

Raman Optical Activity. Computation of Circular Intensity Differentials by the Atom-Dipole Interaction Model

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Abstract: The atom-dipole interaction (ADI) model for molecular optical properties has been extended to provide a generally applicable method for computation of Raman optical activity parameters. This model requires only a minimum number of parameters, i.e., atomic polarizabilities and their derivatives in Cartesian space, which are transferable among similar molecules. Optimization of these parameters from experimental Raman scattering parameters is discussed. The resultant parameters are then incorporated into the ADI model to formulate the tensors necessary for computing the Raman circular intensity differentials for all the fundamental vibrations of any general molecule. Thus, for the first time, a means of directly correlating molecular structural features with observed Raman optical activity is available to guide experimental observation.

Introduction

The potential for vibrational optical activity (VOA) to provide unique information about the intricate details of molecular stereochemistry has fostered widespread interest in the phenomenon. Raman optical activity^{1,2} (ROA) was predicted by Barron and Buckingham^{3,4} and subsequently observed by several groups.⁵⁻¹⁶ Complementary developments in infrared vibrational circular dichroism (VCD) have also occurred.¹⁷⁻³¹

Realization of the full potential of VOA requires that some direct means be available to correlate the structural features and internal dynamics of molecules (absolute configurations, skeletal conformations, functional groups, and vibrational modes) with signs and magnitudes of the chiroptical parameters as measured by ROA or VCD. For VCD, models have been developed to compute the rotatory strength of a vibrational transition in the infrared. Models using a fixed point charge approximation,^{18,22,30} a polar tensor formalism,³⁰ or coupled oscillator interactions^{28,32} have been utilized with varying degrees of success. For ROA, however, no generally applicable models have been available to predict the signs and magnitudes of the circular intensity differentials (CIDs). The general expressions^{1,2} for the Raman CID are of limited utility as such since a priori knowledge of several polarizability derivative components is required. Practical application of the ROA two-group model is^{1,2,33} limited to identical groups and even then it does not distinguish among the several types of vibrational motion. Furthermore, lack of knowledge of the magnitude of the many pairwise interactions required for general application precludes its use with the majority of structures of interest.

Here we describe an inherently general method for computation of the sign and magnitude of the Raman CID for any vibrational mode of an arbitrary molecule. Thus, a powerful yet practical means is now available for correlation of structural/stereochemical features with observed Raman optical activity.

An examination of viable models for other chiroptical phenomena suggests the utility of casting any description of ROA in terms of the properties and interactions of subunits of the molecule. For molar rotation,³⁴⁻³⁸ atomic refractivities (or polarizabilities) are useful parameters, whereas for VCD, net atomic charges (or atomic polar tensors)^{18,30} have been utilized. Raman scattering is a manifestation of the changes in the molecular polarizability ellipsoid which can be expressed as a function of the corresponding atomic or bond polarizability

ellipsoids. Use of bond polarizabilities and their derivatives presents practical difficulties because of the necessity of specifying their three different components. If, on the other hand, atomic polarizabilities of spherical symmetry are utilized, any anisotropy of the molecular polarizability ellipsoid can be introduced through interatomic interactions via a suitable function. Therefore, it seems that the most direct path to a useful computational model for ROA is adoption of an atomic parameter, namely, the atomic polarizability derivative tensor.

Fortunately, the basic framework of this approach is available in the atom-dipole interaction (ADI) model as developed by Applequist and co-workers.³⁶⁻⁴⁰ In this model, the nonspherical molecular polarizability tensor is obtained from spherical atomic polarizabilities and the dipolar interactions between atoms. Optimized atomic polarizabilities (for 5893 Å), which are *transferable* among molecules for prediction of molecular polarizability, have been reported.³⁹ Calculation of the optical rotatory power of a molecule from atomic polarizabilities and molecular structure via the ADI model is practical and remarkably reliable.³⁶⁻³⁸ A further extension of this model shows that the molecular polarizability derivative tensors required for prediction of Raman scattering parameters can be obtained, provided that a knowledge of certain atomic polarizability derivatives is available.^{40,41} As a corollary, knowledge of Raman scattering parameters should provide the necessary atomic polarizability derivative tensor values; appropriate manipulation of these tensors will yield individual values of the molecular polarizability derivative tensors. In addition to the latter tensor, the gyration tensor and the tensor describing the induced quadrupole moment are essential for prediction of Raman CIDs;^{1,2} each of these tensors can be evaluated via the ADI model.

The remarkable utility of the ADI model for Raman CID prediction is further substantiated by other considerations. (1) The ADI model is inherently a completely general model⁴⁰ that is not restricted to a small class of molecular structures. (2) The ADI model is the only available sophisticated description of molecular polarizability which has been sufficiently well elaborated theoretically to provide the parameters required for computation of chirality-related properties.³⁶⁻³⁸ The interactions giving rise to these chiroptical properties are inherent in the model. (3) Numerical computation using established procedures and optimized empirical parameters is straightforward. Simplification using partial structures and numerical differentiation is readily accommodated if proven reliable.

We have combined the ADI formalism with the classical scattering description of ROA due to Barron and Buckingham.² Specifically, we use the CID expressions derived by

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Barron and Buckingham² and evaluate the parameters therein via the ADI model. Here we describe the details of this approach; applications to bromochlorofluoromethane⁴² and to several molecular segments are presented in separate papers.

Circular Intensity Differentials

Since this report describes the first effort to compute Raman circular intensity differentials, it is appropriate to cast the problem in a general form which illustrates that the Raman CID is another manifestation of optical activity. Thus we feel it necessary to follow a basic outline of the theory of optical activity.⁴³⁻⁴⁶ We use SI units throughout this development.

The ordinary effects of an electric field, \mathbf{E} , in a highly dilute, transparent medium can be described by a linear expression:

$$\boldsymbol{\mu}_c = \boldsymbol{\alpha} \mathbf{E} \quad (1)$$

where $\boldsymbol{\mu}_c$ is the induced electric moment and $\boldsymbol{\alpha}$ is the polarizability tensor. In an optically active medium, the applied electric field vector is rotated by the chiral molecule, producing new microscopic effects. These effects are easily accommodated by use of the curl of a vector quantity.^{43,44} Thus, eq 1 becomes

$$\boldsymbol{\mu}_c = \boldsymbol{\alpha} \mathbf{E} + \boldsymbol{\beta} \nabla \times \mathbf{E} \quad (2)$$

where $\boldsymbol{\beta}$ is the rotatory polarizability tensor.

Dependence of the induced moment on the electric field component that is rotated by the chiral part of the molecule requires the molecule to also exhibit a nonvanishing magnetic moment, $\boldsymbol{\mu}_m$:

$$\boldsymbol{\mu}_m = \delta \mathbf{H} + \boldsymbol{\beta}_1 \nabla \times \mathbf{H} \quad (3)$$

Here \mathbf{H} is the internal magnetic field vector, δ is the magnetic polarizability tensor which vanishes in nonmagnetic substances, and $\boldsymbol{\beta}_1$ is a polarizability tensor similar $\boldsymbol{\beta}$ in eq. 2. Application of Maxwell's laws, assuming a nonmagnetic and nonconducting medium, permits transformation for eq 2 and 3:

$$\boldsymbol{\mu}_c = \boldsymbol{\alpha} \mathbf{E} - \boldsymbol{\beta} \dot{\mathbf{B}} \quad (4)$$

$$\boldsymbol{\mu}_m = \epsilon \epsilon_0 \boldsymbol{\beta}_1 \dot{\mathbf{E}} \quad (5)$$

where \mathbf{B} is the magnetic flux, ϵ is the dielectric constant, and ϵ_0 is the permittivity of free space.

If the complex field vectors of the incident light beam (propagating along the z axis) are described as

$$\mathbf{E} = \mathbf{E}^\circ \exp[-i\omega(t - z/c)] \quad (6)$$

$$\mathbf{B} = \mathbf{B}^\circ \exp[-i\omega(t - z/c)] \quad (7)$$

eq 4 and 5 can be rewritten in terms of the amplitudes of the field oscillations:²

$$\boldsymbol{\mu}_c = \boldsymbol{\alpha} \mathbf{E}^\circ + \mathbf{G} \mathbf{B}^\circ \quad (8)$$

and

$$\boldsymbol{\mu}_m = \tilde{\mathbf{G}} \mathbf{E}^\circ \quad (9)$$

where

$$\mathbf{G} = i\omega\boldsymbol{\beta} = -i\omega\epsilon\epsilon_0\tilde{\boldsymbol{\beta}}_1 \quad (10)$$

The quantity \mathbf{G} is the gyration tensor and the mean of the tensor $\boldsymbol{\beta}$ is related directly to the optical rotation.⁴⁶ Although the induced quadrupole moment makes no major contribution to electronic optical activity in fluids, it does contribute to that of ordered arrays and to the Raman optical activity of fluids.³ Thus eq 8 becomes²

$$\boldsymbol{\mu}_c = \boldsymbol{\alpha} \mathbf{E}^\circ + \mathbf{G} \mathbf{B}^\circ + \frac{1}{3} \mathbf{A} \nabla \mathbf{E} \quad (11)$$

where \mathbf{A} represents the tensor for the induced quadrupole moment and $\nabla \mathbf{E}$ is the gradient of the applied field.

The intensity and polarization properties of any monochromatic light beam are most conveniently described by the Stokes vector;^{43,47} the components of the Stokes vector are directly related to the total intensity, I , the degree of polarization, P , the azimuthal angle, θ , and the ellipticity, η , of the polarization ellipse. The ellipticity, η , takes on the values $\pi/4$ and $-\pi/4$ for right and left circularly polarized light, respectively, and zero for linearly polarized light. Since scattered radiation is regarded as having been emitted by the induced multipole moments, the properties (I, P, θ, η) of the scattered light can be related to those of the incident light through the induced moments. Barron and Buckingham,² using the Stokes formalism, have derived expressions for the intensity of light scattered at 90° by the multipole moments in eq 11. In Cartesian tensor notation the scattered intensity components,⁴⁸ polarized perpendicular (s) and parallel (p) to the scattering plane, are²

$$I_s = \frac{K}{2} [(7\alpha_{\alpha\beta}\alpha_{\alpha\beta} + \alpha_{\alpha\alpha}\alpha_{\beta\beta}) + (\alpha_{\alpha\beta}\alpha_{\alpha\beta} + 3\alpha_{\alpha\alpha}\alpha_{\beta\beta}) P \cos 2\eta \cos 2\theta + 2/c(7\alpha_{\alpha\beta}G_{\alpha\beta} + \alpha_{\alpha\alpha}G_{\beta\beta} + \frac{1}{3}\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}) P \sin 2\eta] \quad (12)$$

$$I_p = K[(3\alpha_{\alpha\beta}\alpha_{\alpha\beta} + \alpha_{\alpha\alpha}\alpha_{\beta\beta}) + 2/c(3\alpha_{\alpha\beta}G_{\alpha\beta} - \alpha_{\alpha\alpha}G_{\beta\beta} - \frac{1}{3}\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}) P \sin 2\eta] \quad (13)$$

Here $\alpha_{\alpha\beta}$, $G_{\alpha\beta}$, and $A_{\gamma\alpha\beta}$ are the elements of the tensors $\boldsymbol{\alpha}$, \mathbf{G} , and \mathbf{A} in eq 11, and K is a constant characteristic of the incident light. These equations apply equally well to Raman scattering if $\boldsymbol{\alpha}$, \mathbf{G} , and \mathbf{A} are replaced by the corresponding normal coordinate derivatives $\boldsymbol{\alpha}'$ ($\partial\boldsymbol{\alpha}/\partial Q$), \mathbf{G}' ($\partial\mathbf{G}/\partial Q$), and \mathbf{A}' ($\partial\mathbf{A}/\partial Q$).² The Raman optical activity is then described by a normalized circular intensity differential (CID):²

$$\Delta = I^R - I^L / I^R + I^L \quad (14)$$

where I^R and I^L represent the scattered intensity for right ($\eta = \pi/4$) and left ($\eta = -\pi/4$) circularly polarized incident light. Thus the Raman CIDs, expressed in terms of the normal coordinate derivatives of the multipole moments, are given by²

$$\Delta_s(Q_k) = \frac{2(7\alpha'_{\alpha\beta}G'_{\alpha\beta} + \alpha'_{\alpha\alpha}G'_{\beta\beta} + \frac{1}{3}\omega\alpha'_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A'_{\gamma\delta\beta})}{c(7\alpha'_{\lambda\mu}\alpha'_{\lambda\mu} + \alpha'_{\lambda\lambda}\alpha'_{\mu\mu})} \quad (15)$$

$$\Delta_p(Q_k) = \frac{2(3\alpha'_{\alpha\beta}G'_{\alpha\beta} - \alpha'_{\alpha\alpha}G'_{\beta\beta} - \frac{1}{3}\omega\alpha'_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A'_{\gamma\delta\beta})}{c(3\alpha'_{\lambda\mu}\alpha'_{\lambda\mu} - \alpha'_{\lambda\lambda}\alpha'_{\mu\mu})} \quad (16)$$

By substituting eq 10 and dropping the imaginary term i , eq 15 and 16 become

$$\Delta_s(Q_k) = \frac{4\pi}{n\lambda_c} \frac{7\alpha'_{\alpha\beta}\beta'_{\alpha\beta} + \alpha'_{\alpha\alpha}\beta'_{\beta\beta} + \frac{1}{3}\alpha'_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A'_{\gamma\delta\beta}}{7\alpha'_{\lambda\mu}\alpha'_{\lambda\mu} + \alpha'_{\lambda\lambda}\alpha'_{\mu\mu}} \quad (17)$$

$$\Delta_p(Q_k) = \frac{4\pi}{n\lambda_c} \frac{3\alpha'_{\alpha\beta}\beta'_{\alpha\beta} - \alpha'_{\alpha\alpha}\beta'_{\beta\beta} - \frac{1}{3}\alpha'_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A'_{\gamma\delta\beta}}{3\alpha'_{\lambda\mu}\alpha'_{\lambda\mu} - \alpha'_{\lambda\lambda}\alpha'_{\mu\mu}} \quad (18)$$

Here $\beta'_{\alpha\beta}$ are the elements of the derivative tensor $\partial\boldsymbol{\beta}/\partial Q_k$, λ_c is the wavelength of the exciting monochromatic radiation, and n is the refractive index of the medium. From eq 17 and 18 it can be seen that the individual elements of the derivative tensors $\boldsymbol{\alpha}'$, $\boldsymbol{\beta}'$, and \mathbf{A}' are necessary for evaluation of Raman CIDs. We find that these quantities can be obtained from the ADI model; in the following section we outline the process.

The ADI Model and Its Extension to ROA

In the ADI model, interactions among spherical atomic polarizabilities, α_i , are assumed to be dipolar in form.^{39,40} With such interactions the effective field at atom i is different from the applied field, \mathbf{E}_i , at atom i . Accordingly, the induced electric moment, $\boldsymbol{\mu}_i$, is described by³⁹

$$\boldsymbol{\mu}_i = \alpha_i \left(\mathbf{E}_i - \sum_{j \neq i} \mathbf{T}_{ij} \boldsymbol{\mu}_j \right) \quad (19)$$

Here \mathbf{T}_{ij} is the dipolar interaction function given as follows.

$$\mathbf{T}_{ij} = r_{ij}^{-3} \mathbf{I} - 3r_{ij}^{-5} \mathbf{r}_{ij} \mathbf{r}_{ij} \quad (20)$$

Equation 19 can be rearranged to the following form:³⁹

$$\mathbf{C} \boldsymbol{\mu} = \mathbf{E} \quad (21)$$

where \mathbf{C} , a matrix containing $N \times N$ tensors each of 3×3 size, has the following form:

$$\begin{bmatrix} \alpha_1^{-1} & \mathbf{T}_{12} & \cdots & \mathbf{T}_{1N} \\ \mathbf{T}_{21} & \alpha_2^{-1} & \cdots & \mathbf{T}_{2N} \\ \cdots & \cdots & \cdots & \cdots \\ \mathbf{T}_{N1} & \cdots & \cdots & \alpha_N^{-1} \end{bmatrix} \quad (22)$$

Equation 21 can be written as

$$\boldsymbol{\mu} = \mathbf{B} \mathbf{E} \quad (23)$$

where \mathbf{B} , the inverse of the \mathbf{C} matrix, is known as the relay tensor matrix.³⁹ The induced electric moments in the molecule can be expressed as a linear sum of the induced electric moments on atoms. Therefore,

$$\boldsymbol{\mu}_{\text{mol}} = \sum_i \boldsymbol{\mu}_i = \sum_i \sum_j \mathbf{B}_{ij} \mathbf{E} = \alpha_{\text{mol}} \mathbf{E} \quad (24)$$

where molecular and atomic polarizabilities are obtained as

$$\alpha_{\text{mol}} = \sum_i \sum_j \mathbf{B}_{ij} \quad (25)$$

$$\alpha_i = \sum_j \mathbf{B}_{ij} \quad (26)$$

This equation permits evaluation of the individual elements of the molecular polarizability tensor from a knowledge of spherical atomic polarizabilities and the molecular geometry.³⁹

The utility of the ADI model for ROA calculations arises from the possibility of casting the rotatory polarizability tensor, $\boldsymbol{\beta}$, and the quadrupole polarizability tensor, \mathbf{A} , in terms of the relay tensor matrix, \mathbf{B} .

The scalar rotatory parameter, β , which is the mean of the tensor $\boldsymbol{\beta}$, has been shown to be³⁶

$$\beta = 1/6 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \mathbf{r}_{ij} \cdot \mathbf{b}_{ij} \quad (27)$$

where \mathbf{b}_{ij} is a vector with components $(B_{ij}^{zy} - B_{ij}^{yz}, B_{ij}^{xz} - B_{ij}^{zx}, B_{ij}^{yx} - B_{ij}^{xy})$. Here, for instance, B_{ij}^{zy} represents an element of the third row and second column in the tensor between atoms i and j of the relay tensor matrix \mathbf{B} . By extending the principle which underlies eq 27, the tensor $\boldsymbol{\beta}$ can be formulated as

$$\boldsymbol{\beta} = 1/2 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \mathbf{r} \mathbf{b}_{ij} \quad (28)$$

where $\mathbf{r} \mathbf{b}$ is the dyadic formulated from the vectors \mathbf{r}_{ij} and \mathbf{b}_{ij} .

At this point it is necessary to recognize that $\boldsymbol{\beta}$ as formulated in eq 28 is origin independent. However, since the magnetic moment is origin dependent, it is essential to incorporate this character into the $\boldsymbol{\beta}$ tensor (this was pointed out to us by Dr. L. D. Barron). The elements of the $\boldsymbol{\beta}$ tensor are, therefore,

modified as follows:

$$\beta_{\alpha\beta} \rightarrow \beta_{\alpha\beta} - 1/2 \epsilon_{\beta\gamma\delta} \sum_i^N r_{i\gamma} \alpha_{i\alpha\delta} \quad (29)$$

where ϵ is a two-valued Levi-Civita density function. In other words, eq 28 becomes

$$\boldsymbol{\beta} = 1/2 \left[\sum_{i=1}^{N-1} \sum_{j=i+1}^N \mathbf{r} \mathbf{b}_{ij} - \sum_i^N (\mathbf{r}_i \times \widetilde{\alpha}_i) \right] \quad (30)$$

where the tilde denotes the transpose; the atomic polarizability tensor can be obtained from eq 26.

The induced quadrupolar contributions to the ROA are obtained in a similar fashion by adaptation of the ADI model. Applequist⁴⁰ has shown that the molecular quadrupole polarizability, \mathbf{A} , is related to the relay tensor matrix \mathbf{B} through the equation

$$\mathbf{A} = \sum_{i,j} (3/2 \mathbf{r}_i \mathbf{B}_{ij} + 3/2 \widetilde{\mathbf{r}_i} \mathbf{B}_{ij} - \mathbf{I} \mathbf{r}_i \cdot \mathbf{B}_{ij}) \quad (31)$$

Owing to the origin dependence of the quadrupole moment, it has been shown that the elements of the \mathbf{A} tensor should be modified¹ as follows:

$$\begin{aligned} A_{\alpha\beta\gamma} \rightarrow & A_{\alpha\beta\gamma} + 3/2 \sum_i^N r_{i\beta} \alpha_{i\alpha\gamma} \\ & + 3/2 \sum_i^N r_{i\gamma} \alpha_{i\alpha\beta} - \sum_i^N r_{i\delta} \alpha_{i\alpha\gamma} \delta_{\beta\gamma} \end{aligned} \quad (32)$$

where δ is the Kronecker δ .

Thus it is apparent that eq 25–32 offer a particularly powerful means of evaluating the tensors $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, and \mathbf{A} which are required for computing the scattered intensity components described by eq 12 and 13. Computation of the Raman CIDs (eq 17 and 18) requires evaluation of the normal coordinate derivatives of each of these tensors. From eq 25

$$\alpha_{\text{mol}} = \partial \alpha_{\text{mol}} / \partial Q_k = \partial \mathbf{B} / \partial Q_k = -\mathbf{B} \mathbf{C}' \quad (33)$$

where \mathbf{C}' is the normal coordinate derivative of the matrix \mathbf{C} in eq 22. Similarly, from eq 30

$$\begin{aligned} \boldsymbol{\beta}' = \partial \boldsymbol{\beta} / \partial Q_k = & 1/2 \left[\sum_{i=1}^{N-1} \sum_{j=i+1}^N (\mathbf{r}' \mathbf{b}_{ij} + \mathbf{r} \mathbf{b}_{ij}') \right. \\ & \left. - \sum_i^N (\mathbf{r}_i' \times \widetilde{\alpha}_i) - \sum_i^N (\mathbf{r}_i \times \widetilde{\alpha}_i') \right] \end{aligned} \quad (34)$$

Likewise, a lengthy yet simple expression for the normal coordinate derivatives of \mathbf{A} can be obtained directly from eq 31 and 32.

Optimization of Atomic Polarizability Derivative Tensors

Evaluation of the individual elements of the $\boldsymbol{\alpha}'$, $\boldsymbol{\beta}'$, and \mathbf{A}' tensors (cf. eq 25–34) needs to be discussed in some detail. The derivative of \mathbf{C} (eq 21 and 22) is required and represented by^{40,41}

$$\mathbf{C}' = \partial \mathbf{C} / \partial Q$$

$$= \begin{bmatrix} -\alpha_1^{-2} \cdot \nabla_Q \alpha_1 & \mathbf{T}'_{12} & \cdots & \mathbf{T}'_{1N} \\ \mathbf{T}'_{21} & -\alpha_2^{-2} \nabla_Q \alpha_2 & \cdots & \mathbf{T}'_{2N} \\ \cdots & \cdots & \cdots & \cdots \\ \mathbf{T}'_{N1} & \mathbf{T}'_{N2} & \cdots & -\alpha_N^{-2} \nabla_Q \alpha_N \end{bmatrix} \quad (35)$$

where $\nabla_Q \alpha_i$ represents the derivative of α_i with respect to normal coordinates, Q_k . The off-diagonal tensors \mathbf{T}'_{ij} in the \mathbf{C}' matrix, obtained by differentiating eq 20 with respect to the normal coordinates, Q_k , involve the terms $\partial \mathbf{r}_{ij} / \partial Q_k$ which are obtained from

$$\partial \mathbf{r}_{ij} / \partial Q = \Delta \mathbf{D} \mathbf{L} \quad (36)$$

Here Δ is a row matrix with +1 in column j , -1 in column i ,

and zero in all other locations; \mathbf{D} is the inverse of the familiar Wilson \mathbf{B} matrix⁴⁹ which is constructed from s-vectors; and \mathbf{L} is the eigenvector matrix of the vibrational secular equation. While the evaluation of \mathbf{T}'_{ij} does not involve any approximations (except those inherent in the normal coordinate analysis), an evaluation of the diagonal tensors of the \mathbf{C}' matrix does require an approximation. The diagonal tensors of the \mathbf{C}' matrix are represented as follows.

$$-\alpha_i^{-2} \nabla_Q \alpha_i = \begin{bmatrix} -\alpha_i^{-2} & 0 & 0 \\ & -\alpha_i^{-2} & 0 \\ \text{sym} & & -\alpha_i^{-2} \end{bmatrix} \times \begin{bmatrix} (\partial \alpha_i^{xx} / \partial Q_k) & (\partial \alpha_i^{xy} / \partial Q_k) & (\partial \alpha_i^{xz} / \partial Q_k) \\ & (\partial \alpha_i^{yy} / \partial Q_k) & (\partial \alpha_i^{yz} / \partial Q_k) \\ \text{sym} & & (\partial \alpha_i^{zz} / \partial Q_k) \end{bmatrix} \quad (37)$$

In the context of the ADI model, the elements $\partial \alpha_i^{g'g} / \partial Q_k$ for $g \neq g'$ can be considered to arise from the interaction function \mathbf{T}'_{ij} and as such are already included in eq 33. Therefore, in eq 37 the off-diagonal elements $\partial \alpha_i^{g'g} / \partial Q_k$ have zero values. The remaining nonvanishing normal coordinate derivatives $\partial \alpha_i^{g'g} / \partial Q_k$ are related to the internal coordinate derivatives by

$$\partial \alpha_i^{g'g} / \partial Q_k = \sum_l \partial \alpha_i^{g'g} / \partial R_l \cdot L_{lk} \quad (38)$$

where R_l represents the l th internal coordinate and L_{lk} represents the elements of the \mathbf{L} matrix as used in eq 36. A knowledge of these $\partial \alpha_i^{g'g} / \partial Q_k$ parameters is necessary to obtain the α' , β' , and \mathbf{A}' tensors, but there is no a priori source which can provide their values.

Applequist and Quicksall⁴¹ have used experimental Raman intensities in an attempt to obtain optimized values for $\partial \alpha_i^{g'g} / \partial Q_k$ in a series which included methane and several halomethanes. Such an optimization procedure includes the evaluation of Raman scattering parameters from eq 33 with trial values of $\partial \alpha_i / \partial R_l$. The appropriate Raman scattering parameters are the mean derivative $\bar{\alpha}'_{\text{mol}}$ and the anisotropy γ'^2 or the depolarization ratio ρ for all Raman active modes of the molecule:

$$\begin{aligned} \bar{\alpha}'_{\text{mol}} &= 1/3 (\alpha'_{\text{mol}}{}^{xx} + \alpha'_{\text{mol}}{}^{yy} + \alpha'_{\text{mol}}{}^{zz}) \\ \gamma'^2 &= 1/2 \{ (\alpha'_{\text{mol}}{}^{xx} - \alpha'_{\text{mol}}{}^{yy})^2 \\ &+ (\alpha'_{\text{mol}}{}^{yy} - \alpha'_{\text{mol}}{}^{zz})^2 + (\alpha'_{\text{mol}}{}^{zz} - \alpha'_{\text{mol}}{}^{xx})^2 \\ &+ 6 [(\alpha'_{\text{mol}}{}^{xy})^2 + (\alpha'_{\text{mol}}{}^{xz})^2 + (\alpha'_{\text{mol}}{}^{yz})^2] \} \\ \rho &= 3\gamma'^2 / (45\bar{\alpha}'_{\text{mol}} + 4\gamma'^2) \end{aligned} \quad (39)$$

The differences between calculated and experimental values of these parameters are used to modify the trial values of $\partial \alpha_i / \partial R_l$ until the calculated and the observed Raman scattering parameters are found to be in good agreement. The resultant $\partial \alpha_i / \partial R_l$ values are assumed to be good approximations of the true values if they predict the observed quantities reasonably well.

In this optimization process, however, the number of variables is generally larger than the number of experimental observables available. Applequist and Quicksall⁴¹ incorporated the following approximations to accommodate this situation.

(1) The parameters $\partial \alpha_i^{g'g} / \partial R_l$ for $g = x, y,$ and z are assumed to be equal so that each internal coordinate derivative tensor, $\partial \alpha_i / \partial R_l$, is represented by a single scalar quantity $\partial \alpha_i / \partial R_l$. As a result, the diagonal values $\partial \alpha_i^{g'g} / \partial Q_k$ in eq 37 are degenerate.

(2) The parameters $\partial \alpha_i / \partial R_l$ are assumed to vanish unless

the internal coordinate, R_l , represents a stretching coordinate containing atom i .

(3) The nonvanishing $\partial \alpha_i / \partial R_l$ values for an atom i are assumed to remain independent of the environment, i.e., the $\partial \alpha_i / \partial R_l$ parameters are transferable in a series of similar molecules. These approximations reduce the number of $\partial \alpha_i / \partial R_l$ parameters to a considerable extent. For example, with a molecule such as HCB₃ClF, these approximations reduce the procedure to optimization of only five parameters, namely, $\partial \alpha_{\text{H}} / \partial R_{\text{C-H}}$, $\partial \alpha_{\text{F}} / \partial R_{\text{C-F}}$, $\partial \alpha_{\text{Cl}} / \partial R_{\text{C-Cl}}$, $\partial \alpha_{\text{Br}} / \partial R_{\text{C-Br}}$, and $\partial \alpha_{\text{C}} / \partial R$, instead of 150. Applequist and Quicksall⁴¹ have optimized these five parameters using experimental Raman intensities of 29 symmetric modes in methane and several halomethanes.

Although approximations are unavoidable if the number of variables is to be reduced to a manageable size, sound justification for such approximations is required. One consequence of this particular set of approximations is the ambiguous nature of the internal coordinate derivative of the polarizability for the central atom, e.g., $\partial \alpha_{\text{C}} / \partial R$ in substituted methanes. Since the carbon atom is bonded to different types of atoms in halomethanes, assignment of only one parameter, $\partial \alpha_{\text{C}} / \partial R$, to the carbon atom is ambiguous. This ambiguity would vanish if optimization of the independent values of $\partial \alpha_{\text{C}} / \partial R$ for all bonds to carbon were carried out. However, since such derivatives are dependent on the inherently different electrostatic interactions which prevail in each molecule, it is highly doubtful that such derivatives have the same values in a series of molecules such as the substituted methanes. Since these particular approximations appear to degrade the transferability of the polarizability derivatives, they are not really suitable for use with the ADI model. We present an alternate procedure which not only preserves parameter transferability but also capitalizes on the interaction feature of the ADI model.

Some molecular properties when expressed in Cartesian space are consistently found to be fairly independent of the environment. For instance, atomic force constants⁵⁰ and atomic polar tensors,⁵¹ which are Cartesian derivatives of the molecular potential energy and the electric moment, respectively, have been shown to be transferable, to some extent, among similar molecules. If the Cartesian derivatives of the molecular potential energy and electric moment were further reduced to the Cartesian derivatives of the corresponding atomic contributions, the latter parameters unambiguously become characteristic of the atoms and remain independent of the environment. With respect to molecular polarizability, the ADI model permits reduction of the molecular polarizability as well as its derivatives to atomic polarizability components and also incorporates the interatomic interactions through a reasonable interaction function. Therefore, the Cartesian derivative tensors of atomic polarizability would certainly be characteristic of the atoms and transferable within a series of molecules.

Accordingly, we assume that each atom in a vibrating molecule has a characteristic Cartesian polarizability derivative tensor $\nabla_X \alpha_i$, as defined in

$$\nabla_X \alpha_i = \begin{bmatrix} \frac{\partial \alpha_i^{xx}}{\partial x_i} & \frac{\partial \alpha_i^{xy}}{\partial y_i} & \frac{\partial \alpha_i^{xz}}{\partial z_i} \\ \frac{\partial \alpha_i^{xy}}{\partial x_i} & \frac{\partial \alpha_i^{yy}}{\partial y_i} & \frac{\partial \alpha_i^{yz}}{\partial z_i} \\ \frac{\partial \alpha_i^{xz}}{\partial x_i} & \frac{\partial \alpha_i^{yz}}{\partial y_i} & \frac{\partial \alpha_i^{zz}}{\partial z_i} \end{bmatrix} \quad (40)$$

where $\nabla_X \alpha_i$ represents the derivative of α_i with respect to the Cartesian coordinates \mathbf{X} . Then the derivatives $\nabla_Q \alpha_i$ required in eq 33 and 35 can be expressed in terms of the $\nabla_X \alpha_i$ tensors:

$$\nabla_Q \alpha_i = \nabla_X \alpha_i \mathbf{DL} \quad (41)$$

where \mathbf{D} and \mathbf{L} are as defined in eq 36. In reality, the derivative of an atomic polarizability tensor with respect to the Cartesian coordinates yields a higher order tensor than shown in eq 40. The simplified form of eq 40 results from our extension of some of the constraints of the ADI model. (1) Terms such as $\partial\alpha_i/\partial X_j$, where X_j represents the position vector of atom j , vanish for $i \neq j$. These terms vanish since changes in atomic polarizability caused by neighboring atom displacements from equilibrium positions are presumed to arise only through changes in the dipolar interaction function. Such effects are automatically incorporated in the T'_{ij} terms in eq 35. (2) Terms such as $\partial\alpha_i^{gg'}/\partial X_j$ for $g \neq g'$ are also incorporated into the dipolar interactions, so as to be consistent with the basic framework of the ADI model. These constraints, thereby, become an integral part of the framework of the ADI model as applied to the vibrational problem; they are expressed mathematically as

$$\partial\alpha_i/\partial X_j = \partial\alpha_i^{gg'}/\partial X_j \cdot \delta_{gg'} \cdot \delta_{ij} \quad (42)$$

where δ is Kronecker δ .

It is now appropriate to examine the optimization procedures in further detail. Applequist and Quicksall⁴¹ made the approximation that $\partial\alpha_i^{xx}/\partial Q_k$, $\partial\alpha_i^{yy}/\partial Q_k$, and $\partial\alpha_i^{zz}/\partial Q_k$ (eq 37) for any k th normal coordinate are degenerate. This approximation implies that all elements in each column of the tensor $\nabla_X\alpha_i$ (eq 40) are equal. Consequently, unit displacement of atom i in the x direction, for example, would produce a uniform change in its polarizability sphere in all three directions. In other words, the atomic polarizability would retain its spherical symmetry during atomic displacements. This, however, is a gross approximation because there are several factors which distort the atomic polarizability sphere during molecular vibrations. In the ADI model, some of these effects are taken into account through the normal coordinate derivative of the dipolar interaction function, T'_{ij} . Effects which are not incorporated into T'_{ij} include incoherent displacements of a nucleus with its associated polarizability and charge reorganization in various parts of the molecule. The ADI model, and for that matter any classical model, does not take cognizance of these effects because, in a classical description of molecular vibrations, a molecule is considered to consist of rigid atoms where the interactions among electrons on different atoms are ignored. In a quantum mechanical picture, during a molecular vibration the changes in overlap of atomic orbitals result in changes in population densities of electrons. These effects result in the so-called "nonfollowing" contributions⁵² to the polarizability sphere. Such effects on the electric moment have been well discussed in the literature.⁵³ Although explicit inclusion of nonfollowing contributions in a classical model is not practical, these effects could be incorporated in a gross sense, either by introducing new constraints or by removing some of the constraints present in the model. For example, in the present situation we could introduce an approximation to this type of an effect by not requiring the elements in each column of the tensor $\nabla_X\alpha_i$ to be equal. This procedure would ensure that during atomic displacements the atomic polarizability sphere would be distorted, hopefully, by an amount equivalent to that due to the nonfollowing effects. As a result the terms $\partial\alpha_i^{gg'}/\partial Q_k$ for $g = x, y,$ and z would not be degenerate.

We suggest that the optimization of the $\nabla_X\alpha_i$ tensors is more advantageous than optimization of $\partial\alpha_i/\partial R_l$ values because not only are the $\nabla_X\alpha_i$ tensors more prone to be transferable but no problematical approximations are involved. It is apparent that the constraints involved in formulating the $\nabla_X\alpha_i$ tensor, in eq 40, are introduced as an integral part of the basic framework of the ADI model, and do not constitute a separate set of approximations. Moreover, as seen from eq 41,

the complete set of $\partial\alpha_i/\partial R_l$ values can also be obtained from the optimized $\nabla_X\alpha_i$ tensors.

The utility of our proposed procedure now depends on resolving the problem of the number of variables in the optimization process. As an example, for HCBrc1F, we need to construct a $\nabla_X\alpha_i$ tensor for each of the five atoms. Since each such tensor requires nine independent parameters, a total of 45 parameters needs to be optimized from experimental Raman scattering parameters. If "nonfollowing" contributions are ignored, only three parameters are required to define the complete tensor for each atom so that only 15 parameters would need to be optimized for HCBrc1F.

The optimized tensors which predict a consistent set of Raman scattering parameters close to the experimental values can be considered as being close to the true ones. The final set of these polarizability derivative tensors permits the evaluation (cf. eq 25-34) of the tensors α' , β' , and A' . Thus the parameters required for computation of Raman CIDs (eq 17 and 18) can be obtained through an ADI model using measured Raman intensities and depolarization ratios for the molecule of interest.

Discussion

When considering application of this ADI model to the computation of the Raman CIDs in an arbitrary chiral molecule, it is apparent that several practical limitations will prevail if additional simplifications are not introduced. First of all, a comprehensive normal coordinate analysis is required. Since molecules of interest to ROA are of C_n , D_n , T , O , or I symmetry, reliable vibrational analyses are quite difficult. Although some progress has been made in empirically optimizing the molecular force field of simple molecules using vibrational band contours and intensities,⁵⁴ such techniques are not practical with the terpenes,⁵ camphors,^{8,13} phenyl-substituted ethanes,^{6,7,9,10,12} aryl sulfoxides,¹⁵ or tartaric acid derivatives¹⁶ where Raman CIDs have been observed. A utilitarian approach which consists of treating simple model molecules and using the results in a semiquantitative fashion with more complex molecules by assuming perturbed group modes, completely transferable force constants, and/or kinematic coordinates may be the only way out of this dilemma. Since the computation of Raman CIDs will become less reliable if the normal coordinates are ill defined, it appears that this factor is likely to be the major limitation to effective employment of this model or any other model for VOA in general.

A second difficulty is encountered in optimization of the Cartesian derivative tensors of atomic polarizability, $\nabla_X\alpha_i$. This optimization depends largely on our assumption of transferability of atomic polarizabilities and their Cartesian derivatives among similar molecules. A reasonable degree of transferability in atomic polarizabilities has been demonstrated by their utility in prediction of molecular polarizability and molar rotation. Unfortunately, however, there are several types of atoms, most noticeably S and C (unsaturated), for which ADI optimized atomic polarizabilities are not presently available. For the $\nabla_X\alpha_i$ tensors, the situation is more complex, however, since accurate experimental values of Raman intensities and depolarization ratios are required for optimization. Except for a few small molecules there are few reliable data on Raman scattering parameters in the literature and, moreover, acquisition of such data for most chiral molecules would be a formidable task. Reliance on transferability for Cartesian derivative tensors from simple molecules to complex ones must be adopted. It should be remembered, however, that the optimization of transferable $\nabla_X\alpha_i$ tensors from limited experimental data may not be unique. The only solution to this problem is to undertake a systematic measurement of Raman intensities and optimization of these tensors in a large series of simple chemically similar molecules.

It is appropriate to inquire about the reliability of the computed Raman CIDs in the event that all the necessary parameters are available. Although resort to comparison with experimental observation is the only means of really answering such a query, some insight into the situation can be gained by consideration of the inherent capacities of the model. Even though the ADI model assumes spherically symmetrical atomic polarizabilities, the intramolecular interactions are reasonably well represented by the dipolar interactions between all pairs of atomic polarizability spheres. Such a representation might appear crude from a quantum mechanical viewpoint but is quite reasonable classically. A major difficulty, however, is incorporation of the *intermolecular* interactions. The model, as developed, assumes the molecule to be free except for the gross medium dependence of refractive index. The small magnitude of Raman CIDs, however, requires that measurements be made on condensed phases where intermolecular interactions are not negligible. Thus incorporation of macroscopic medium effects will be required for detailed comparison of computed CIDs with observed values. It is not clear as to how such effects are most effectively accommodated since a simple Lorentz factor or other similar parameter is not likely to be sufficient. Hopefully, such effects will be minor in some cases at least and simple consideration of the array of molecular geometric possibilities will be adequate for comparison with experiment.

After consideration of these factors, the prospects of applying the complete ADI treatment to very many molecules do not appear very practical. Thus a much more approximate approach would seem to have considerable utility. If the necessary atomic polarizabilities and a molecular structure are available, a numerical evaluation of the α' , β' , and A' tensors can be carried out where the normal vibration is simulated by a suitable distortion of the structure of the molecule or molecular segment. Calculation of the Raman CIDs then involves computation of α , β , and A tensors for equilibrium and for distorted configurations and numerical evaluation of the gradients of the resultant tensors. This procedure avoids a priori knowledge of the normal coordinates and the $\nabla \chi \alpha_i$ tensors but the resultant CIDs can be only qualitative, at best. By sacrificing accuracy and, to some extent, reliability as well, the computations can easily be extended to any large molecule wherein the atomic polarizabilities are known. The results of the numerical method, although qualitative in nature, should be more reliable and more generally applicable than those for a simple two-group model. A direct comparison of the results of the complete analytical procedure with those of the numerical procedure is worthwhile. If a correspondence indeed exists, the numerical procedure will become quite useful because it can be extended to large molecules fairly easily. Treatment of large molecules of biological significance may even be practical.

In the subsequent article, the results of application of the analytical procedure are presented for HCB₂ClF and DCB₂ClF. The utility of the numerical procedure is under active investigation and will be communicated soon.

Acknowledgments. The authors gratefully acknowledge the financial support for this work provided by the National Science Foundation and helpful correspondence with Dr. L. D. Barron.

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