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The *A Priori* Prediction of Vibrational Circular Dichroism Spectra: a New Approach to the Study of the Stereochemistry of Chiral Molecules

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A theory of Vibrational Circular Dichroism (VCD) has been developed by the author and implemented at the *ab initio* self-consistent field (SCF) level of approximation. VCD spectra calculated from this theory for several small chiral organic molecules are in excellent overall agreement with experiment, when basis sets of adequate sophistication are used and when the *ab initio* SCF force fields are scaled following the procedure of Pulay and coworkers. VCD spectroscopy, together with *a priori* theoretical calculations, now affords a new technique for the study of the stereochemistry of chiral molecules.

Vibrational Circular Dichroism (VCD) is the circular dichroism of vibrational transitions. Circular dichroism is a phenomenon specific to chiral molecules. In the case of fundamental vibrational transitions of molecules, VCD occurs in the infrared spectral region. VCD was first observed in chiral organic molecules in 1974¹. Since that time the technology for the measurement of infrared circular dichroism has advanced very considerably². It is now possible to measure VCD spectra from frequencies below 700 cm⁻¹ throughout the infrared spectral region.³

The theoretical prediction of VCD spectra has advanced somewhat more slowly. A number of theoretical approaches have been proposed, leading to relatively simple equations, but have not proven to be satisfactory⁴. Very recently, however, a theory has been developed, placing the theory of VCD on the same level of rigor as the theory of vibrational absorption intensities⁵. Further, the calculational machinery required for the implementation of this theory at the *ab initio* self-consistent field (SCF) level of approximation has been developed⁶ and applied to the prediction of the VCD spectra of a number of small chiral organic molecules⁷. Where compared, predicted and experimental VCD spectra have been in remarkably good agreement.

At the present time, therefore, it is possible both to measure and to predict the VCD spectra of simple chiral molecules with substantial accuracy. Clearly, the potential of the VCD phenomenon to enable the stereochemistry of chiral molecules to be elucidated is now capable of realisation.

In this article, we will summarise the fundamental equations used in the prediction of vibrational absorption and circular dichroism spectra. The technology currently available for their implementation will be described. Spectra predicted for a small organic molecule will be presented and compared to experimental spectra. The limitations of current techniques and foreseeable developments in the prediction of VCD spectra will be commented upon.

THEORY

The general form of the vibrational absorption spectrum of a molecule can be written⁸:

$$\varepsilon(\nu) = \gamma \sum_i \nu D_i f_i(\nu_i, \nu) \quad (1)$$

where ε is the extinction coefficient, γ is a constant, D_i is the dipole strength of the i th transition, and f_i is a normalized line shape function:

$$\int f_i(\nu_i) d\nu = 1. \quad (2)$$

Equation 1 is appropriate to a dilute, isotropic solution of randomly oriented molecules, obeying Beer's Law. It ignores the effect of the solvent on the molecular absorption. The molecular property D_i is given by

$$D_i = |\langle g | \overrightarrow{\mu_{ei}} | e \rangle|^2 \quad (3)$$

where g and e are the ground and excited states involved in the i th transition and $\overrightarrow{\mu_{ei}}$ is the electric dipole moment operator. As is extremely wellknown, within the harmonic approximation for molecular vibrational motion, for the fundamental ($0 \rightarrow 1$) transition in the i th mode D_i is given by

$$D_i^{0 \rightarrow 1} = \left(\frac{\hbar}{2\omega_i} \right) \left| \left(\frac{\partial \overrightarrow{\mu_{ei}}^G}{\partial Q_i} \right)_0 \right|^2 \quad (4)$$

where $\hbar\omega_i$ is the energy of the i th mode and Q_i is its normal coordinate. $(\partial \overrightarrow{\mu_{ei}}^G / \partial Q_i)_0$ is the derivative with respect to the normal coordinate Q_i of the electric dipole moment of the ground electronic state G of the molecule, evaluated at the equilibrium molecular geometry.

Using the relationship between the normal coordinates Q_i and the set of Cartesian nuclear displacement coordinates, $X_{\lambda\alpha}$ ($\lambda = \text{nucleus}$; $\alpha = x, y, z$):

$$X_{\lambda\alpha} = \sum_i S_{\lambda\alpha,i} Q_i \quad (5)$$

where $S_{\lambda\alpha,i}$ is determined by the force field of the molecule, equation 4 can be written alternatively as

$$D_i^{0 \rightarrow 1} = \left(\frac{\hbar}{2\omega_i} \right) \sum_{\beta} \left\{ \sum_{\lambda\alpha} P_{\alpha\beta}^{\lambda} S_{\lambda\alpha,i} \right\} \left\{ \sum_{\lambda'\alpha'} P_{\alpha'\beta'}^{\lambda'} S_{\lambda'\alpha',i} \right\} \quad (6)$$

where

$$P_{\alpha\beta}^{\lambda} = \left(\frac{\partial (\mu_{ei}^G)_{\beta}}{\partial X_{\lambda\alpha}} \right)_0 \quad (\alpha, \beta = x, y, z) \quad (7)$$

is referred to as the atomic polar tensor of nucleus λ ⁹.

The prediction of the fundamental absorption spectrum, $\varepsilon(\nu)$, thus involves the prediction of the vibrational absorption frequencies, ω_i , the normal coordinates, Q_i , or (equivalently) the $S_{\lambda\alpha,i}$ matrix, and the atomic polar tensors $P_{\alpha\beta}^\lambda$. Both ω_i and $S_{\lambda\alpha,i}$ follow from the vibrational force field. If this is written in terms of the Cartesian displacement coordinates, $X_{\lambda\alpha}$:

$$W_G = W_G^0 + \frac{1}{2} \sum_{\lambda\alpha, \lambda'\alpha'} k_{\lambda\alpha, \lambda'\alpha'} X_{\lambda\alpha} X_{\lambda'\alpha'} + \dots \quad (8)$$

where W_G^0 is the energy at the equilibrium molecular geometry, ω_i and $S_{\lambda\alpha,i}$ are obtained *via* diagonalisation of the mass-weighted force constant matrix $k_{\lambda\alpha, \lambda'\alpha'}$. In the end, therefore, prediction of $\varepsilon(\nu)$ requires calculation of the force constant matrix $k_{\lambda\alpha, \lambda'\alpha'}$ and the atomic polar tensors, $P_{\alpha\beta}^\lambda$. $k_{\lambda\alpha, \lambda'\alpha'}$ is the matrix of second-derivatives of the molecular energy:

$$k_{\lambda\alpha, \lambda'\alpha'} \equiv \frac{\partial^2 W_G}{\partial X_{\lambda\alpha} \partial X_{\lambda'\alpha'}} \quad (9)$$

$P_{\alpha\beta}^\lambda$ is the matrix of first derivatives of the molecular electric dipole moment

$$\vec{\mu}_{\text{el}}^G = \langle \psi_G | \vec{\mu}_{\text{el}} | \psi_G \rangle \quad (10)$$

where ψ_G is the electronic wavefunction of the ground state of the molecule.

The general form for the vibrational circular dichroism spectrum of a molecule parallels equation 1 and can be written⁸

$$\Delta\varepsilon(\nu) = 4\gamma \sum_i \nu R_i f_i(\nu_i, \nu) \quad (11)$$

where R_i is the rotational strength of the *ith* transition, defined by

$$R_i = \text{Im} [\langle g | \vec{\mu}_{\text{el}} | e \rangle \cdot \langle e | \vec{\mu}_{\text{mag}} | g \rangle] \quad (12)$$

where $\vec{\mu}_{\text{mag}}$ is the magnetic dipole operator. As shown by Stephens⁵, the expression for the rotational strength of the *ith* fundamental transition within the harmonic approximation, paralleling that of equation 6 for the dipole strength, is

$$R_i^{0 \rightarrow 1} = \hbar^2 \text{Im} \sum_{\beta} \left\{ \sum_{\lambda\alpha} P_{\alpha\beta}^\lambda S_{\lambda\alpha,i} \right\} \left\{ \sum_{\lambda'\alpha'} M_{\alpha'\beta}^{\lambda'} S_{\lambda'\alpha',i} \right\} \quad (13)$$

where $M_{\alpha\beta}^{\lambda}$ is termed the atomic axial tensor^{5b} and is a molecular property paralleling the atomic polar tensor. The expression for $M_{\alpha\beta}^{\lambda}$ is somewhat more complex than that for $P_{\alpha\beta}^\lambda$. It is

$$\begin{aligned} M_{\alpha\beta}^{\lambda} &= I_{\alpha\beta}^{\lambda} + J_{\alpha\beta}^{\lambda} \\ I_{\alpha\beta}^{\lambda} &= \left\langle \left(\frac{\partial \psi_G}{\partial X_{\lambda\alpha}} \right)_0 \middle| \left(\frac{\partial \psi_G(H_\beta)}{\partial H_\beta} \right)_0 \right\rangle \\ J_{\alpha\beta}^{\lambda} &= \frac{i}{4\hbar c} \sum_{\gamma} \varepsilon(Z_\lambda e) R_{\alpha\beta\gamma}^0 \end{aligned} \quad (14)$$

Here, $I_{\alpha\beta}^{\lambda}$ and $J_{\alpha\beta}^{\lambda}$ are electronic and nuclear contributions to $M_{\alpha\beta}^{\lambda}$. $I_{\alpha\beta}^{\lambda}$ involves the overlap of two derivative wavefunctions: $(\partial \psi_G / \partial X_{\lambda\alpha})_0$ and $(\partial \psi_G / \partial H_\beta)_0$.

$/\partial H_\beta)_0$. The former represents the linear variation of the electronic wavefunction of the molecular ground state G with respect to nuclear displacement at the molecular equilibrium geometry. The latter represents the linear variation of the electronic wavefunction of the molecular ground state G at the equilibrium geometry with respect to magnetic field, H , when a magnetic field perturbation of the form

$$H'(H_\beta) = -(\mu_{\text{mag}}^e)_\beta H_\beta \quad (15)$$

is applied to the molecule. In equation 15, μ_{mag}^e is the electronic contribution to the magnetic moment operator. $J_{\alpha\beta}^{\lambda}$ simply involves nuclear charges, $Z_\lambda e$, and equilibrium positions, R_λ^0 .

Atomic axial tensors differ from atomic polar tensors in being intrinsically origin dependent. When the origin dependence of $M_{\alpha\beta}^\lambda$ is examined, it transpires that it can be written^{5b}

$$(M_{\alpha\beta}^\lambda)^0 = (M_{\alpha\beta}^\lambda)^{0'} + \frac{i}{4\hbar c} \sum_{\gamma\delta} \varepsilon_{\beta\lambda\delta} \vec{\Delta}_\gamma P_{\alpha\delta}^\lambda \quad (16)$$

where O and O' are two origins and $\vec{\Delta}$ is the vector from O to O' . Equation 16 is an example of the fascinating interrelationship between the electric and magnetic properties of a molecule. Stephens has used equation 16 to define a more sophisticated expression for the atomic axial tensors, with respect to an origin O ,^{5b}:

$$(M_{\alpha\beta}^\lambda) = (M_{\alpha\delta}^\lambda)^\lambda + \frac{i}{4\hbar c} \sum_{\gamma\delta} \varepsilon_{\beta\gamma\delta} R_{\lambda\gamma}^0 P_{\alpha\delta}^\lambda \quad (17)$$

where $(M_{\alpha\beta}^\lambda)^\lambda$ is given by equation 14 and the superscript indicates that each $(M_{\alpha\beta}^\lambda)^\lambda$ tensor is evaluated with the origin at the equilibrium position of nucleus λ — the position R_λ^0 relative to O . Equation 17 is termed the equation for the atomic axial tensor in the Distributed Origin with origins at nuclei gauge. There are two reasons for the use of equation 17. First, when substituted into equation 13 it leads to rotational strengths that are independent of origin — a necessary property for any physical observable! Second, using the methods to be described below, it provides the most accurate algorithm for the calculation of $M_{\alpha\beta}^\lambda$ tensors yet known.

In sum, to predict the fundamental VCD spectrum, $\Delta\varepsilon(\nu)$, requires all of the quantities involved in the prediction of the absorption spectrum, $\varepsilon(\nu)$, together with the atomic axial tensors, $(M_{\alpha\beta}^\lambda)^\lambda$. The absorption spectrum is automatically available whenever all quantities required for calculating the VCD spectrum are at hand.

IMPLEMENTATION

One of the most dramatic developments in quantum chemistry in the last decade has been the improvement in the techniques and computational programs for *ab initio* molecular orbital calculation of molecular properties¹⁰. It has become routine to calculate the first and second derivatives of the ground state energy at the self-consistent field (SCF) level of approximation, and thence to calculate equilibrium molecular geometries and vibrational

force fields. In addition, not only dipole moments but also atomic polar tensors can be routinely calculated at the SCF level. Thus, it is possible to calculate the frequencies and intensities of a vibrational absorption spectrum entirely *ab initio* at the SCF level of approximation.

For very simple molecules, predicted vibrational frequencies and intensities recognisably resemble experiment¹⁰. However, frequencies calculated at the SCF level are typically 10–15% higher than experimental frequencies, implying that force constants are in error by as much as 20–30%. As molecular size and the number of vibrational frequencies increase, the relationship between theory and experiment becomes less perfect, reflecting increasing error in the normal coordinates due to the errors in the force field.

There are two ways in which the residual errors in vibrational force fields, frequencies and normal coordinates calculated at the SCF level can be removed. One is to improve the level of *ab initio* approximation. A variety of methods exist by which correlation corrections can be included, such as Møller-Plesset (MP) perturbation theory, configuration interaction (CI) and so on. Methods for the efficient calculation of vibrational frequencies at post-SCF levels of approximation are being developed and implemented at this time¹¹ and are starting to appear in the most up-to-date *ab initio* molecular orbital programs. Results reported so far are very impressive, in the extent to which the errors found at the SCF level are reduced and to which predicted frequencies are in agreement with experiment. In addition, post-SCF methods for the calculation of atomic polar tensors are being developed simultaneously¹² leading to improved agreement between predicted and experimental absorption intensities. It is very likely that post-SCF methods will soon become as routine as SCF methods are now. However, at this time, post-SCF calculations are still restricted to a small number of programs and are practical only for quite small molecules.

An alternative method by which SCF force fields, frequencies and normal coordinates can be improved has been popularised by Pulay and coworkers¹³. In this method the SCF force field is empirically refined to fit experimental frequencies, somewhat in the manner of traditional methods for deriving vibrational force fields. However, the procedure of Pulay is constrained in two ways which eliminate most of the ambiguity of the traditional empirical force field. First, the fact that the initial guess is a SCF calculated force field, and therefore already quite close to the true force field, enormously constrains the outcome. Second, the refinements is carried out using a very simple algorithm, in which it is required that true force constant matrix elements, k_{ij} , expressed with respect to a basis of internal (not Cartesian) coordinates, are related to SCF ones, K_{ij} , by

$$k_{ii} = \alpha_i K_{ii}; \quad k_{ij} = \sqrt{\alpha_i \alpha_j} K_{ij} \quad (18)$$

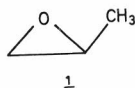
where α_i are so-called scaling factors. This procedure has by now been used to analyse the vibrational spectra of a substantial number of molecules. It has the advantage that post-SCF calculations are not required. Its disadvantages are that it is empirical and nonunique. Not only does the force field depend on an assignment of the experimental spectrum, but also on the specific choice of coordinates in terms of which the force field is expressed and on the number of scaling factors adopted. In addition, the Pulay pro-

cedure is not applicable to the atomic polar tensors and does not address the errors in intensities arising from errors in the SCF atomic polar tensors.

Predictions of VCD spectra require in addition calculation of atomic axial tensors. Following the introduction of these tensors by Stephens, their calculation has been implemented at the SCF level of approximation⁶. At this time, the most efficient implementation is contained in the CADPAC program, an *ab initio* molecular orbital program developed at Cambridge University by Drs. R. D. Amos, N. C. Handy and their coworkers¹⁴. CADPAC is a mnemonic for Cambridge Analytical Derivatives Package. In addition to atomic axial tensors, CADPAC also enables state-of-the-art calculations of energy first and second derivatives with respect to nuclear coordinates and of atomic polar tensors at the SCF level. All molecular properties required for the prediction of vibrational absorption and circular dichroism spectra based on SCF calculations are thus available from the CADPAC program.

APPLICATION

We describe here a single application of the theory described above. The molecule of interest is propylene oxide (epoxypropane)



a small, simple, chiral organic molecule. The VCD of this molecule has probably been more thoroughly studied than any other at this time¹⁵.

VCD spectra have been obtained¹⁵ over the frequency ranges 650—1600 cm^{-1} and 2800—3200 cm^{-1} , which span all but three of the fundamental transitions of propylene oxide (those lying $< 500 \text{ cm}^{-1}$). The spectra have been studied for the neat liquid and for dilute solutions in CS_2 and CCl_4 . The spectra are qualitatively identical and quantitatively very similar. The absorption and VCD spectra of the neat liquid over the range 700—1600 cm^{-1} are shown in Figures 1 and 2.

VCD and absorption spectra have been calculated¹⁵ using SCF atomic polar and axial tensors and force fields obtained from SCF force fields using the methodology of Pulay. In doing so, the following choices exist. First the equilibrium molecular geometry can be either taken from experiment, calculated or obtained by empirical correction of calculated geometries. In the case of propylene oxide, an experimental geometry does not exist and we have used the latter two approaches. The correction of theoretically calculated geometries using corrections obtained from comparison of calculated and experimental geometries for other molecules has been advocated by Pulay and coworkers in the derivation of vibrational force fields¹³. Second, in deriving a scaled force field from an *ab initio* calculation, a set of internal coordinates and, subsequently, the number and distribution of independent scaling factors must be chosen. In our work, we have carried out scaling in stages, each one incrementing the number of scaling factors over the previous number. We start with one scaling factor, which scales all frequencies by the same amount and does not change the normal coordinates. Then a small number of independent scaling factors is introduced, such that chemically similar internal coordinates (e. g. all C—H stretching coordi-

notes) receive identical scaling factors. Following this, the number of scaling factors is gradually incremented until no further improvement in the fit between calculated and experimental frequencies is obtained. In the case of propylene oxide we have used a maximum of 10 scaling factors. Thirdly, an assignment of the vibrational spectrum must be chosen before the scaled force field can be derived. This involves the differentiation of fundamental and overtone/combination transitions and the evaluation of the relationship between the *ab initio* calculated and observed frequencies (as it does in the development of a vibrational force field by any empirical method). In our work on propylene oxide we were assisted by the availability of matrix-

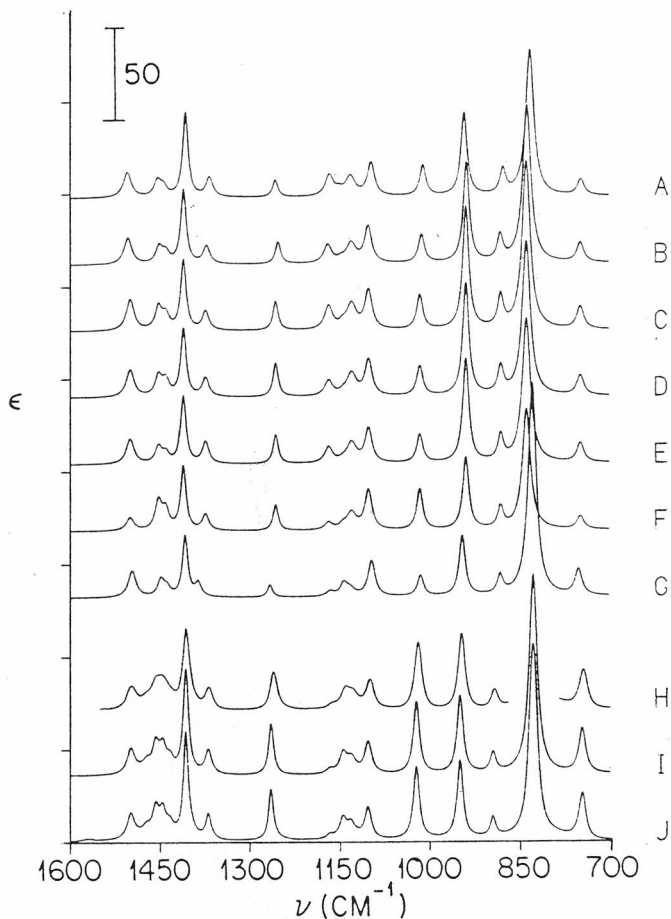


Figure 1. Calculated (A-G) and experimental (H-J) absorption spectra of propylene oxide. **A.** STO-3G optimised geometry, 6-31G** vibrational force field and 6-31G** atomic polar and axial tensors: STO-3G/6-31G**/6-31G**. **B.** 6-31G**/6-31G**/6-31G**. **C.** CORR/6-31G**/DZ/IP. **D.** CORR/6-31G**/6-311G**. **E.** CORR/6-31G**/61-31G**. **F.** CORR/6-31G**/4-31G. **G.** CORR/4-31G/6-31G**. (CORR is a corrected 4-31G optimised geometry). **H** and **J.** Experimental spectra at resolution used for VCD measurement (Figure 2) and 1 cm^{-1} respectively. **I.** Lorentzian fit to spectrum **J.** Spectra A-G are calculated using Lorentzian line shapes obtained from fit I.

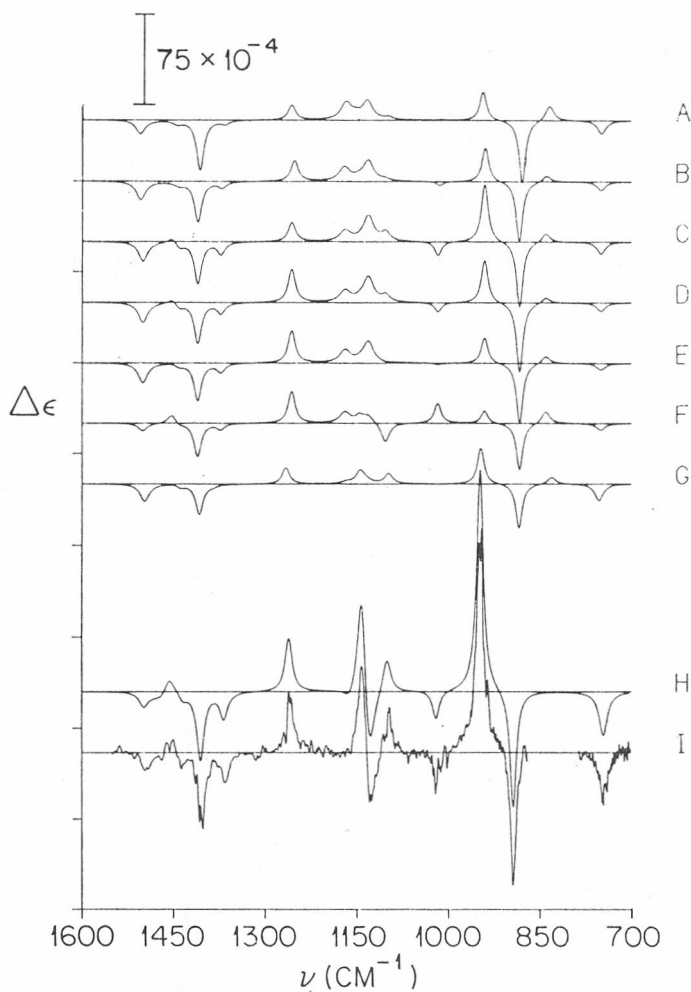


Figure 2. Calculated (A-G) and experimental (H, I) VCD spectra of S-(−)-propylene oxide. A-G as in Figure 1. I. Experimental VCD spectrum (resolution varying from 6–10 cm^{-1}). H. Lorentzian fit to spectrum I. Spectra A-G are calculated using Lorentzian line shapes obtained from fit H.

isolation spectra in N_2 and Ar matrices, in which line widths were much less than in liquid phase spectra and spectral resolution consequently superior.¹⁵ Fourthly, in calculating geometry, force field and atomic polar and axial tensors a basis set must be chosen. This need not be the same for different properties. In our work on propylene oxide we have used predominantly the basis sets developed by Pople and coworkers: STO-3G, 3-21G, 4-31G, 6-31G, 6-31G*, 6-31G** and 6-311G**¹⁰. STO-3G is a minimal basis set. 3-21G, 4-31G and 6-31G are split-valence basis sets and those bearing asterisks are split-valence basis sets to which polarisation functions are added. One asterisk indicates polarisation functions are added only to »heavy« atoms (i.e. the first row atoms C, N, O etc.). Two asterisks implies polarisation

functions are also added to H atoms. Lastly, there may be a practical choice of computer program and machine. In our studies of propylene oxide, for pragmatic, historical reasons, geometry optimisation and vibrational force field calculations were carried out using the GAUSSIAN 82 program,¹⁰ while atomic polar and axial tensors were calculated using version 3.0 of CADPAC. In both cases, calculations were executed using the San Diego Supercomputer Center CRAY-XMP machine.

Selected results from our studies are shown in Figures 1. and 2. In all cases, vibrational force fields were obtained by fitting absorption frequencies. Absorption and VCD intensities were then calculated with no further use of experimental data. Predicted spectra assume Lorentzian line shapes and use line widths obtained by fitting experimental absorption spectra. (Note that absorption spectra are measured at 1 cm⁻¹ resolution, while VCD are measured at lower resolution in order to achieve adequate signal-to-noise ratios).

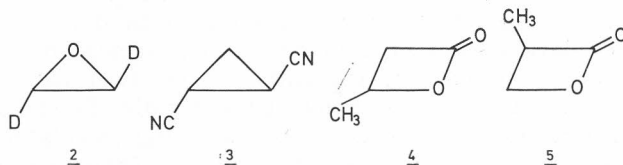
We find that

- 1) all force fields give similar results, with the exception of STO-3G force fields which yield a worse fit to experimental frequencies and absorption and VCD spectra in worse agreement with experiment;
- 2) with respect to the basis set used in calculating atomic polar and axial tensors, basis sets containing polarisation functions yield superior results to split-valence basis sets and enormously superior results to minimal basis sets;
- 3) all choices of geometry yield similar results
- 4) when the force field is derived using basis sets larger than minimal and the atomic polar and axial tensors are calculated using basis sets containing polarisation functions, predicted absorption and VCD spectra are in excellent overall agreement with experiment. The principal disagreement occurs in the region 1100—1170 cm⁻¹. In this region, the results are particularly sensitive to the choices of basis set made in calculating geometry, force field and atomic polar and axial tensors.

Similar conclusions are reached from the study of the C—H stretching region¹⁵. Theory and experiment are in moderately good agreement. However, here the comparison is complicated by the existence of Fermi resonance involving fundamentals and overtone/combinations.

DISCUSSION

Comparison of VCD spectra predicted via SCF calculations, along the lines described in the previous section, and experimental VCD spectra have by now been carried out for several molecules, including¹⁶



With the qualifications that

- 1) force fields are calculated using split-valence or larger basis sets and scaled, and
- 2) $P^{\lambda}_{\alpha\beta}$ and $M^{\lambda}_{\alpha\beta}$ tensors are calculated using split-valence-plus-polarisation-functions-on-heavy-atoms or larger basis sets,

predicted spectra are *overall* in excellent agreement with experiment. By this we mean that in the large majority of cases signs (+ or -) are correctly predicted, relative magnitudes of VCD intensities are qualitatively correct, and the absolute magnitudes of rotational strengths are within a factor of 2–3. In each case, some parts of the VCD spectrum are better predicted than others. In general, predictions are less effective for vibrations whose normal coordinates are a very sensitive function of the force field. This is most often the case when other modes are close in energy. Thus, predictions are more likely to err, the more congested the region of the vibrational spectrum. In addition, regions of the spectrum subject to significant Fermi resonance are naturally difficult to reproduce using a theory in which anharmonicity is neglected. The C—H stretching region is usually the one most prone to Fermi resonance. Since the C—H stretching region is also typically more congested than any other region, it is generally the region where predictions and experiment differ the most.

On the one hand, the results obtained to date are very encouraging. There is no reason to believe that the same level of success will not occur in other molecules. There is every reason to believe that improvements in theoretical techniques will lead to closer agreement between theory and experiment. On the other hand, the data base currently available is obviously extremely limited. A substantial expansion of this data base is clearly mandatory. In particular, a wider *variety* of molecular structures must be studied. Parts of the periodic table not encompassed so far must be included. More varied types of bonding must be examined. Ions, weakly-bound aggregates (dimers, ...) and other different categories of molecules require study. At the present time, we are studying several molecules containing second-row atoms (Cl, S, ...) and internal hydrogen bonding, in an effort to broaden the current data base. It is our hope that many more molecules will soon be enlisted in this endeavor.

At the present time, the SCF calculations described above when carried out using the current generation of supercomputers (such as the CRAY-XMP used in our work) are limited to about ~ 150 basis functions. For molecules whose formula is X_nH_{2n} , where $X = C, N, O \dots$, the number of basis functions when split valence basis sets are used is $13n$. For split-valence-plus-polarisation-functions-on-heavy-atom basis sets, the number is $19n$. In these two cases, n is thus limited to ~ 12 and ~ 8 respectively. At this time, SCF calculations using basis sets of adequate size are therefore limited to fairly small molecules. This limitation can be expected to be short lived, however. First, the rate of development of both *ab initio* molecular orbital programming and computer hardware is currently extremely rapid. The frontier of feasibility will undoubtedly be pushed back rapidly. Secondly, it is very likely that approximations can be developed allowing calculations for much larger molecules without serious loss of accuracy. There are two obvious approximations which will probably be the first to be explored. First, semi-

-empirical methods can be employed in place of the more rigorous *ab initio* methods. Second, properties of larger molecules can be obtained from calculations on smaller molecular fragments. Consider, for example, atomic polar tensors, $P_{\alpha\beta}^{\lambda}$, defining the change in the molecular electric dipole moment as a result of the displacement of nucleus λ . Clearly in most molecules $P_{\alpha\beta}^{\lambda}$ will not be sensitive to the nature of atoms in the molecule distant from nucleus λ . Such atoms can then therefore be deleted or replaced by H atoms and a smaller molecule used to calculate $P_{\alpha\beta}^{\lambda}$. In this way, all $P_{\alpha\beta}^{\lambda}$ tensors for a large molecule can be obtained by a series of calculations of fragments of this molecule (no more than N for an N-atom molecule). Of course, these are not the only approaches possible and it would be premature to judge which will be the most successful. It is only sure that this topic will receive intense attention in the near future.

Given the feasibility of predicting the VCD spectrum of molecules of substantial size, a new technique is available for the study of molecular stereochemistry. Of course, vibrational spectroscopy has been used by chemists for many years in studying molecular structure. However this usage has until recently been entirely empirical. Very recently, *a priori* calculations of vibrational absorption spectra have begun to be used by organic chemists, notably in elucidating the structure of novel, unstable small molecules.¹⁷ *A priori* calculations of VCD spectra further extends the utility of vibrational spectroscopy. VCD only exists in chiral molecules, of course. However, within this category, the use of VCD substantially enhances the information content of vibrational spectroscopy. Specifically, VCD is uniquely dependent on the absolute configuration of a chiral molecule. In addition, VCD can be expected to be generally more sensitive to molecular conformation than absorption spectra and therefore to be more discriminating in distinguishing alternative conformations.

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SAŽETAK

A priori prognoza spektara vibracijskog cirkularnog dikroizma: novi pristup proučavanju stereokemije kiralnih molekula

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Autor je razvio teoriju vibracijskog cirkularnog dikroizma (VCD) i ugradio na »*ab initio* self-consistent field« (SCF) stupnju aproksimacije. VCD spektri, proračunani prema toj teoriji za različite male kiralne organske molekule, izvanredno se dobro slažu s eksperimentom, kada se koriste bazni skupovi odgovarajuće složenosti i kada su *ab initio* SCF polja sila rangirana prema postupku Pulaya i sur. VCD spektroskopija zajedno s *a priori* teorijskim proračunima pružaju sada novu tehniku za proučavanje stereokemije kiralnih molekula.