} \tag{104}$$

where $\vec{\mu}_i$ is the transition moment for bond i .

Similarly the magnetic transition moment for the molecule can be given as a sum of group contributions. There are no group magnetic transition moments, and so the only contribution to the molecular magnetic moment comes from the choice of molecular origin.

$$\vec{m}_{0K} = (\pi i/c) \sum_j c_{jK} \nu_j \vec{R}_j \times \vec{\mu}_j \quad (105)$$

where ν_j is the frequency of the transition $0a$ of bond j and c is the speed of light, and \vec{R}_j is the vector distance from the molecular origin to the center of the bond.

Equations (104) and (105) are substituted into the definition for the rotational strength, Eq. (23), giving

$$R_{0K} = -(\pi/c) \sum_{i=1}^N \sum_{j>i}^N c_{iK} c_{jK} \nu_j [(\vec{R}_j - \vec{R}_i) \cdot (\vec{\mu}_i \times \vec{\mu}_j)] \quad (106)$$

The terms for the pairs $i < j$ and $i > j$ have been combined to show the lack of origin dependency in R_{0K} as long as the bond transition moments are origin independent.

B. Calculations and Results

The rotational strength of the DKP's is calculated for a model made by replacing all C-N, C-O and C-C bonds with C-C bonds of length 1.5 Å. All interior bond angles in the planar DKP ring are taken to be 120°. The C-C bond replacing C-O is also 120° from either adjoining bond. The plane of one "pseudo-amide" group is then folded by the value suggested by our results from $\pi_0 \pi_-$. The C^α-C^β side chain bonds are placed out of the DKP plane by 55°. They are

then appropriately folded as the DKP ring is folded. The interior prolyl ring angles are assumed to be about 105° with the C^β atom out of the plane by 0.5 \AA . The number of bonds and therefore the number of $\sigma\sigma^*$ transitions for AGDKP is 9, for AADKP is 10, and for PPDKP is 16.

This data was used to generate the positions of atoms in the model compounds. Figure 7 shows the numbering of atoms and ordering of bonds used in the calculations. This data was then used in a computer program to calculate the transition energies and the rotational strengths for the various transitions.

The program solves the eigenvalue problem by diagonalizing a matrix of the form $(H-ES)$. $(H-ES)$ is the matrix form of Eq. (103) where H is a matrix containing the α 's and β 's, E is a scalar, and S is the overlap matrix which in the independent systems approach is the unity matrix. All of the matrices are symmetric, and so to save on storage in the computer's memory, the matrices are entered as a diagonal and the off-diagonal terms below the diagonal.

The atomic positions (\AA), bond transition moments ($e\text{\AA}$), monopole charges (e) and positions, H matrix (kK) and S matrix for AGCC9, AACCC10 and PPCC16 are given below.

Table XIII gives the transition wavelengths and the calculated rotational strengths for the three model compounds. It is clear that the $\sigma\sigma^*$ transition can account for the large rotational strengths

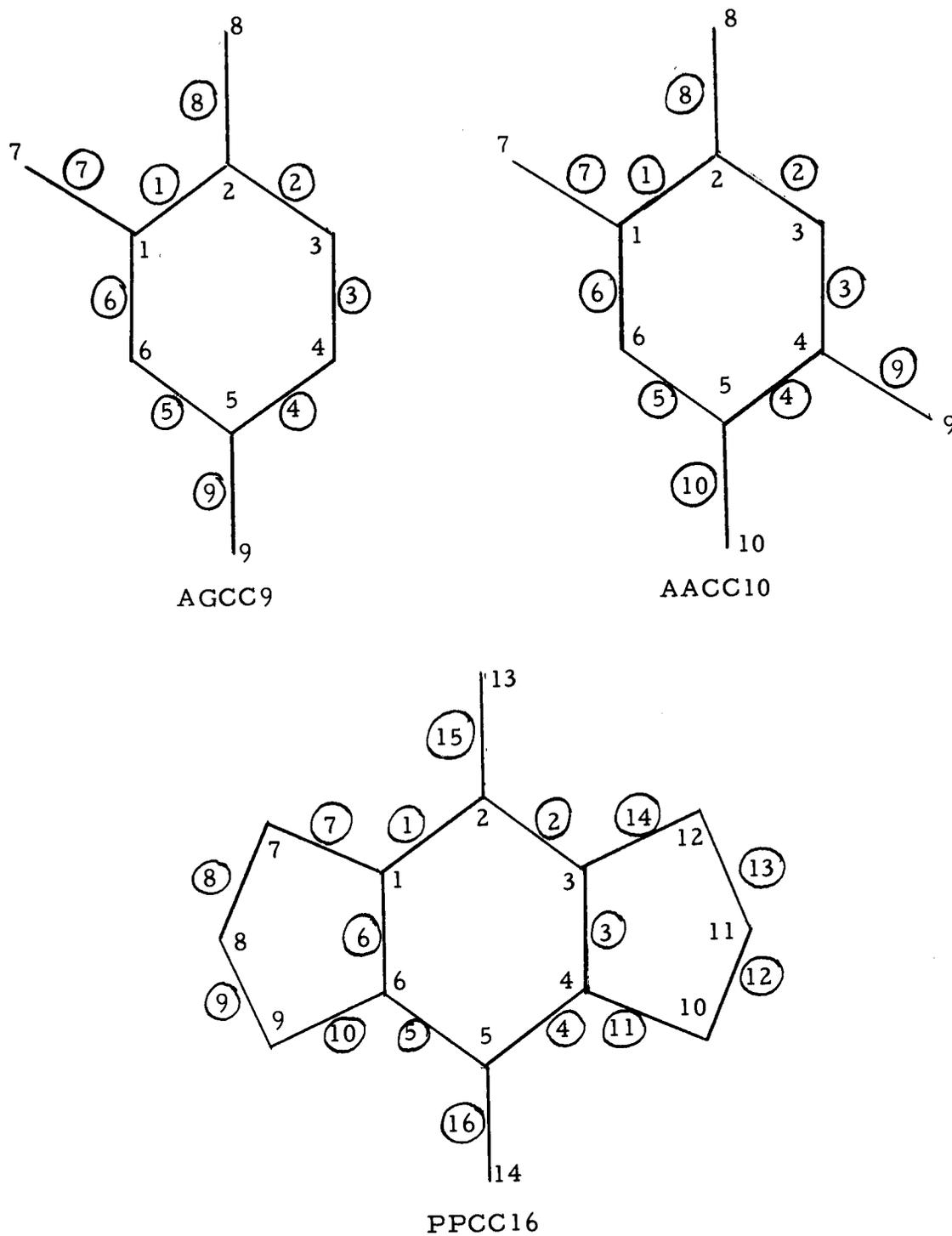


Figure 7. Model alkane compounds and numbering of the atoms and bonds.

ATOM	POSITION(X,Y,Z)		
1	-1.5000	0	0
2	-0.7500	1.0649	.7456
3	.7500	1.0649	.7456
4	1.5000	0	0
5	.7500	-1.3000	0
6	-0.7500	-1.3000	0
7	-2.8950	-0.2336	.5000
8	-3.1050	-1.6170	0
9	-1.8100	-2.3590	0
10	2.8950	-0.0959	.5432
11	3.1050	1.3246	.9275
12	1.8100	1.9324	1.3531
13	-1.5000	2.1298	1.4913
14	1.5000	-2.6000	0

BOND	T.M.(E*A)	DIRECTION(X,Y,Z)		
1 TO 2	.435	.2174	.3086	.2161
2 TO 3	.435	.4350	0	0
3 TO 4	.435	.2174	-0.3086	-0.2161
4 TO 5	.435	-0.2174	-0.3768	0
5 TO 6	.435	-0.4350	0	0
6 TO 7	.435	-0.2174	.3768	0
7 TO 8	.435	-0.4045	-0.0676	.1450
8 TO 9	.435	-0.0615	-0.4050	-0.1463
9 TO 10	.435	.3774	-0.2163	0
10 TO 11	.435	.3077	.3074	0
11 TO 12	.435	.4045	-0.0270	.1575
12 TO 13	.435	.0615	.4157	.1124
13 TO 14	.435	-0.3774	.1771	.1240
14 TO 1	.435	-0.3077	-0.2518	-0.1763
1 TO 14	.435	-0.2174	.3086	.2161
14 TO 1	.435	.2174	-0.3768	0

BOND	RHO	POSITION(X,Y,Z)		
1	-1.00	-1.234	.378	.265
	1.00	-1.016	.687	.481
2	-1.00	-0.217	1.065	.746
	1.00	.217	1.065	.746
3	-1.00	1.016	.687	.481
	1.00	1.234	.378	.265
4	-1.00	1.234	-0.462	0
	1.00	1.016	-0.838	0
5	-1.00	-0.217	-1.300	0
	1.00	-1.016	-1.300	0
6	-1.00	-1.016	-0.838	0
	1.00	-1.234	-0.462	0
7	-1.00	-1.999	-0.083	.178
	1.00	-2.400	-0.150	.322
8	-1.00	-2.969	-0.722	.323
	1.00	-3.031	-1.128	.177
9	-1.00	-2.646	-1.880	0
	1.00	-2.269	-2.096	0
10	-1.00	-1.434	-1.983	0
	1.00	-1.126	-1.676	0
11	-1.00	1.999	-0.034	.193
	1.00	2.400	-0.062	.350
12	-1.00	2.969	.406	.679
	1.00	3.031	.822	.792
13	-1.00	2.646	1.540	1.078
	1.00	2.269	1.717	1.202
14	-1.00	1.434	1.625	1.138
	1.00	1.126	1.373	.961
15	-1.00	-1.016	1.443	1.010
	1.00	-1.234	1.752	1.227
16	-1.00	1.016	-1.762	0
	1.00	1.234	-2.138	0

observed below 180 nm, while the various transitions of the amide groups (Tables X-XII) could not account for them.

Table XIII. $\sigma\sigma^*$ rotational strengths for three model compounds.

AGCC9 ^a		AACCC10 ^b		PPCC16 ^c	
λ [nm]	$\Delta\epsilon_{\max}$	λ [nm]	$\Delta\epsilon_{\max}$	λ [nm]	$\Delta\epsilon_{\max}$
159.0	0.1	159.0	0.2	180.3	-5.0
142.9	46.6	146.5	32.3	180.2	1.1
138.5	-57.1	139.0	-54.7	161.1	6.6
122.0	-3.8	135.9	-0.4	149.9	22.6
110.7	12.3	113.6	0.3	139.5	-46.5
95.3	2.0	109.3	17.0	136.2	1.8
77.7	4.0	88.0	15.2	110.1	-4.2
71.2	2.1	75.5	-0.1	110.0	-18.0
64.2	-6.2	68.0	0.1	107.0	47.0
		63.1	-9.8	101.8	-8.9
				84.8	15.9
				75.9	-3.8
				71.6	9.8
				67.9	1.6
				65.8	-23.8
				60.3	3.8

^aAGCC9 is a model for AGDKP.

^bAACCC10 is a model for AADKP.

^cPPCC16 is a model for PPDKP.

In the case of AGCC9 and AACCC10 the first transition was a ring transition. For PPCC16 the first two transitions were degenerate "prolyl" ring transitions while the third transition was essentially a transition in the central ring of 6 C-C bonds. All planar ring transitions contribute no rotational strength, so any rotational strength comes from the rings' departure from planarity.

These calculations provide validity to assigning the 140 band in AG- and AADKP and the 140 to 160 band in PPDKP to $\sigma\sigma^*$ transitions. The second transition for AGCC9 occurs at 142.9 nm with $\Delta\epsilon = 46.6$ followed closely at 138.5 nm by a negative band of $\Delta\epsilon = -57.1$. Similarly for AACCC10, the second transition occurs at 146.5 nm with $\Delta\epsilon = 32.3$ followed by a negative band at 139.0 of $\Delta\epsilon = -54.7$. Thus, the 140 nm band in both AG- and AADKP can be assigned to a $\sigma\sigma^*$ transition. An intense negative band is also predicted for the 130-135 nm region just beyond the limits of the experimental spectra. For PPCC16 the third and fourth transitions give positive CD bands. The third transition is at 161.1 nm with $\Delta\epsilon = 6.6$, and the fourth one is at 149.9 nm with $\Delta\epsilon = 22.6$. The fifth transition, at 139.5 nm, gives a band with $\Delta\epsilon = -46.5$. Therefore, the 160 nm positive band and 140 nm negative band in the experimental spectrum of PPDKP are assignable to $\sigma\sigma^*$ transitions.

C. The 180 nm PPDKP Band

PPCC16 did have two transitions at 180 nm. However, their rotational strengths calculated by Eq. (106) were small. As noted above these transitions are "prolyl" transitions. If the prolyl rings are thought of as two separate groups in the PPDKP molecule just as the two amide groups are, then their group magnetic and electric

transition moments can be calculated and interacted with the amide transitions.

Since the prolyl groups are rings and each bond electric transition moment contributes about equally, there exists a magnetic transition moment for the group placed at the center of the ring. The magnetic moment is given by Eq. (105) where ν_j is the frequency of the prolyl group transition. The electric transition moment for the group is given by Eq. (104). We investigated the interaction between these electric and magnetic moments and the two strongest electrically-allowed amide transitions, $\pi_0\pi_-$ and $\pi_+\pi_-$.

One of the group magnetic moments differ in sign between the two degenerate $\sigma\sigma^*$ transitions at 180 nm. However, the associated monopoles will also differ in sign. Therefore both transitions make identical contributions to the rotational strength for the 180 nm band.

Table XIV lists the contributions of the $\pi_0\pi_-$ and $\pi_+\pi_-$ transitions to the $\sigma\sigma^*$ rotational strength at 180 nm through interaction with $\vec{\mu}_{\sigma\sigma^*K}$. The interaction of $\vec{\mu}_{\sigma\sigma^*K}$ and $\vec{\mu}_{\pi_0\pi_-}$ gives the largest contribution, $\Delta\epsilon = -8.2$. The total $\Delta\epsilon$ is -12.1 . This allows the assignment of the 180 nm band as the lowest lying $\sigma\sigma^*$.

Table XIV. $\Delta\epsilon_{\max}$ values for the 180 nm $\sigma\sigma^*$ band in PPDKP.

Interaction	Interacting Transition	$\Delta\epsilon_{\max}$ ($\beta = 35^\circ$)
Degenerate $\sigma\sigma^*$ (106)		-3.9
Nondegenerate (elec.) (54a)	$\pi_0\pi_-$ $\pi_+\pi_-$	-8.2 -1.0
Dynamic field (mag.) ^a (55a)	$\pi_0\pi_-$ $\pi_+\pi_-$	0.9 <u>0.1</u>
	Total $\Delta\epsilon =$	-12.1

^aThe magnetic transition moment for prolyl group two is (0, 00001, -0, 00001, 0.00011) [eA].

D. Interaction of $\pi_0\pi_-$ and Various $\sigma\sigma^*$ Transitions

The use of polarizabilities to estimate the effect of $\sigma\sigma^*$ transitions on the transitions of the amide group has a major defect. Group polarizabilities are calculated at zero energies from experiment. However, in our calculations these polarizabilities are used at energies very close to the actual $\sigma\sigma^*$ energies. Due to the close proximity of the $\sigma\sigma^*$ transitions and the transitions under study, the actual shape of the polarizabilities will be distorted from that at zero energy.³⁵ The above calculations have shown that the low lying $\sigma\sigma^*$ transitions do occur very close in energy to the transitions on the amide group.

Thus, with the apparent breakdown of the polarizability approximation for the $\pi_0\pi_-$ transition in AG- and AADKP (see Table IX) and with the results of Section V B for $\sigma\sigma^*$ transitions, we decided to explicitly interact $\vec{\mu}_{\pi_0\pi_-}$ and various $\vec{\mu}_{\sigma\sigma^*K}$'s. Already calculated is the result for K equal one and two, the 180 transitions in PPDKP. The 180 transition makes the main contribution, so only the first six transitions are considered. There is also a natural break in energy values between transition six and transition seven. The number of transitions is much less for AG- and AADKP. Therefore, all of the contributions for these molecules are calculated.

Table XV is a list of the various contributions to the $\pi_0\pi_-$ transition due to the interaction with $\vec{\mu}_{\sigma\sigma^*K}$'s. The $\Delta\epsilon$ values of -1.7 (AGDKP) and 0.2 (AADKP) for $\beta = -15^\circ$ are significantly different from the -4.8 and -7.2 results for $\beta = -10^\circ$ and the even more negative values for $\beta = -20^\circ$. PPDKP has a $\Delta\epsilon = 8.0$ which is close to 6.6 found by the use of polarizabilities. Included also in the list is the nonconservative term from the explicit interaction of the amide transitions. The final outcome for all three molecules is a non-conservative term with the appropriate sign and magnitude to fit the experimental spectra: 4.0 (AGDKP), 5.9 (AADKP) and -6.6 (PPDKP).

Table XV. Interaction of $\widehat{\mu}_{\sigma\sigma^*K}$ and $\widehat{\mu}_{\pi_0\pi_-}$.

AGDKP (185 nm) ($\beta = -15^\circ$)		AADKP (185 nm) ($\beta = -15^\circ$)		PPDKP (190 nm) ($\beta = 35^\circ$)	
K	$\Delta\epsilon$	K	$\Delta\epsilon$	K	$\Delta\epsilon$
1	-1.1	1	-1.1	1, 2	8.2
2	-0.3	2	0.2	3	0.9
3	0.6	3	0.2	4	-1.4
4	-0.2	4	1.0	5	0.9
5	-0.1	5	0.0	6	-0.6
6	-0.4	6	-0.2		
7	-0.2	7	0.1		
8	0.0	8	-0.2		
9	0.0	9	0.2		
		10	0.0		
	<hr/>		<hr/>		<hr/>
	-1.7		0.2		0.8
Nonconservative term (Table IX)					
	5.7 ^a		5.7 ^a		-14.6
	<hr/>		<hr/>		<hr/>
Total	4.0		5.9		-6.6

^aAverage of values for $\beta = -10^\circ$ and -20° .

VI. CONCLUSION

Independent systems theory has been used successfully in this study to interpret the CD spectra of AGDKP, AADKP and PPDKP in the vacuum uv. Of special interest is the assignment of the intense bands below 180 nm to $\sigma\sigma^*$ transitions. The explicit interaction of the $\sigma\sigma^*$ transitions with the $\pi_0\pi_-$ transition also corrects the non-conservative part of the $\pi_0\pi_-$ couplet centered at 185 nm in AG- and AADKP. These interactions replace the use of polarizabilities which gives non-conservative components of the wrong sign.

The experimental and theoretical spectra are presented in Figures 8 to 10. The theoretical spectra for AG- and AADKP are for a folding of $\beta = -15^\circ$. The methyl groups are in an axial position. The spectrum calculated for PPDKP is for $\beta = 35^\circ$. Only the results for the $\pi_0\pi_-$ couplet and the $\sigma\sigma^*$ bands are plotted. Our $n\pi_-$ values are too small to show up on the theoretical curve. The $n\sigma^*$ and $\pi_0\sigma^*$, if they occur in this region, are well buried under the more intense $\sigma\sigma^*$ transitions. The $\pi_+\pi_-$ transition possibly contributes to the 160 nm band in PPDKP but its value is still less than the $\sigma\sigma^*$ bands.

The theoretical curve for AGDKP is in excellent agreement with the experimental spectrum predicting three CD bands of correct sign and magnitude at 148 nm ($\sigma\sigma^*$), 178 nm ($\pi_0\pi_-$) and 195 nm ($\pi_0\pi_-$). The shoulder at 155 nm on the $\sigma\sigma^*$ band is not reproduced. The theoretical

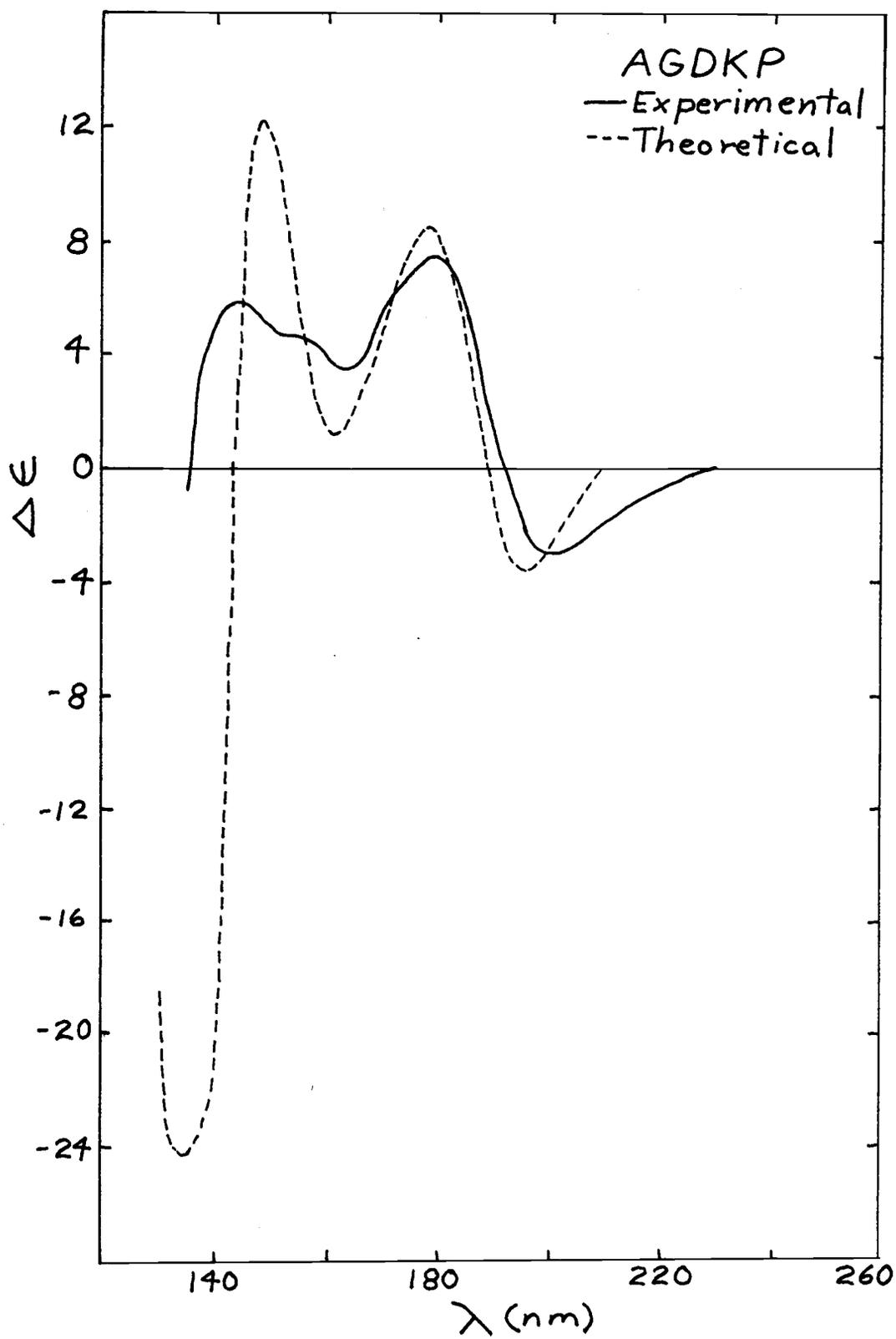


Figure 8. Theoretical and experimental (in HFIP) CD spectra of AGDKP.

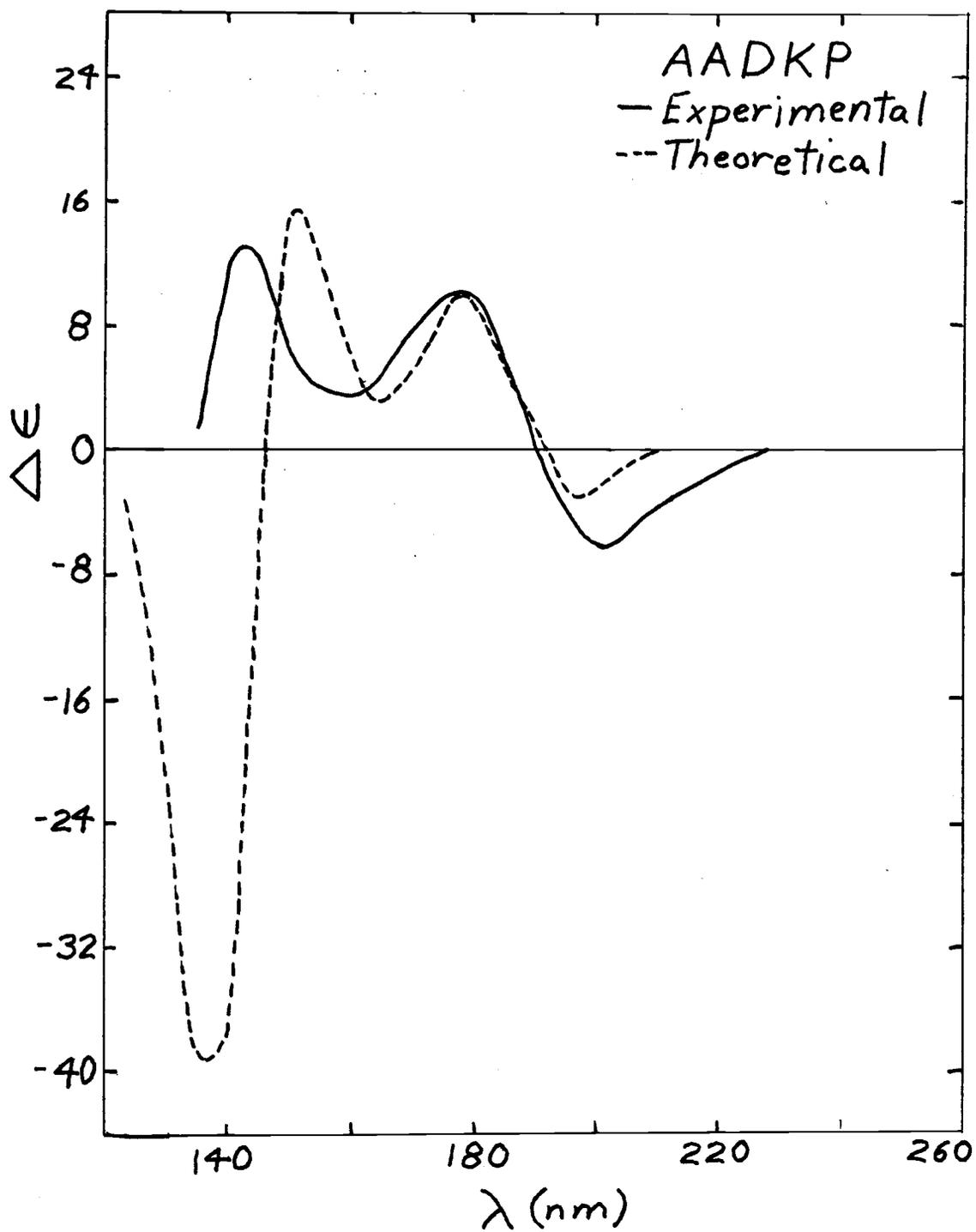


Figure 9. Theoretical and experimental (in HFIP) CD spectra of AADKP.

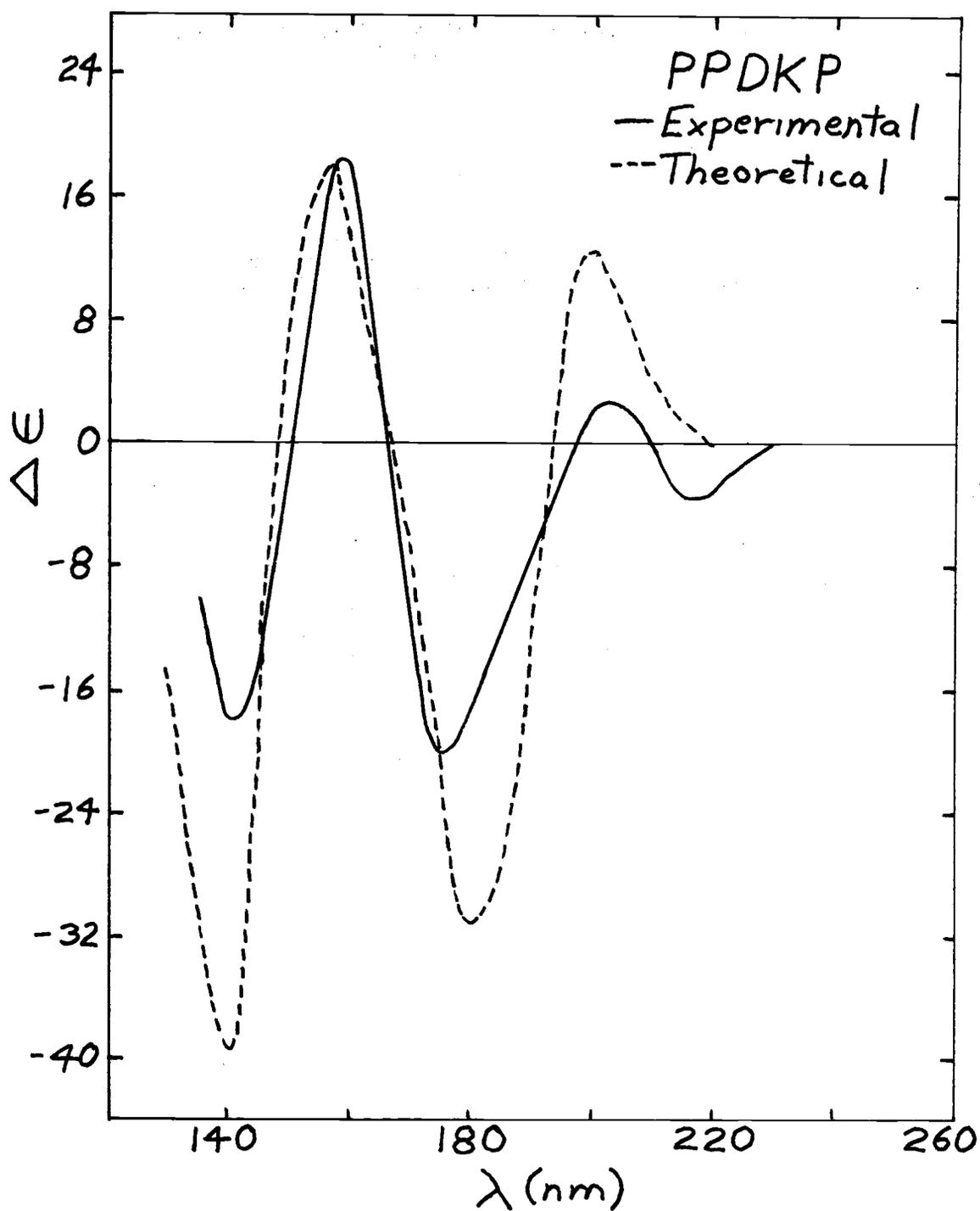


Figure 10. Theoretical and experimental (in HFIP) CD spectra of PPDKP.

curve for AADKP is also in very good agreement with experiment. The three CD bands predicted are at 151 nm ($\sigma\sigma^*$), 179 nm ($\pi_0\pi_-$) and 197 nm ($\pi_0\pi_-$). The magnitude of the 151 nm and 179 nm bands agree well with that found experimentally. With a $\Delta\epsilon = -3$, the 197 nm band is about half that of the experimental value. This indicates that AADKP may on the average be more folded than AGDKP.

For PPDKP, the agreement is good. The theoretical curve predicts the correct number of bands and sign and approximate magnitude for the bands except for the $n\pi_-$ band at 220 nm in the experimental spectrum which is too small to show up on the theoretical curve. The predicted bands are at 139 nm ($\sigma\sigma^*$), 155 nm ($\sigma\sigma^*$), 182 nm ($\sigma\sigma^*$ and $\pi_0\pi_-$) and 200 nm ($\pi_0\pi_-$). All of the bands except the 155 nm band (which probably has a positive contribution from $\pi_+\pi_-$ that has not been included) are too large by factors of 1.5 to 3. The long wavelength $\pi_0\pi_-$ band is the one most too large, but a negative $n\pi_-$ band of experimental magnitude centered at 210 nm would help to lower the apparent size of the $\pi_0\pi_-$ band. In solution PPDKP may be somewhat less folded than L-prolyl-L-leucine diketopiperazine in the crystal. This would lower the magnitudes of all bands. However, considering the approximations in the theory used here, the agreement between theory and experiment for all three compounds is excellent.

The success of the $\sigma\sigma^*$ transitions in explaining the short wavelength region of the spectra suggests a similar interpretation of the

higher energy CD bands in other molecules such as the α -helix. The use of interacting the $\sigma\sigma^*$ transitions explicitly with other transitions instead of using the polarizability approximation should be investigated further. Also, the first order corrections to the zeroth order conservative CD bands, as derived in the theoretical section, could be calculated for some simple dimers to see how significant it is.

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