

An interacting segment model of molecular electric tensor properties: Theory and application to electric dipole moments of the halogenated methanes^{a)}

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A model is developed to describe trends in molecular properties such as electric dipole moment, polarizabilities, and hyperpolarizabilities for series of structurally related molecules. The model takes account of intramolecular electrostatic interactions, which give rise to induced electric moments in the various segments of the molecule. For this purpose each molecular segment is ascribed a set of "bare" electric tensor properties, which describe the hypothetical situation where intersegment interactions are absent, and a corresponding set of "dressed" properties, which include the effects of the intramolecular field. Any overall molecular electric tensor property is then obtained by summing the appropriate dressed segment properties. After theoretical development the model is used to fit electric dipole moment data for the 12 halogenated methanes CX_nY_{4-n} ($X, Y = H, F, Cl; n = 0-4$), for which a simple bond additivity model is known to be inadequate and which severely test any theory of induced dipole moments. The results of such an analysis are highly satisfactory and indicate that the model should also give an adequate description of higher-order electric tensor properties.

I. INTRODUCTION

Many significant molecular processes depend on the interaction between a molecule and a uniform electric field, and can conveniently be described by expanding the total electric dipole moment $\mu(\mathbf{E})$ in powers of the electric field strength \mathbf{E} :

$$\mu(\mathbf{E}) = \mu + \alpha \mathbf{E} + \zeta \beta \mathbf{E}^2 + \lambda \gamma \mathbf{E}^3 + \dots \quad (1)$$

The leading term μ is the permanent electric dipole moment of the molecule in the absence of the field \mathbf{E} and subsequent terms involve the molecular polarizability tensor α and molecular hyperpolarizability tensors β , γ , \dots .¹ It suffices in the present discussion to regard \mathbf{E} as a dc field, in which case ζ , λ , \dots are numbers of order unity whose assignment depends on convention.² Extension to the case of time-dependent fields is straightforward, involving only the definition of \mathbf{E} as a field amplitude and reassignment of the values of ζ , λ , \dots . These details are set out in the Appendix.

Experimental data on the molecular electric properties μ , α , β , and γ are now available from a wide range of sources,¹ and permit comparisons to be made from molecule to molecule. For simple molecules, such as those of the first-row elements, *ab initio* quantum mechanical calculations are able to predict the properties μ and α and are generally consistent with corresponding experimental data. The few *ab initio* computations of molecular β and γ data which exist yield only order-of-magnitude agreement with experiment. As molecules increase in size and complexity accurate *ab initio* calculations become increasingly difficult, so that it is customary to analyze observed results for such molecules in terms of semiempirical correlations with other chemically and physically similar molecules. The most widely used correlation scheme is the bond ad-

ditivity approximation (BAA), in which a molecule is subdivided into a number of segments i , corresponding to its individual bonds and/or functional groups, and a given molecular tensor property χ is assumed to be the sum of its corresponding segment tensors χ_i :

$$\chi = \sum_i \chi_i \quad (2)$$

The application of such an approximation to molecular electric properties has a long history, particularly in relation to electric dipole moments μ and to the isotropic part α of the molecular polarizability tensor. In the former case the fact that Eq. (2) is a vectorial sum of segment electric dipole moments μ_i has enabled electric dipole moment determinations to provide useful information about molecular geometries.³ In the latter case α conforms closely to scalar bond additivity laws within a given homologous series of molecules and is recognized as a characteristic molecular property which is independent of structural geometry.^{4,5} The BAA has also been applied to the anisotropic part of the polarizability α and extensively employed in studies of molecular structure.⁵ More recently versions of the BAA have been proposed⁶ and applied⁷⁻¹⁰ with mixed success to the hyperpolarizabilities β and γ , which can be obtained¹ from various nonlinear optical experiments.

The conceptual division of a molecule into individual segments, which is the basis for the BAA, is inherent in discussions of such accepted and useful quantities as bond energies, group vibrational frequencies, and molecular geometric parameters. For the BAA to be valid for electric tensor properties it is necessary that characteristic electric tensors can be assigned to individual segments and that these should not be modified by interactions with neighboring segments. There is no *a priori* justification for the assumption of negligible electrostatic intersegment interaction, as can be demonstrated by a simple calculation. Consider, for example, the electric dipole moment $\Delta\mu_A$ induced in a molecular segment A by its interaction with an adjacent segment B at distance R . The electric field at A due to the electric

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dipole moment μ_B of segment B is approximately $\mu_B R^{-3}$, so that the induced moment $\Delta\mu_A$ is of order $\alpha_A \mu_B R^{-3}$, where α_A is the polarizability (assumed isotropic) of segment A. Both α_A and R^3 are measures of a molecular bond or group volume and their ratio is of order unity, so that the induced moment $\Delta\mu_A$ is comparable in magnitude to its source μ_B . Attempts to assess the role of such inductive effects in determining molecular electric dipole moments have been reviewed by Smith.³ Several workers¹¹⁻¹⁵ have indicated the consequences of neglecting interactions between segments within a molecule, with regard to molecular polarizability. It is a feature of any treatment of intramolecular electrostatic interactions that αR^{-3} , the parameter which scales the effect of such interactions, is comparable in magnitude to unity and that the interactions are therefore not in general negligible.

In view of the above it is remarkable that simple BAA schemes have achieved their generally accepted level of success in treating electric dipole moment and polarizability data. The early criticism of Pitzer¹¹ that "some fortuitous cancellation of conflicting factors" probably accounts for the applicability of the BAA to a limited range of molecules, remains valid. Such a situation is indeed suggested by the need to assign, within the framework of the BAA, different bond and group polarizabilities for markedly different molecular environments⁵ and by the inadequacy of the simple BAA in treating the electric dipole moments of such molecules as those in the halogenated methane series.³ It would appear that empirical electric tensor properties for a given species of segment, deduced from experimental data for a series of molecules, must contain, in addition to the intrinsic segment contribution, a substantial but undetermined contribution arising from interactions between segments.

There is some recent theoretical support for the proposition that individual bond contributions to molecular electric dipole moments^{16,17} and polarizabilities¹⁸ may in certain instances be identified and transferred from molecule to molecule. These studies are based on localized molecular orbital theory and are confined to the contributions of $\mu(\text{C-H})$, $\alpha(\text{C-H})$, and $\alpha(\text{C-C})$ in simple hydrocarbon molecules.

A further factor which may assist the apparent validity of the BAA in certain circumstances arises from local field effects in condensed phases. Discrepancies have recently been noted¹⁵ between the gas- and liquid-phase results obtained from light scattering or electric birefringence measurements of simple alkanes. The discrepancies have been attributed¹⁵ to the more symmetrical environment of a molecular segment when it is surrounded by a random distribution of nearby molecules in the condensed phase, compared to the relatively anisotropic environment of the segment in an isolated (gas-phase) molecule. A similar argument¹⁹ might explain why a simple BAA scheme appears to be much more successful in fitting hyperpolarizability data obtained in condensed phases¹⁰ than in fitting those determined for isolated molecules in the gas phase.⁷⁻⁹ Our present concern is with the understanding of electric dipole

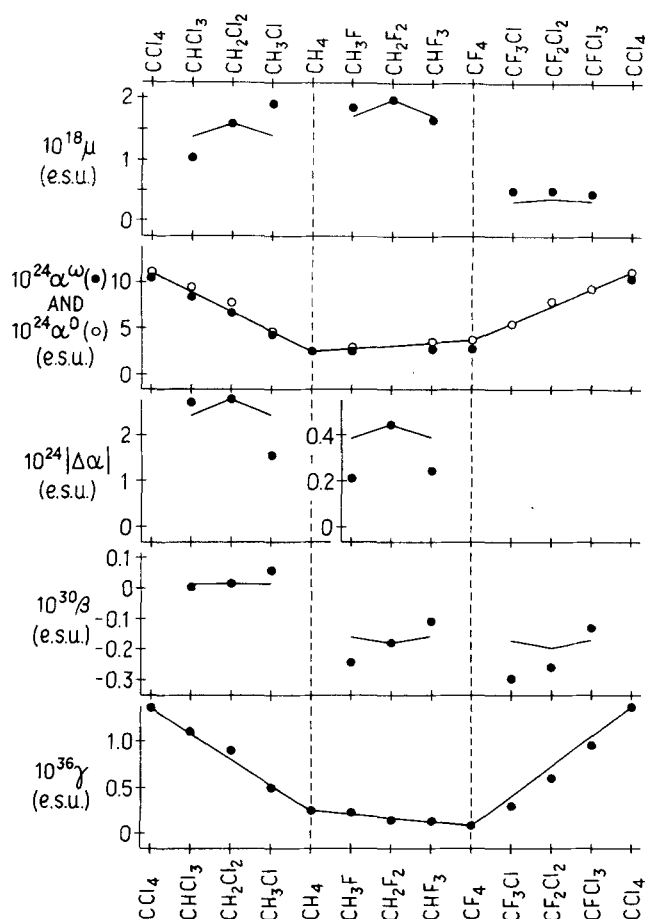


FIG. 1. Electric dipole properties of the halogenated methanes. The definitions of the molecular observables, μ , α^ω , α^0 , $\Delta\alpha$, β , and γ are given in the Appendix and sources of data are indicated in the text. The solid lines are fitted by application of the simple bond additivity approximation (BAA) to the data for CH_2X_2 (in the case of μ , $|\Delta\alpha|$, and β) and CX_4 molecules (in the case of α^0 and γ), with the assumption of tetrahedral bond angles.

properties of isolated molecules, so that in the discussion which follows only gas-phase experimental data are considered.

We shall concentrate attention on the halogenated derivatives of methane, which have provided a severe test of semiempirical correlation schemes for electric dipole moments μ and, more recently, for polarizabilities α and hyperpolarizabilities β and γ . The understanding of trends in the electric dipole moments within this series of molecules has advanced relatively little since the classic work of Smyth and McAlpine²⁰ in 1933, in which approximate account was taken of mutual inductive effects between C-H, C-F, and C-Cl bond dipole moments. Of subsequent developments³ the best fit to experimental electric dipole moments of the halogenated methanes appears to have been achieved by a model²¹ which treats the inductive effect semiclassically in terms of screened nuclear charges. Although this model proves consistent with dipole moment data for molecules $\text{CH}_n\text{X}_{4-n}$ ($\text{X} = \text{halogen}$), it is inadequate for molecules such as $\text{CF}_n\text{Cl}_{4-n}$, in which inductive contributions are known²⁰ to be dominant. In Fig. 1 we summarize the molecular observables of a number of electric dipole

tensor properties, for 12 chloro and fluoro derivatives of methane. The observables and their sources of determination²² are the permanent electric dipole moment μ from microwave spectra and dielectric constant data,^{23,24} the mean optical polarizability α^ω determined from refractivity data for $\lambda \sim 640$ nm,²⁵⁻²⁷ the mean static polarizability α^0 from dielectric constant data,^{1,28-30} the polarizability anisotropy parameter²² $|\Delta\alpha| = 3\alpha^\omega|\kappa|$ from studies of depolarization of Rayleigh scattering³¹ and from the temperature dependence of the electric birefringence,⁷ and the hyperpolarizabilities²² β and γ from dc-induced second harmonic generation studies.^{9,32} Also shown in Fig. 1 are lines indicating the application of a simple BAA correlation scheme. For the isotropic properties α^ω , α^0 , and γ the BAA predicts a linear relationship in the number of substituents, whereas anisotropic properties such as μ , $|\Delta\alpha|$, or $\beta(=\chi)$, say) would be expected to fit relationships of the type $\chi(CX_3Y) = \chi(CXY_3) = \sqrt{3}/2\chi(CX_2Y_2)$, assuming tetrahedral valence angles. It is evident that α^ω and α^0 appear remarkably consistent with the BAA, and that the trends in γ are also well represented by the BAA. The anisotropic properties μ , $|\Delta\alpha|$, and β , on the other hand, are noteworthy for their marked inconsistency with any simple BAA relationship. In fact, the BAA is hardly any better in these cases than a crude dimensional argument, which would predict that a given observable should be of the same order of magnitude within a set of molecules.

In this paper we develop an interacting-segment model (ISM) to seek better agreement with data such as those displayed in Fig. 1, without completely abandoning the simplicity of the BAA. The theoretical framework of the ISM is presented in Sec. II, and in Sec. III the model is applied in detail to the electric dipole moments of the halogenated methanes. A full-scale application of the ISM to all of the properties μ , α , $\Delta\alpha$, β , and γ shown in Fig. 1 will be reported in a subsequent paper.³³ A simplified version of the ISM has also been used to provide a preliminary analysis of the hyperpolarizabilities β of the halogenated methanes.³²

Very recently, Sundberg³⁴ has developed a group-dipole interaction model which is formally similar to our ISM.

II. THEORY

We consider a molecular model comprising a number of segments, corresponding to the individual bonds and/or functional groups of the molecule. In the absence of intersegment interactions we suppose that the segment i can be characterized by a set of "bare" segment parameters μ_i , α_i , β_i , γ_i , ...; these are tensor properties which conform to the symmetry of the isolated segment, so that a heteronuclear σ bond would have undressed tensor properties with C_∞ symmetry about the bond axis. When account is taken of intersegment interactions the same segment is characterized by a different set of parameters $\hat{\mu}_i$, $\hat{\alpha}_i$, $\hat{\beta}_i$, $\hat{\gamma}_i$, ... which are "dressed" by electrostatic interactions with neighboring segments of the molecule; the dressed tensors conform in general to a lower symmetry than that of the undressed segment, in view of the anisotropy of the intra-

molecular interactions. The resultant molecular tensor property χ will then be given by the sum over segments of the corresponding dressed segment tensors $\hat{\chi}_i$.

The electric dipole moment of the i th segment in the presence of a uniform applied electric field \mathbf{E} may be written in terms of the dressed tensors and the applied field:

$$\begin{aligned}\mu_i(\mathbf{E}) &= \hat{\mu}_i + \hat{\alpha}_i \mathbf{E} + \hat{\beta}_i \mathbf{E}^2 + \hat{\gamma}_i \mathbf{E}^3 + \dots \\ &= \sum_{n=0}^{\infty} \hat{\chi}_i^{(n)} \mathbf{E}^n.\end{aligned}\quad (3)$$

This equation is the same as Eq. (1) except that here it is applied to individual segments rather than the complete molecule, and ζ , λ have been set equal to unity. This choice of ζ and λ and the relevance of Eq. (3) to the case where time varying fields are present is discussed in the Appendix. $\hat{\chi}_i^{(n)}$ is defined by Eq. (3) to be $\hat{\mu}_i$, $\hat{\alpha}_i$, $\hat{\beta}_i$, $\hat{\gamma}_i$, ... for $n=0, 1, 2, 3, \dots$, respectively. $\mu_i(\mathbf{E})$ can equally well be expressed in terms of the total electric field \mathbf{E}_i which is the sum of the external applied field \mathbf{E} and fields produced at segment i by polarized neighboring segments. This expression involves the bare parameters of the i th segment and is

$$\begin{aligned}\mu_i(\mathbf{E}) &= \mu_i + \alpha_i \mathbf{E}_i + \beta_i \mathbf{E}_i^2 + \gamma_i \mathbf{E}_i^3 + \dots \\ &= \sum_{n=0}^{\infty} \chi_i^{(n)} \mathbf{E}_i^n.\end{aligned}\quad (4)$$

In Eqs. (3) and (4) we ignore nonclassical short-range interactions, of the type known³⁵ to be significant at distances as short as those between segments in a typical molecule, and assume intersegment interactions to be electrostatic in origin. In order more simply to evaluate \mathbf{E}_i we will further assume that all segment tensors are localized within the segment at a single point, which we call the "active center," and that contributions from segment electric multipoles of order higher than dipole can be neglected. Such drastic approximations must, of course, be justified by the ability of the model to reproduce molecular observables and to provide a set of empirical undressed parameters μ_i , α_i , β_i , γ_i , ... which are transferable, for a given species of bond or functional group, from one molecule to another. With these approximations the electric field $\mathbf{F}_i^{(ij)}$ induced at the active center of segment i due to the dressed point electric dipole $\hat{\mu}_j$ at the active center of a neighboring segment j is $T_{ij} \hat{\mu}_j$ or, more explicitly,^{36,37}

$$\mathbf{F}_i^{(ij)} = T_{ij} \hat{\mu}_j, \quad (5)$$

where

$$\begin{aligned}T_{ij} &= T_{j\ell\eta} = (3R_{ij\ell} R_{ij\eta} - R_{ij}^2 \delta_{\ell\eta}) R_{ij}^{-5}, \quad j \neq i \\ &= 0, \quad j = i,\end{aligned}\quad (6)$$

and \mathbf{R}_{ij} is the distance vector between the active centers of segments i and j .

The total electric field \mathbf{E}_i at a segment i , resulting from the application of a uniform electric field \mathbf{E} external to the molecule, may now be written as

$$\mathbf{E}_i = \mathbf{E} + \sum_{j \neq i} T_{ij} \mu_j(\mathbf{E}). \quad (7)$$

Combination with Eq. (3) yields

$$\mathbf{E}_i = \mathbf{E} + \sum_{j \neq i} \mathbf{T}_{ij} \sum_{n=0}^{\infty} \hat{\chi}_j^{(n)} \mathbf{E}^n. \quad (8)$$

Substitution of this expression for \mathbf{E}_i into Eq. (4) gives a polynomial in \mathbf{E} which can be compared term by term with Eq. (3) to yield the relations between the dressed and bare quantities which we seek. Equivalently, Eq. (8) can be used together with

$$\hat{\chi}_i^{(m)} = \sum_{n=0}^{\infty} \chi_i^{(n)} \lim_{\mathbf{E} \rightarrow 0} [\partial^m (\mathbf{E}_i^n) / \partial (\mathbf{E})^m] / m!, \quad (9)$$

which follows from Eqs. (3) and (4). Introducing an abbreviated notation³⁸ the results are

$$\hat{\mu}_i = \mu_i + \alpha_i \langle \mathbf{T} \cdot \hat{\mu} \rangle_i + \beta_i \langle \mathbf{T} \cdot \hat{\mu} \rangle_i^2 + \gamma_i \langle \mathbf{T} \cdot \hat{\mu} \rangle_i^3 + \dots, \quad (10)$$

$$\hat{\alpha}_i = (\alpha_i + 2\beta_i \langle \mathbf{T} \cdot \hat{\mu} \rangle_i + 3\gamma_i \langle \mathbf{T} \cdot \hat{\mu} \rangle_i^2 + \dots)(1 + \langle \mathbf{T} \cdot \hat{\alpha} \rangle_i), \quad (11)$$

$$\hat{\beta}_i = \alpha_i \langle \mathbf{T} \cdot \hat{\beta} \rangle_i + \beta_i [2 \langle \mathbf{T} \cdot \hat{\mu} \rangle_i \langle \mathbf{T} \cdot \hat{\beta} \rangle_i + (1 + \langle \mathbf{T} \cdot \hat{\alpha} \rangle_i)^2] + 3\gamma_i \langle \mathbf{T} \cdot \hat{\mu} \rangle_i [\langle \mathbf{T} \cdot \hat{\mu} \rangle_i \langle \mathbf{T} \cdot \hat{\beta} \rangle_i + (1 + \langle \mathbf{T} \cdot \hat{\alpha} \rangle_i)^2] + \dots, \quad (12)$$

$$\hat{\gamma}_i = \alpha_i \langle \mathbf{T} \cdot \hat{\gamma} \rangle_i + 2\beta_i [\langle \mathbf{T} \cdot \hat{\mu} \rangle_i \langle \mathbf{T} \cdot \hat{\gamma} \rangle_i + (1 + \langle \mathbf{T} \cdot \hat{\alpha} \rangle_i) \langle \mathbf{T} \cdot \hat{\beta} \rangle_i] + \gamma_i [3 \langle \mathbf{T} \cdot \hat{\mu} \rangle_i^2 \langle \mathbf{T} \cdot \hat{\gamma} \rangle_i + 6 \langle \mathbf{T} \cdot \hat{\mu} \rangle_i (1 + \langle \mathbf{T} \cdot \hat{\alpha} \rangle_i) \langle \mathbf{T} \cdot \hat{\beta} \rangle_i + (1 + \langle \mathbf{T} \cdot \hat{\alpha} \rangle_i)^3] + \dots. \quad (13)$$

The only contributions which are not specified in Eqs. (10)–(13) are those which would arise from terms in Eqs. (7) and (8) involving $\hat{\chi}_i^{(n)}$ and $\chi_i^{(n)}$ with $n > 3$, i. e., the above equations are complete through the order of hyperpolarizabilities $\hat{\gamma}_i$ and γ_i .

The above set of coupled equations forms the basis for attempts to determine self-consistent sets of dressed and undressed electric tensors from appropriate molecular observables. To achieve this it is desirable to rearrange the equations so that the expression for a given dressed tensor $\hat{\chi}_i^{(m)}$ is not functionally dependent on terms which contain $\langle \mathbf{T} \cdot \hat{\chi}^{(m)} \rangle_i$. In the present paper we consider this problem for the electric dipole moment $\hat{\mu}_i$. The corresponding situations for $\hat{\alpha}_i$, $\hat{\beta}_i$, and $\hat{\gamma}_i$ will be dealt with in a subsequent paper.³³

Equation (10) may be rearranged as follows:

$$\sum_j \{ \alpha_j^{-1} \delta_{ij} - \mathbf{T}_{ij} \} \hat{\mu}_j = \alpha_i^{-1} (\mu_i + \beta_i \langle \mathbf{T} \cdot \hat{\mu} \rangle_i^2 + \gamma_i \langle \mathbf{T} \cdot \hat{\mu} \rangle_i^3). \quad (14)$$

An expression for $\hat{\mu}_i$ is then obtained by forming the inverse \mathbf{M} of the matrix quantity $\{ \dots \}$ in Eq. (14), in the manner exploited in polarizability calculations by Applequist *et al.*^{14,39}

$$\hat{\mu}_i = \sum_j \mathbf{M}_{ij} \alpha_j^{-1} (\mu_j + \beta_j \langle \mathbf{T} \cdot \hat{\mu} \rangle_j^2 + \gamma_j \langle \mathbf{T} \cdot \hat{\mu} \rangle_j^3). \quad (15)$$

The significance of \mathbf{M} can be demonstrated by manipulating Eq. (11) with β_i , $\gamma_i = 0$ to yield

$$\sum_j \mathbf{M}_{ij} = \hat{\alpha}_i. \quad (16)$$

This is identical to the result of Applequist *et al.*¹⁴ Further manipulation of Eq. (16) also reproduces the results of the Silberstein model,^{40,41} which first demonstrated how intramolecular electrostatic interactions can produce an anisotropic polarizability tensor for a

molecule composed of isotropically polarizable atomic segments.

The previously stated objective, of casting the expression for $\hat{\mu}_i$ in a form which is independent of terms containing $\langle \mathbf{T} \cdot \hat{\mu} \rangle_i$, has not been satisfied by Eq. (15), since $\hat{\mu}_i$ is a nonlinear function of $\langle \mathbf{T} \cdot \hat{\mu} \rangle_j$. However, Eq. (15) does provide a suitable basis for computations of $\hat{\mu}_i$ and details of its application will be considered in the next section.

III. APPLICATION TO THE DIPOLE MOMENTS OF SOME HALOGENATED METHANES

We wish to understand the measured dipole moments of nine halogenated-methane molecules (a list is given in Table III) in terms of the interacting segment model (ISM) as expressed by Eq. (15). The procedure may be summarized as follows: (1) Select a set of parameters \mathbf{T}_{ij} which describe the interaction geometry for each pair of bonds in each molecule; (2) select electric tensor parameters α_i , β_i , γ_i for each type of bond; and (3) compute values of bare bond moments μ_i which, using Eq. (15), yield values for molecular dipole moments μ' that best fit the experimental molecular moments μ for the set of molecules considered. The steps in this procedure will now be considered in more detail before presenting the results.

A reference set of parameters is shown in Table I. Since a simultaneous fit to all hyperpolarizability data is not being attempted at this stage, it has been necessary to estimate bare bond parameters other than μ_i . The nature of these estimates is indicated in the table. The choice of active center locations \mathbf{r}_i forms part of the statement of the model. Rather than adjusting these parameters for best fit we elect to use a specific, arbitrary set of locations consistent with intuition and similar to those selected by Smyth and McAlpine.²⁰ Other reasonable choices of the \mathbf{r}_i lead to qualitatively similar results. The effect of using bond angles and polarizability anisotropies differing from the reference set will be discussed briefly later.

Dimensional arguments discussed in Sec. I. lead to the conclusion that terms μ_i , $\beta_i \langle \mathbf{T} \cdot \hat{\mu} \rangle_i^2$, and $\gamma_i \langle \mathbf{T} \cdot \hat{\mu} \rangle_i^3$ appearing in Eq. (15) are all of comparable magnitude. However, we adopt the hypothesis that μ_i and β_i , which vanish in centrosymmetric systems, are overestimated by the dimensional arguments so that $\beta_i \langle \mathbf{T} \cdot \hat{\mu} \rangle_i^2$ and $\gamma_i \langle \mathbf{T} \cdot \hat{\mu} \rangle_i^3$ may both be smaller than μ_i . Any cancellation within the vector sum over bonds $\langle \mathbf{T} \cdot \hat{\mu} \rangle_i$ will reinforce this tendency. This hypothesis allows an iterative solution of Eq. (15) which yields, as the result of the p th iteration, the bare and dressed bond moments $\mu_i^{(p)}$ and $\hat{\mu}_i^{(p)}$, respectively. The procedure is described by the sequence of Eqs. (17)–(20), where the steps indicated by Eqs. (18) and (19) are carried out iteratively

$$\hat{\mu}_i^{(0)} = 0, \quad (17)$$

$$\mu - \sum_{i,j} \mathbf{M}_{ij} \alpha_j^{-1} (\beta_j \langle \mathbf{T} \cdot \hat{\mu}^{(p-1)} \rangle_j^2 + \gamma_j \langle \mathbf{T} \cdot \hat{\mu}^{(p-1)} \rangle_j^3) \Leftarrow \sum_{i,j} \mathbf{M}_{ij} \alpha_j^{-1} \mu_j^{(p)}. \quad (18)$$

TABLE I. Reference set of bond and structural parameter values for the halogenated methanes.^a

Parameter	C-X bond			Comments
	C-F	C-Cl	C-H	
$10^{24}\alpha(\text{C-X})/\text{cm}^3$	0.96	2.8	0.65	The isotropic bare bond polarizability $\alpha(\text{C-X})$ is approximated by the dressed polarizability $\hat{\alpha}^0(\text{C-X}) = \frac{1}{4}\alpha^0(\text{CX}_4)$ from Refs. 29 and 1.
$10^{24}[\alpha_{\parallel} - \alpha_{\perp}](\text{C-X})/\text{cm}^3$	0.75	2.00	0.35	The bare bond polarizability anisotropy $(\alpha_{\parallel} - \alpha_{\perp})(\text{C-X})$ is approximated by the dressed anisotropy $(\hat{\alpha}_{\parallel}^0 - \hat{\alpha}_{\perp}^0)(\text{C-X}) = \hat{\alpha}^0(\text{C-X})(\hat{\alpha}_{\parallel}^{\omega} - \hat{\alpha}_{\perp}^{\omega})(\text{C-X})/\hat{\alpha}^{\omega}(\text{C-X})$, where $\hat{\alpha}^{\omega}(\text{C-X}) = \frac{1}{4}\alpha^{\omega}(\text{CX}_4)$ from Refs. 25-27 and $(\hat{\alpha}_{\parallel}^{\omega} - \hat{\alpha}_{\perp}^{\omega})(\text{C-X})$ is determined crudely from a combination of theoretical ¹⁸ and Raman intensity ⁴² data from molecules CX_4 .
$10^{30}\beta_{\parallel}(\text{C-X})/\text{esu}$	+0.103	+0.223	+0.303	$\beta_{\parallel}(\text{C-X}) = \beta_{xxx}(\text{C-X})$ and $\beta_{\perp}(\text{C-X}) = \beta_{xxx}(\text{C-X}) = \beta_{yyy}(\text{C-X}) = \dots$ (where the bond z axis points from X to C) are determined from a preliminary fit of experimental hyperpolarizabilities β^{EHG} to Eq. (12).
$10^{30}\beta_{\perp}(\text{C-X})/\text{esu}$	-0.127	-0.265	+0.104	
$10^{36}\gamma(\text{C-X})/\text{esu}$	0.023	0.342	0.066	The bare bond hyperpolarizability $\gamma(\text{C-X})$ is approximated by the dressed hyperpolarizability $\hat{\gamma}^{\text{ESHG}}(\text{C-X}) = \frac{1}{4}\gamma^{\text{ESHG}}(\text{CX}_4)$ from Ref. 32. $\gamma(\text{C-X})$ is assumed to be isotropic.
$10^9 R(\text{C-X})/\text{cm}$	1.36	1.77	1.10	Representative internuclear distances for C-X bonds in the halogenated methane series. See Ref. 43.
f	1.0	1.0	0.5	$f = r(\text{C-X})/R(\text{C-X})$ defines the fractional position of the active center along the C-X bond. The choice of f is discussed in the text.
$\theta(\text{X-C-X})$ in CX_3Y	108.0°, Y = H 108.6°, Y = Cl	110.9°, Y = H 111.7°, Y = F	110.9°, Y = Cl 110.1°, Y = F	X-C-X bond angles for the halogenated methane series from Ref. 43.
$\theta(\text{X-C-X})$ in CX_2Y_2	108.5°, Y = H 109.5°, Y = Cl	111.8°, Y = H 108.5°, Y = F	112.0°, Y = Cl 111.9°, Y = F	

^aThe parameter values listed in this table are used as a basis for describing in the text various choices of the parameter set.

We use the symbol \rightleftharpoons to indicate that the $\mu_j^{(p)}$ on the right are varied for best (least squares) fit of the expression on the right to that on the left for the set of molecules considered. Equation (19) is similar to Eq. (18) but serves, in this step, to calculate the value of $\hat{\mu}_i^{(p)}$ for use in Eq. (18) for the next iteration

$$\hat{\mu}_i^{(p)} = \sum_j \mathbf{M}_{ij} \alpha_j^{-1} (\mu_j^{(p)} + \beta_j \langle \mathbf{T} \cdot \hat{\mu}^{(p-1)} \rangle_j^2 + \gamma_j \langle \mathbf{T} \cdot \hat{\mu}^{(p-1)} \rangle_j^3). \quad (19)$$

After sufficient iteration the $\hat{\mu}_i^{(p)}$ converge to a value $\hat{\mu}_i$ and the molecular moment μ' is calculated as

$$\mu' = \sum_i \hat{\mu}_i. \quad (20)$$

This algorithm is carried out numerically noting that in Eqs. (18) and (19) $\hat{\mu}_i$ is a 12 component vector ($\hat{\mu}_{x1}, \hat{\mu}_{y1}, \dots, \hat{\mu}_{z4}$) and $(\mathbf{M}_{ij} \alpha_j^{-1})$ is a 12×12 matrix operator in the same space. The number of components can be reduced from 12 to three (for CXY_3 type molecules) or four (for CX_2Y_2 type molecules) by choice of coordinate systems and by noting that each molecule contains bonds of two types only. For all choices of parameter set (with one exception indicated in Table II) there are no changes greater than 1% in any variable from the fifth to the sixth iteration of this procedure. This convergence justifies the approach adopted.

The least squares fit of Eq. (18) involves minimizing χ^2 (the reduced chi-squared parameter) with respect to μ_i . χ^2 is defined by

$$\chi^2 = \nu^{-1} \sum_i (\mu'_i - \mu_i)^2 W_i^2, \quad (21)$$

where the sum is over molecules, ν is the difference between the number of data points and the number of parameters ($\nu = 6$ here), and W_i is a weight. In results quoted explicitly we have used the reciprocals of experimental uncertainties as weights. Arguments can be made for using other weights (all molecules weighted equally, W_i^{-1} proportional to μ for the i th molecule, etc.), but we find that these do not yield qualitatively different fits. The uncertainties listed in parentheses after each μ_i in Table II are as defined by Bevington⁴⁴ and serve mainly to indicate the relative sensitivity of a fit to the various μ_i .

The results of fitting with various choices of parameter set are shown in Tables II-V. In Table II the full range of parameter-set choices is presented, exhibiting μ_i and χ^2 for each. Simple BAA with tetrahedral angles is not included, since only *differences* between the μ_i can be determined in this case. Use of experimental (nontetrahedral) angles lifts this restriction but the results are sensitive to deviations from tetrahedral sym-

TABLE II. Bare bond moments $\mu(\text{C-X})$ obtained by fitting dipole moments of the halogenated methanes.^a

Parameter values	$\mu(\text{C-F})$	$\mu(\text{C-Cl})$	$\mu(\text{C-H})$	χ^2
Simple BAA ($\alpha_i, \beta_i, \gamma_i = 0$); experimental angles ^b	4.75(8)	4.54(9)	3.11(9)	109
Isotropic α_i ; $\beta_i, \gamma_i = 0$; tetrahedral angles	1.75(3)	1.84(4)	0.80(4)	31
Isotropic α_i ; $\beta_i, \gamma_i = 0$; experimental angles	1.70(3)	1.87(3)	0.74(4)	12
Anisotropic α_i ; $\beta_i, \gamma_i = 0$; tetrahedral angles	1.57(2)	1.80(2)	0.64(3)	12
Anisotropic α_i ; $\beta_i, \gamma_i = 0$; experimental angles ^b	1.52(2)	1.76(2)	0.59(2)	8
Isotropic α_i ; $\beta_i, \gamma_i \neq 0$; tetrahedral angles ^c
Isotropic α_i ; $\beta_i, \gamma_i \neq 0$; experimental angles	1.65(3)	1.79(4)	0.42(4)	37
Anisotropic α_i ; $\beta_i, \gamma_i \neq 0$; tetrahedral angles	1.47(2)	1.65(2)	0.34(3)	33
Anisotropic α_i ; $\beta_i, \gamma_i \neq 0$; experimental angles ^b	1.40(2)	1.59(2)	0.28(2)	13

^aThe bare bond moments are in debye units (10^{-18} esu). The positive sign of $\mu(\text{C-X})$ in all cases implies an electric polarization of the bond in the same C^+-X^- .

^bThe fitted molecular dipole moment μ' for each molecule is listed in Table III.

^cCalculation failed to converge satisfactorily.

metry. Some variation of the results with choice of parameters may be noted: Firstly, all of the fits in which interactions are included have significantly smaller χ^2 than the BAA calculation; and secondly, for both isotropic and anisotropic α_i use of experimental bond angles yields a better fit than obtained with tetrahedral angles. It should be emphasized that α_i , β_i , and γ_i have *not* been varied to minimize χ^2 .

The values of bare bond dipole moment $\mu(\text{C-X})$ from Table II can usefully be compared with corresponding results from other sources. Analyses of infrared intensity data⁴⁵ have yielded estimates of $\mu(\text{C-X})$, but the reliability of such estimates based on the bond moment

hypothesis have been strongly criticized.^{46,47} Nevertheless, there appears to be a consensus that $\mu(\text{C-H})$ for CH_4 ⁴⁸ is approximately 0.35 D, in close agreement with the results of Table II for anisotropic α_i and $\beta_i, \gamma_i \neq 0$. Theoretical calculations^{16,17} of $\mu(\text{C-H})$ confirm that it is positive (i.e., polarized in the sense C^+-H^-), but predict a much larger magnitude (~ 2.0 D). Infrared intensity data do not appear to yield physically unambiguous estimates of $\mu(\text{C-F})$ or $\mu(\text{C-Cl})$.

In Table III fitted molecular moments μ' are compared with the experimentally determined values μ for various levels of interaction. All results here are for experimental bond angles and anisotropic α_i . Results

TABLE III. Experimental and fitted electric dipole moments for halogenated methanes.^a

Molecule	μ^b	$\alpha_i, \beta_i, \gamma_i = 0^{c, g}$		$\alpha_i \neq 0; \beta_i, \gamma_i = 0^g$		$\alpha_i, \beta_i, \gamma_i \neq 0^g$		Smith <i>et al.</i> (Ref. 21)	
		μ'	Diff.	μ'	Diff.	μ'	Diff.	μ'^d	Diff. ^e
CHCl_3	1.04(2)	1.10	-0.06	0.98	+0.06	1.14	-0.10	1.12	-0.11
CH_2Cl_2	1.60(3)	1.62	-0.02	1.60	0.0	1.64	-0.04	1.63	-0.06
CH_3Cl	1.90(2)	1.66	+0.24	1.89	+0.01	1.88	+0.02	(1.86) ^f	...
CH_3F	1.85(2)	1.75	+0.10	1.91	-0.06	1.91	-0.06	(1.81) ^f	...
CH_2F_2	1.98(2)	2.07	-0.09	1.93	+0.05	1.92	+0.06	1.91	+0.07 ^g
CHF_3	1.65(2)	1.80	-0.15	1.71	-0.06	1.58	+0.07	1.53	+0.06
CF_3Cl	0.50(1)	0.41	+0.09	0.49	+0.01	0.52	-0.02
CF_2Cl_2	0.51(5)	0.18	+0.33	0.45	+0.06	0.48	+0.03	1.18	-0.67
CFCl_3	0.46(2)	0.73	-0.27	0.42	+0.04	0.43	+0.03	0.95	-0.50

^aExperimental and fitted dipole moments μ and μ' , respectively, and their differences ($\mu - \mu'$) are in debye units (10^{-18} esu).

^bValues of μ are taken from Refs. 23 and 24. μ is directed along the major symmetry axis and is taken to be in the sense $^-\text{F}_n\text{CCl}_{4-n}^+$, $^+\text{H}_n\text{CF}_{4-n}^-$, or $^+\text{H}_n\text{CCl}_{4-n}^-$, which is consistent with the experimentally determined⁴⁹ polarizations $^+\text{HCF}_3$ and $^+\text{H}_3\text{CCl}^-$. Experimental uncertainties are indicated in parentheses.

^cThe approximation $\alpha_i, \beta_i, \gamma_i = 0$ corresponds to the simple BAA situation.

^dValues of μ' from Ref. 21 are those estimated by assuming that $\mu(\text{C-H}) = 0$. Results with $\mu(\text{C-H}) = \pm 0.3$ D are also listed in Ref. 21, but these do not provide a significantly better fit to μ . All angles in this fitting were assumed to be tetrahedral.

^eDifferences are calculated using values of μ cited in Ref. 21, with the exception of CH_2F_2 , for which μ from Ref. 23 was used.

^fThe fitting procedure of Ref. 21 constrains μ' to equal μ for CH_3Cl and CH_3F .

^gExperimental bond angles (see Table I) and anisotropic α_i were used.

TABLE IV. Contributions to $\hat{\mu}_i$ for C-X bonds in halogenated methanes, based on Eq. (10).^a

Molecule	Bond i	μ_i^b	Components parallel to bond axis			Components perpendicular to bond axis ^c		
			$\alpha_i \langle T \cdot \hat{\mu} \rangle_i$	$\beta_i \langle T \cdot \hat{\mu} \rangle_i^2$	$\gamma_i \langle T \cdot \hat{\mu} \rangle_i^3$	$\alpha_i \langle T \cdot \hat{\mu} \rangle_i$	$\beta_i \langle T \cdot \hat{\mu} \rangle_i^2$	$\gamma_i \langle T \cdot \hat{\mu} \rangle_i^3$
CHCl ₃	C-Cl	1.593	-0.534	0.004	-0.001	0.024	-0.001	0.0
	C-H	0.281	-0.438	0.074	-0.008	0.0	0.0	0.0
CH ₂ Cl ₂	C-Cl	1.593	-0.285	0.001	0.0	0.028	0.0	0.0
	C-H	0.281	-0.349	0.049	-0.004	0.072	-0.011	0.001
CH ₃ Cl	C-Cl	1.593	0.119	0.0	0.0	0.0	0.0	0.0
	C-H	0.281	-0.307	0.038	-0.003	0.070	-0.009	0.0
CH ₃ F	C-F	1.406	0.186	-0.002	0.0	0.0	0.0	0.0
	C-H	0.281	-0.370	0.058	-0.005	0.117	-0.019	0.002
CH ₂ F ₂	C-F	1.406	-0.096	0.0	0.0	0.012	0.0	0.0
	C-H	0.281	-0.533	0.119	-0.016	0.153	-0.036	0.004
CHF ₃	C-F	1.406	-0.301	0.004	0.0	0.011	0.001	0.0
	C-H	0.281	-0.962	0.360	-0.085	0.0	0.0	0.0
CF ₃ Cl	C-F	1.406	-0.486	0.011	-0.001	0.013	0.002	0.0
	C-Cl	1.593	-1.116	0.016	-0.007	0.0	0.0	0.0
CF ₂ Cl ₂	C-F	1.406	-0.397	0.008	0.0	0.011	0.001	0.0
	C-Cl	1.593	-0.991	0.013	-0.005	-0.002	0.0	0.0
CFCl ₃	C-F	1.406	-0.324	-0.005	0.0	0.0	0.0	0.0
	C-Cl	1.593	-0.859	0.010	-0.003	0.001	0.0	0.0

^aAll numerical entries are in debye units and are calculated using anisotropic α_i and experimental bond angles. The results correspond to the entries labeled α_i , β_i , $\gamma_i \neq 0$ in Table III and to the final row of Table II. Computed results are shown to three places of decimals to exhibit small components. Physically meaningful precision at this level is not implied.

^bNote that the component of the bare bond moment μ_i perpendicular to the bond axis is identically zero, in contrast to the perpendicular components of the dressed bond moments $\hat{\mu}_i$.

^cPerpendicular components lie in the plane including the bond and the molecular z axis. A positive sign indicates a positive component along the molecular $+z$ direction.

of Smith *et al.*²¹ are included for comparison. In addition to having better χ^2 the cases with interactions included reproduce the experimentally determined ordering of moment values: This is not the case either with BAA or with the calculation of Smith *et al.*²¹ It is conceivable that the method of Smith *et al.*²¹ might more closely reproduce the experimental data if its parameters were determined by a least squares fit to all the data, rather than by constraining the fit to just two molecules (CH₃Cl and CH₃F).

Table IV displays the detailed contributions of the various terms to the dressed moments $\hat{\mu}_i$ of the bonds in each of the molecules included in the fit. Of particular interest are the large $\beta_i \langle T \cdot \hat{\mu} \rangle_i^2$ contributions parallel to the bond axis in the C-H bonds of CHCl₃, CH₂F₂, and CHF₃, due to large dipole moments of C-Cl and C-F bonds acting upon the β_i of the C-H bond. Also, there are large $\alpha_i \langle T \cdot \hat{\mu} \rangle_i$ contributions perpendicular to the bond axes in the C-H bonds of CH₃F and CH₂F₂. In most cases $\alpha_i \langle T \cdot \hat{\mu} \rangle_i$ parallel to the bond axis makes a significant contribution to $\hat{\mu}_i$.

Table V contains fitted molecular moments resolved into contributions arising from various interactions corresponding to the terms in Eq. (10). These data can best be examined in three groups. In the CH_{*n*}Cl_{4-*n*} molecules $\alpha_i \langle T \cdot \hat{\mu} \rangle_i$ contributions are considerably smaller than μ_i terms, and $\beta_i \langle T \cdot \hat{\mu} \rangle_i^2$ terms are fairly small. In

CH_{*n*}F_{4-*n*} molecules the $\alpha_i \langle T \cdot \hat{\mu} \rangle_i$ are somewhat larger in relation to μ_i , and $\beta_i \langle T \cdot \hat{\mu} \rangle_i^2$ becomes appreciable. In CF_{*n*}Cl_{4-*n*} $\alpha_i \langle T \cdot \hat{\mu} \rangle_i$ terms overwhelm μ_i , and the $\beta_i \langle T \cdot \hat{\mu} \rangle_i^2$ terms are small. Looking at results for all nine molecules the largest $\beta_i \langle T \cdot \hat{\mu} \rangle_i^2$ contribution is about 22% of μ' and in all other cases it contributes less than 10%. The average $\gamma_i \langle T \cdot \hat{\mu} \rangle_i^3$ contribution is 1%.

TABLE V. Contributions to the fitted electric dipole moments for halogenated methanes.^a

Molecule	μ'^c	Components parallel to molecular z axis ^b			
		$\sum_i \mu_i$	$\sum_i \alpha_i \langle T \cdot \hat{\mu} \rangle_i$	$\sum_i \beta_i \langle T \cdot \hat{\mu} \rangle_i^2$	$\sum_i \gamma_i \langle T \cdot \hat{\mu} \rangle_i^3$
CHCl ₃	1.141	1.196	0.010	-0.073	0.007
CH ₂ Cl ₂	1.643	1.473	0.238	-0.073	0.006
CH ₃ Cl	1.877	1.333	0.602	-0.062	0.004
CH ₃ F	1.910	1.134	0.875	-0.109	0.009
CH ₂ F ₂	1.918	1.328	0.757	-0.192	0.024
CHF ₃	1.584	1.171	0.681	-0.353	0.085
CF ₃ Cl	0.524	-0.128	0.646	-0.004	0.006
CF ₂ Cl ₂	0.475	-0.239	0.714	-0.004	0.005
CFCl ₃	0.431	0.007	0.439	0.000	0.003

^aFitted electric dipole moments μ' and all contributions are in debye units. Computed results are shown to three places of decimals to exhibit small components. Physically meaningful precision at this level is not implied.

^bMolecular z axis is defined to point in the \rightarrow^* direction of the molecular dipole moment.

^cThe parameters used in this calculation are: anisotropic α_i ; β_i , $\gamma_i \neq 0$; experimental bond angles.

The foregoing results encourage confidence that the ISM approach, in general, and the iterative method of computation, in particular, represent a valid means of understanding the dipole moments of the molecules considered. Moreover, the results are not particularly sensitive to the (poorly determined) values of β_i and γ_i , which in turn justifies the omission of higher order hyperpolarizability contributions. Uncertainties in α_i , however, are important, and more reliable data for these bare bond values will be provided by an ISM study³³ of α analogous to that presented here for μ .

IV. CONCLUSION

We have developed the theory of an interacting segment model (ISM) of the molecular electric dipole moment, polarizability, and hyperpolarizabilities. A detailed ISM for dipole moments with segments taken to be bonds has been applied to the dipole moments of some halogenated methanes. It has been demonstrated that it is possible to treat terms in β_i and γ_i as perturbations and to omit contributions depending on higher order hyperpolarizabilities. The resulting fit has proved to be good and to produce bond dipole moments $\mu(\text{C-X})$ which are reasonably consistent with expectations from other sources, such as infrared intensity data.

The model is characterized by a number of parameters which are not varied for best fit (see Table I). The choice of values for these parameters involves crude estimates of bare values from measured dressed parameters. It is anticipated that the number of such crudely estimated parameters will be reduced in further computations³³ in which the fitting procedure will be extended to include ISM calculations for α_i , β_i , and γ_i . The quality of this overall fit should give a better measure of the usefulness and limitations of the model than can be obtained from the present preliminary computations.

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APPENDIX: EXTENSION TO TIME VARYING FIELDS AND DEFINITION OF MOLECULAR OBSERVABLES

In most experiments used to measure the electric tensor properties μ , α , β , and γ the applied electric field is time dependent and is of the general form

$$\mathbf{E}(t) = \mathbf{E}^0 + \frac{1}{2} \sum_j [\mathbf{E}^{\omega_j} \exp(-i\omega_j t) + \mathbf{E}^{-\omega_j} \exp(+i\omega_j t)]. \quad (\text{A1})$$

The resultant electric dipole moment can be similarly expressed in terms of Fourier components

$$\mu(\mathbf{E}, t) = \mu^0(\mathbf{E}) + \frac{1}{2} \sum_{\sigma} [\mu^{\omega_{\sigma}}(\mathbf{E}) \exp(-i\omega_{\sigma} t) + \mu^{-\omega_{\sigma}}(\mathbf{E}) \exp(+i\omega_{\sigma} t)], \quad (\text{A2})$$

where, for a specific combination $\omega_1, \omega_2, \dots, \omega_n$ of applied field frequencies which together yield a resultant frequency $\omega_{\sigma} = \omega_1 + \omega_2 + \dots + \omega_n$, we can write

$$\mu^{\omega_{\sigma}}(\mathbf{E}) = \sum_{n=0}^{\infty} K(-\omega_{\sigma}; \omega_1, \omega_2, \dots, \omega_n) \times \chi^{(n)}(-\omega_{\sigma}; \omega_1, \omega_2, \dots, \omega_n) \mathbf{E}^{\omega_1} \mathbf{E}^{\omega_2} \dots \mathbf{E}^{\omega_n}. \quad (\text{A3})$$

Equation (A3) is a more general form of Eq. (4), which can now describe phenomena with general time dependence. Definition of the numerical factors $K(-\omega_{\sigma}; \omega_1, \omega_2, \dots)$ may be completed by specifying

$$K(0; 0, \dots, 0) = 1, \quad \text{for all } n, \quad (\text{A4})$$

$$\lim_{\omega \rightarrow 0} \chi^{(n)}(-\omega_{\sigma}; \omega_1, \dots, \omega_n) = \chi^{(n)}(0; 0, \dots, 0). \quad (\text{A5})$$

This definition follows the convention previously adopted by Ward and co-workers and numerical values of these K 's for specific combinations of field frequencies have been evaluated and tabulated.^{2,50} It should be noted however that there is a wide variety of different conventions in current use.^{1,10}

For dc fields Eq. (A4) states that all K 's are unity in this convention and that Eq. (A3) reduces to the form used in Eq. (4) or, in terms of dressed tensors, Eq. (3). Also, by comparison with Eq. (1) it can be seen that the constants ξ and λ used there are unity in this convention.

The derivation in Sec. II leading to the relations between $\hat{\chi}_i^{(n)}$ and $\chi_i^{(n)}$ set out in Eqs. (10)–(13) can be reworked using the more general time-dependent expressions Eqs. (A1)–(A3) in place of the original expressions relevant to dc fields only. A typical result is the segment hyperpolarizability for dc-induced second-harmonic generation, where Eq. (13) is replaced by a far richer expression containing, among other parameters, polarizabilities for all three frequencies involved. The frequency dependent expression is³⁸

$$\begin{aligned} \hat{\gamma}_i(-2\omega; \omega, \omega, 0) = & \alpha_i(-2\omega; 2\omega) \langle \mathbf{T} \cdot \hat{\gamma}(-2\omega; \omega, \omega, 0) \rangle_i + 2\beta_i(-2\omega; 2\omega, 0) \{ \langle \mathbf{T} \cdot \hat{\mu} \rangle_i \langle \mathbf{T} \cdot \hat{\gamma}(-2\omega; \omega, \omega, 0) \rangle_i \\ & + \frac{1}{3} [1 + \langle \mathbf{T} \cdot \hat{\alpha}(0; 0) \rangle_i] \langle \mathbf{T} \cdot \hat{\beta}(-2\omega; \omega, \omega) \rangle_i \} + \frac{4}{3} \beta_i(-2\omega; \omega, \omega) [1 + \langle \mathbf{T} \cdot \hat{\alpha}(-\omega; \omega) \rangle_i] \langle \mathbf{T} \cdot \hat{\beta}(-\omega; \omega, 0) \rangle_i \\ & + \gamma_i(-2\omega; 2\omega, 0, 0) \{ 3 \langle \mathbf{T} \cdot \hat{\mu} \rangle_i^2 \langle \mathbf{T} \cdot \hat{\gamma}(-2\omega; \omega, \omega, 0) \rangle_i + 2 \langle \mathbf{T} \cdot \hat{\mu} \rangle_i [1 + \langle \mathbf{T} \cdot \hat{\alpha}(0; 0) \rangle_i] \langle \mathbf{T} \cdot \hat{\beta}(-2\omega; \omega, \omega) \rangle_i \} \\ & + \gamma_i(-2\omega; \omega, \omega, 0) \{ 4 \langle \mathbf{T} \cdot \hat{\mu} \rangle_i [1 + \langle \mathbf{T} \cdot \hat{\alpha}(-\omega; \omega) \rangle_i] \langle \mathbf{T} \cdot \hat{\beta}(-\omega; \omega, 0) \rangle_i + [1 + \langle \mathbf{T} \cdot \hat{\alpha}(-\omega; \omega) \rangle_i]^2 [1 + \langle \mathbf{T} \cdot \hat{\alpha}(0; 0) \rangle_i] \}. \quad (\text{A6}) \end{aligned}$$

Although polarizabilities and hyperpolarizabilities $\chi^{(n)}$ of a given order n and for a given molecule vary appreciably as a result of dispersion, such variations are in

many cases negligible when compared to the large non-additive contributions from intersegment interactions which vary greatly from molecule to molecule and which

TABLE VI. Definition of observable molecular electric tensor properties.

Electric tensor	Molecular observable ^{a,b}	Experimental source(s) ^c	Comments
μ	$\mu = (\mu_x \mu_x)^{1/2} $	Microwave spectra Dielectric constant	We choose the molecular z axis such that $\mu = \mu_x$.
$\alpha(0; 0)$ $= \alpha^0$	$\alpha^0 = \frac{1}{3} \alpha_{xx}^0 = \frac{1}{3} \text{Tr}(\alpha^0)$	Dielectric constant	α^0 is the isotropic part of α^0 .
$\alpha(-\omega; \omega)$ $= \alpha^\omega$	$\alpha^\omega = \frac{1}{3} \alpha_{xx}^\omega = \frac{1}{3} \text{Tr}(\alpha^\omega)$ $\Delta\alpha = 3\alpha^\omega \kappa$ $= \{3[\alpha_{xx}^\omega \alpha_{yy}^\omega - 3(\alpha^\omega)^2]/2\}^{1/2}$ $(\alpha_{xx}^\omega - \alpha^\omega)$	Refractive index Depolarization ratio for Rayleigh scattering Kerr effect (electric birefringence)	α^ω is the isotropic part of α^ω . $\kappa^2 = [(\alpha_{xx}^\omega - \alpha^\omega)^2 + (\alpha_{yy}^\omega - \alpha^\omega)^2 + (\alpha_{zz}^\omega - \alpha^\omega)^2]/9(\alpha^\omega)^2$. If molecule has three or higher-fold rotational symmetry, $\kappa = (\alpha_{xx}^\omega - \alpha^\omega)/3\alpha^\omega$, so that $\Delta\alpha = \alpha_{xx}^\omega - \alpha^\omega$. If molecule has three or higher-fold rotational symmetry, $(\alpha_{xx}^\omega - \alpha^\omega) = \frac{2}{3}(\alpha_{yy}^\omega - \alpha^\omega) = \frac{2}{3}\Delta\alpha$.
$\beta(-2\omega; \omega, \omega)$ $= \beta^{\text{SHG}}$	$\beta^{\text{SHG}} = \frac{2}{3} \beta_{xxz}(-2\omega; \omega, \omega)$ $+ \frac{1}{3} \beta_{zzx}(-2\omega; \omega, \omega)$	dc-induced second harmonic generation ^d	A second observable, $\beta_1^{\text{SHG}} = \frac{6}{5} \beta_{xxz}(-2\omega; \omega, \omega) - \frac{3}{5} \beta_{zzx}(-2\omega; \omega, \omega)$ can be determined by having E^ω polarized perpendicular to E^0 . Usually, β^{SHG} and β_1^{SHG} differ by less than 5%. ⁹
$\beta(-\omega; \omega, 0)$ $= \beta^K$	$\beta^K = \frac{9}{10} \beta_{xxz}(-\omega; \omega, 0)$ $- \frac{3}{10} \beta_{zzx}(-\omega; \omega, 0)$	Kerr effect (electric birefringence)	
$\gamma(-2\omega; \omega, \omega, 0)$ $= \gamma^{\text{ESHG}}$	$\gamma^{\text{ESHG}} = \frac{2}{15} \gamma_{zz\eta\eta}(-2\omega; \omega, \omega, 0)$ $+ \frac{1}{15} \gamma_{\eta\eta\kappa}(-2\omega; \omega, \omega, 0)$	dc-induced second harmonic generation ^d	A second observable $\gamma_1^{\text{ESHG}} = \frac{2}{5} \gamma_{zz\eta\eta}(-2\omega; \omega, \omega, 0) - \frac{1}{5} \gamma_{\eta\eta\kappa}(-2\omega; \omega, \omega, 0)$ can be determined by having E^ω polarized perpendicular to E^0 . Usually, γ^{ESHG} and γ_1^{ESHG} differ by less than 5%. ⁹
$\gamma(-\omega; \omega, 0, 0)$ $= \gamma^K$	$\gamma^K = \frac{3}{10} \gamma_{zz\eta\eta}(-\omega; \omega, 0, 0)$ $- \frac{1}{10} \gamma_{\eta\eta\kappa}(-\omega; \omega, 0, 0)$	Kerr effect (electric birefringence)	
$\gamma(-3\omega; \omega, \omega, \omega)$ $= \gamma^{\text{THG}}$	$\gamma^{\text{THG}} = \frac{1}{5} \gamma_{zz\eta\eta}(-3\omega; \omega, \omega, \omega)$	Third harmonic generation	

^aCartesian tensor notation³⁶ is used where convenient.

^bAxes x, y, z are principal molecular axes, the z -axis being specified in the definition of μ .

^cSee Ref. 1 for a survey of experimental techniques.

^d β^{SHG} and γ^{ESHG} are determined with E^ω polarized parallel to E^0 .

form the subject of this paper. For example, the chloro- and fluoromethanes do not have electronic absorption bands above 200 nm, so that the differences due to dispersion between pairs of electric tensor properties, such as $\alpha(0; 0)$ and $\alpha(-\omega; \omega)$, $\beta(-2\omega; \omega, \omega)$ and $\beta(-\omega; \omega, 0)$, and $\gamma(-2\omega; \omega, \omega, 0)$ and $\gamma(-\omega; \omega, 0, 0)$, where ω corresponds to wavelengths above 600 nm, are expected to be relatively small.

The hyperpolarizabilities may be expanded as follows:

$$\chi_i^{(n)}(-\omega_\sigma; \omega_1, \dots, \omega_i, \dots, \omega_n) = \lim_{\omega \rightarrow 0} \chi_i^{(n)}(-\omega_\sigma; \omega_1, \dots, \omega_i, \dots, \omega_n) + \sum_i \omega_i \lim_{\omega \rightarrow 0} \frac{\partial}{\partial \omega_i} [\chi_i^{(n)}(-\omega_\sigma; \omega_1, \dots, \omega_i, \dots, \omega_n)] + \dots \quad (\text{A7})$$

As discussed above it is a reasonable approximation to adopt the dispersionless limit by dropping all but the first term on the right of Eq. (A7). Equation (A5) then indicates that, in the present convention, all hyperpolarizabilities of a given order become equal. The frequency labels may therefore be dropped from Eq. (A6), which reduces directly to Eq. (13). It follows that Eqs. (10)–(13) in the body of the text apply in the dispersion-

less limit to hyperpolarizabilities involving time-dependent fields so long as the hyperpolarizabilities are defined in accordance with Eqs. (A1)–(A5).

It is also relevant in this Appendix to define a number of observable linear combinations of electric tensor elements. These definitions are given in Table VI.

¹For a recent review of much of the relevant literature see M. P. Bogaard and B. J. Orr, *International Review of Science. Physical Chemistry*, edited by A. D. Buckingham (Butterworths, London, 1975), Ser. 2, Vol. 2, p. 149.

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