Molecular vibrational and rotational motion in static and dynamic electric fields

David M. Bishop

Department of Chemistry, University of Ottawa, Ottawa, Canada K1N 6N5

For many years the effects of a static or dynamic electric field upon electronic motion in a molecule have been studied. These effects have been described in terms of multipolar electronic polarizabilities and higher-order hyperpolarizabilities. Much less attention, however, has been paid to the effects of an electric field upon vibrational and rotational motion. It is the aim of this review to consider, in some detail, these effects. As in the electronic work, they too will be described in terms of polarizabilities and hyperpolarizabilities (the latter being particularly important for the study of nonlinear optics). The theory will be developed so as to bring together the different methods that have been used in various calculations. Examples drawn from the recent literature will be discussed and it will be seen that in many cases vibrational and rotational changes with an electric field are as important as electronic ones, if not more so. Examples of experimental work relevant to this review include research on the Kerr effect, electric-field-induced second-harmonic generation, and third-harmonic generation.

CONTENTS

I. INTRODUCTION

A. Objective

The study of molecular electronic polarizabilities has had a long and honorable history. In particular, the simplest polarizability α has long been a useful property, since it characterizes the ability of an electric field to distort the electronic distribution of a molecule. It and other polarizabilities are not, however, properties that can be experimentally measured directly because, when an electric field is applied, the molecule as a *whole* (nuclei included) is perturbed. This means that in addition to electronic distortion there will be a change to the equilibrium nuclear geometry and (as a result of there being a different potential-energy curve or surface in the presence of the field) a change to the vibrational motion. Similarly, the rotational motion will be altered—in classical terms, it will show an orientational effect. This is the subject that will be discussed in this review.

The question of vibration involves much more than the usual requirement of averaging an electronic property over the vibrational motion, e.g., the zero-point vibrational correction, which usually changes polarizability values by roughly a few percent. The distortion of the vibrational motion contributes its own vibrational polarizabilities, which are quite distinct from the averaged electronic ones and often quite dramatic. For example, for SF_6 (Shelton and Ulivi, 1988) this independent contribution to the second hyperpolarizability γ is twenty times the electronic γ; in H_2^+ (Bishop *et al.*, 1986) it is ten times as great; and in certain H-bonded systems (Eckert and Zundel, 1987, 1988) the vibrational polarizability is two orders of magnitude larger than its electronic counterpart.

The converse is also true, namely, that we cannot ignore the effect of an electric field on electronic and vibrational motions when studying its effect on rotational motion, as, for example, in rotational Stark spectroscopy. Brieger (Brieger *et al.*, 1983; Brieger, 1984) has stressed this point eloquently in two enlightening articles concerned with the theory and measurement of the dipole moment (μ) of LiH. He maintains that omitting consideration of electronic and vibrational effects in deducing μ from the rotational-state shifts and splittings caused by an electric field may lead to erroneous and questionable values and that what is thus measured "actually has nothing to do with dipole moments." The role of rotation or orientation in the theory of polarizabilities is as old as the classical formula of Debye (Debye, 1912, 1929; Smyth, 1955), $\alpha=\alpha_0+\mu^2/3kT$, which was derived for use in dielectric measurements.

When the electric field is oscillating, as in a light or laser beam, the corresponding properties are the dynamic polarizabilities, and the higher-order ones are fundamental to the understanding of nonlinear optics. This is an area of immense importance, with applications ranging from communications to medicine. The need for materials with specific optical properties that can alter the characteristics of transmitted electromagnetic radiation leads to pressure on theorists to predict likely candidates. This can only be done through the calculation of the higher-order polarizabilities. Again, the roles of vibration and rotation must be considered; for example, Kang *et al.* (1976) found that in the third-harmonic generation of SF_6 with the CO_2 transversely excited atmospheric (TEA) laser, the enhancement from vibrational-rotational transitions completely dominated the electronic nonlinear polarizability.

This review will be concerned with the effects of uniform and, to a lesser extent, nonuniform static and oscillating electric fields on molecular vibrational and rotational motions. The interaction between electric fields and electronic motion has already been well covered. Here we shall largely limit ourselves, with the exception of a brief mention of H-bonding, to single molecules, and the results will therefore be most directly related to experiments on dilute gases. Intermolecular interactions, which we ignore, are nonetheless intimately connected to these single-molecule properties. The only context in which more than one molecule will be considered is the averaging of a property over a Boltzmann distribution of molecules among the rotational states and when necessary, as in one case, to account for the change in this distribution due to the presence of the electric field. Our emphasis will be on theory, and an attempt will be made to synthesize several methods of calculation that have often been thought to be more different than they really are. Results will be given merely as examples, and little discussion of their quality, in terms of basis-set size, etc., will be made. Naturally, most previous work in this area has been concerned with diatomics and small polyatomics, and this will also be our focus.

The subject is still, in many respects, in its infancy and it is hoped that this review will stimulate further interest—there is much to be done.

B. Definitions and units

Our definitions of the static polarizabilities will follow those of Buckingham (1967) and are most conveniently introduced by considering a molecule in weak interaction with fixed external charges. The Hamiltonian describing such a situation is

$$H=H^0-\hat{\mu}_\alpha F_\alpha-\tfrac{1}{3}\hat{\Theta}_{\alpha\beta}F_{\alpha\beta}-\cdots , \qquad (1)$$

where H^0 is that for the free molecule and $\hat{\mu}_\alpha=\sum_i q_i r_{i\alpha}$ and

$$\hat{\Theta}_{\alpha\beta}=\hat{\Theta}_{\beta\alpha}=\tfrac{1}{2}\sum_i q_i(3r_{i\alpha}r_{i\beta}-r_i^2\delta_{\alpha\beta})$$

are the dipole- and quadrupole-moment operators; q_i is the ith element of charge at the point $\underline{r}_i$ relative to an origin fixed at some point in the molecule. The Greek subscripts denote vector or tensor components and can be equal to x, y, or z; a repeated Greek subscript denotes summation over all three Cartesian components (Einstein summation), so that

$$\tfrac{1}{3}\hat{\Theta}_{\alpha\beta}F_{\alpha\beta}=\tfrac{1}{3}\sum_{\alpha,\beta=x,y,z}\hat{\Theta}_{\alpha\beta}F_{\alpha\beta} ,$$

which equals a scalar quantity (the quadrupolar interaction with the field gradient). F_α and $F_{\alpha\beta}$ are the electric field and field gradient at the origin due to the external charges. If the molecule is in the internal quantum state Ψ, its energy for a fixed position and orientation is

$$\begin{aligned}E=E^0&-\mu_\alpha F_\alpha-\tfrac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta-\tfrac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma-\tfrac{1}{24}\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta-\tfrac{1}{3}\Theta_{\alpha\beta}F_{\alpha\beta}\\&-\tfrac{1}{3}A_{\gamma,\alpha\beta}F_\gamma F_{\alpha\beta}-\tfrac{1}{6}B_{\alpha\beta,\gamma\delta}F_\alpha F_\beta F_{\gamma\delta}-\tfrac{1}{6}C_{\alpha\beta,\gamma\delta}F_{\alpha\beta}F_{\gamma\delta}-\cdots ,\end{aligned} \qquad (2)$$

where $\mu_\alpha=\langle\Psi^0|\hat{\mu}_\alpha|\Psi^0\rangle$ and $\Theta_{\alpha\beta}=\langle\Psi^0|\hat{\Theta}_{\alpha\beta}|\Psi^0\rangle$ are dipole- and quadrupole-moment functions, Ψ^0 being the unperturbed wave function; $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, $\gamma_{\alpha\beta\gamma\delta}$ and $A_{\alpha,\beta\gamma}$, $B_{\alpha\beta,\gamma\delta}$, $C_{\alpha\beta,\gamma\delta}$ are molecular polarizabilities describing distortion by the external electric field and field gradient. α, β, and γ are symmetric in all suffixes, $A_{\alpha,\beta\gamma}$ in $\beta\gamma$, $B_{\alpha\beta,\gamma\delta}$ in $\alpha\beta$ and $\gamma\delta$, and $C_{\alpha\beta,\gamma\delta}$ in $\alpha\beta$ and $\gamma\delta$, and in the pairs $(\alpha\beta),(\gamma\delta)$.

α is often referred to as the dipole polarizability and β and γ as the first and second dipole hyperpolarizabilities (a name first coined by Coulson *et al.*, 1952). The terms in Eq. (2) up to γ denote the energy of a molecule in a uniform external field. A, B, and C are field-gradient polarizabilities as opposed to dipole polarizabilities. The definitions implicit in Eq. (2) will be used irrespective of whether we are considering simply the electronic energy or the total molecular energy. The reader is cautioned that Ward and co-workers (e.g., Orr and Ward, 1971) define β and γ in such a way that they are $\frac{1}{2}$ and $\frac{1}{6}$, respectively, of the above definitions.

Recently, Logan (1982) and Applequist (1983,1984) have introduced into the subject the notation of Cartesian polytensors and with it the use of *traced* quadrupole-moment operators as contrasted to the *traceless* ones above. This has the effect of changing the definitions of A, B, and C, and the traced properties will be distinguished by a tilde: $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$. Apart from the work of Dykstra and co-workers, this convention has not yet been widely used, though it has its convenience for high-order polarizabilities, and, consequently, we will stay with the definitions implied by Eq. (2). The relations between A, B, C and $\tilde{A}$, $\tilde{B}$, $\tilde{C}$ will be given in Sec. VI, where we discuss nonuniform fields and field-gradient polarizabilities. There is also a simple connection between C and the so-called quadrupole polarizability α^q as defined by Sternheimer (1954) and others (e.g., Dalgarno, 1962); this will also be given in Sec. VI.

When it comes to the dynamic polarizabilities, the notation is necessarily somewhat more complex, since it must indicate the process of interest by stating the frequencies involved and the dependence of the polarization on the perturbation (Orr and Ward, 1971; Bogaard and Orr, 1975). For a third-order process, for example, the perturbation Hamiltonian will involve three terms of the form $H'(\omega_j)=-\underline{\mu}\cdot\underline{E}_0^{\omega_j}$ $(j=1,2,3)$, where $\underline{E}_0^{\omega_j}$ is the electric field oscillating with a frequency ω_j. The induced dipole moment may be resolved into Fourier components and the one of interest identified with the frequency $\omega_\sigma=\omega_1+\omega_2+\omega_3$. In this way we have $\alpha_{\alpha\beta}(-\omega_\sigma;\omega_1)$ and $\omega_\sigma=\omega_1$; $\beta_{\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2)$ and $\omega_\sigma=\omega_1+\omega_2$; and $\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)$ and $\omega_\sigma=\omega_1+\omega_2+\omega_3$. When all the frequencies are zero, these terms are identical to the static polarizability and hyperpolarizabilities α, β, and γ given before; i.e., $\alpha(0;0)=\alpha$, $\beta(0;0,0)=\beta$, and $\gamma(0;0,0,0)=\gamma$. The two nonlinear optical effects to which we shall refer the most are (a) the Kerr effect, which introduces $\beta_{\alpha\beta\gamma}(-\omega;\omega,0)$ and $\gamma_{\alpha\beta\gamma\delta}(-\omega;\omega,0,0)$, and (b) electric-field-induced second-harmonic generation (ESHG), which involves $\beta_{\alpha\beta\gamma}(-2\omega;\omega,\omega)$ and $\gamma_{\alpha\beta\gamma\delta}(-2\omega;\omega,\omega,0)$. The Greek subscripts identify the axes of the induced-dipole-moment component and the perturbing fields. When lower-case letters (x,y,z) are used, this will mean molecular axes (with z being the one of highest symmetry), and when upper-case letters (X,Y,Z) are used, this will imply laboratory- or space-fixed axes. We might note here that in the Kerr experiment the actual quantity measured is

$$\gamma^K=\tfrac{3}{2}(\gamma_{\parallel}^K-\gamma_{\perp}^K)\ , \tag{3}$$

where

$$\gamma_{\parallel}^K=\gamma_{ZZZZ}(-\omega;\omega,0,0) \tag{4}$$

and

$$\gamma_{\perp}^K=\gamma_{XXZZ}(-\omega;\omega,0,0)\ . \tag{5}$$

The last term would be interpreted as the second hyperpolarizability in an experiment in which a static electric field lies along the Z axis and a dynamic one (a light beam) of frequency ω lies along X, which is the axis along which polarization of frequency ω is being measured.

We have employed both the atomic unit system and the Système Internationale d'Unités (SI units). The equivalences are given in Table I and are based on the 1986 adjustment of the fundamental physical constants (Cohen and Taylor, 1987). In this regard it should be noted that the older literature often gives α in units of cm^3 or a_0^3—this is not correct, though $4\pi\varepsilon_0$ cm^3 and $4\pi\varepsilon_0 a_0^3$ would be (ε_0=permittivity of vacuum); see Mills, 1988. For high-precision calculations on atoms, the atomic units may be modified by using the reduced nuclear mass in place of the infinite nuclear mass. Finally, ω will be understood to be a circular frequency, so that conversion to energy is by way of $E=\hbar\omega$.

C. Outline

The review begins in Sec. II with a general discussion of some of the concepts and techniques that repeatedly occur in calculations of both the static (nonoscillating

TABLE I. Units.

Property	Symbol	Atomic unit	SI equivalent
Length		a_0	$5.291\,77\times10^{-11}$ m
Energy		E_h	$4.359\,75\times10^{-18}$ J
Dipole moment	μ	ea_0	$8.478\,36\times10^{-30}$ C m[a]
Quadrupole moment	Θ	ea_0^2	$4.486\,55\times10^{-40}$ C m^2
Dipole-dipole polarizability	α	$e^2a_0^2E_h^{-1}$[b]	$1.648\,78\times10^{-41}$ C^2 m^2 J^{-1}
First hyperpolarizability	β	$e^3a_0^3E_h^{-2}$	$3.206\,36\times10^{-53}$ C^3 m^{3}J^{-2}
Second hyperpolarizability	γ	$e^4a_0^4E_h^{-3}$	$6.235\,38\times10^{-65}$ C^4 m^4 J^{-3}
Dipole-quadrupole polarizability	A	$e^2a_0^3E_h^{-1}$	$8.724\,96\times10^{-52}$ C^2 m^3 J^{-1}
Dipole-dipole-quadrupole polarizability	B	$e^3a_0^4E_h^{-2}$	$1.696\,73\times10^{-63}$ C^3 m^4 J^{-2}
Quadrupole-quadrupole polarizability	C	$e^2a_0^4E_h^{-1}$	$4.617\,05\times10^{-62}$ C^2 m^4 J^{-1}

[a] Also 2.541 75 Debye.

[b] Note that $e^2a_0^2E_h^{-1}=4\pi\varepsilon_0a_0^3$.

electric field) and dynamic (oscillating field) vibrational and rotational polarizabilities. This is followed in Sec. III by a brief look at the effects of vibration and rotation with respect to standard averaging of the electronic polarizabilities over these motions. This usually makes changes of only a few percent. We then consider, in detail, the pure vibrational and rotational contributions to the static and dynamic α polarizability (Sec. IV) and to the static and dynamic hyperpolarizabilities β and γ (Sec. V). The effects of vibration and rotation when a nonuniform field is present, which are therefore relevant to field-gradient polarizabilities, are looked at in Sec. VI. Up to this point, the Born-Oppenheimer approximation is used, but in the penultimate section a brief description is given of the only extant non-Born-Oppenheimer calculation (Bishop and Solunac, 1985)—that of the second hyperpolarizability of H_2^+. We end with our conclusions and some indications of where future work in this subject lies.

D. Previous reviews

Previously there have been no reviews specifically devoted to vibrational and rotational polarizabilities, although an article by Bishop *et al.* (1986) contains some material of a review nature. There are, however, several that deal with polarizabilities in general, including reviews by Buckingham on permanent and induced molecular moments (1967), on electric moments of molecules (1970), and on the Stark effect (1972); by Bogaard and Orr (1975) on electric dipole polarizabilities (especially useful for its discussion of dynamic hyperpolarizabilities) and by Orr and Ward (1971; similarly very useful). A recent review by Dykstra *et al.* (1990), deals in part with the role of vibration.

For nonlinear optical properties, from both experimental and theoretical points of view, the books by Hanna *et al.* (1979), Levenson (1982), Shen (1984), and Chemla and Zyss (1987) serve as a good introduction. For very early work on polarizabilities, the books by Debye (1929), Smyth (1955), and Van Vleck (1932) are extremely valuable and of great historic interest. In this review, only articles that were available prior to January 1989 have been considered.

II. GENERAL CONCEPTS

A. Techniques

There are, in principle, two basic ways in which we can calculate *total* polarizabilities for a molecule and whereby vibration and rotation are acknowledged as well as electronic motion (Bishop *et al.*, 1980). In both we assume the Born-Oppenheimer approximation, that is to say, the total molecular rovibronic wave function is written as a product of separate electronic, vibrational, and rotational wave functions.

In the first, we consider the molecule as a *whole* to be perturbed by an electric field and consider a single perturbed Hamiltonian and its concomitant Schrödinger equation. From perturbation theory (Hirschfelder *et al.*, 1964) we can then extract energy terms to various orders in the field and with Eq. (2) these can be associated with polarizabilities of different orders, e.g., the second-order energy correction is related to α. Dissection of these perturbation energies into electronic, vibrational, and rotational components can then be carried out. This is the approach of Brieger (Brieger *et al.*, 1983; Brieger, 1984) and of an earlier, less rigorous treatment by Bishop and Cheung (1980, 1982a)—we shall call it the *sum-over-states method.* A more precise name would be the *sum-over-rovibronic-states method.*

The second method follows more closely the standard Born-Oppenheimer methodology by solving the Schrödinger equation in *two* steps. We think of the molecule first in terms of its electronic motion perturbed by the electric field and solve the appropriate Schrödinger equation to obtain the perturbed potential-energy curve or surface. If we stopped here, we could extract from the energy the well-known electronic polarizabilities—they would, in fact, be only slightly different from those obtained in the first method (Bishop *et al.*, 1980). However, since our interest is in vibration and rotation, we go on to the second step, which is to solve the rovibrational Schrödinger equation and obtain rovibronic energies for the molecule in the presence of the electric field. From these energies we can extract the total polarizabilities (electronic+vibrational+rotational); we call this the *clamped-nucleus method.* There are several ways in which this procedure can be carried out, though they really differ only in technique and not in principle, and in the limit they will give the same results. One way is to choose a variety of field strengths, run the problem through for each, and then numerically differentiate the final total energies to obtain the total polarizabilities; this may also be done just after the first (electronic) step to obtain the electronic polarizabilities and is known as the *finite-field method* (Cohen and Roothaan, 1965). Alternatively, one may determine a set of perturbation-theory expressions at each step, which will have components (electronic from the first step and vibrational and rotational from the second) that can be evaluated from a knowledge (*ab initio* or experimental) of the electronic-transition dipole-moment functions and energies, etc. Finally, an alternative second step can be carried out semianalytically by using a derivative Numerov-Cooley (DNC) technique (Dykstra and Malik, 1987).

Both of these basic methods are capable of giving the same values of the vibrational and rotational polarizabilities, and only approximations made along the way may make this not so. It is simply that in the first method one obtains the property directly from a second-, third-, etc., order energy from a *single* perturbation step, and in the second method one is obliged to find the perturbation to the electronic energy and afterwards the effect of this perturbation on the vibrational-rotational motion. If, in the first step of the second method, the electric field is aligned with a molecular axis, then the effects of rotation will have to be handled by classical averaging. If, however, the field is initially defined with respect to space-fixed axes, then rotation will necessarily be taken into account automatically.

One technique that does not directly fit into the above schemes is the one that is sometimes used to evaluate the Kerr constant. Here consideration is made, by way of perturbation theory, of the change that occurs to the polarizability itself, rather than the energy, by the presence of an electric field; the resulting expressions (Buckingham, 1962a) are, nonetheless, completely equivalent to those obtained via the energy.

B. Coordinate frames

Obviously an extremely important aspect of the subject under review is the relation between polarizabilities calculated with respect to space-fixed axes and those calculated with respect to molecule-fixed axes. For example, what is the connection between α_{ZZ} (Z space-fixed), a quantity we may call "macroscopic" and which is capable of experimental observation, and α_{zz} (z molecule-fixed), which is a theoretical quantity incapable of being directly observed and "microscopic" in nature? Whether we use the sum-over-states or the clamped-nucleus method, the question requires consideration of both rotation (or, classically, orientation) and thermal averaging over the populated rotational states; we assume, for the present, that all molecules are in the ground electronic state and a single vibrational state v.

The classical answer (Debye, 1929; Smyth, 1955) is that

$$\bar{\alpha}_{ZZ}=\frac{\int_0^{2\pi}\int_0^{\pi}\alpha_{\alpha\beta}k_\alpha k_\beta \exp(-\Delta E/kT)\sin\theta\, d\theta\, d\phi}{\int_0^{2\pi}\int_0^{\pi}\exp(-\Delta E/kT)\sin\theta\, d\theta\, d\phi} , \tag{6}$$

where Einstein summation and the Boltzmann law are assumed, θ and ϕ are the usual spherical coordinates that define the molecule's orientation with respect to X, Y and Z, ΔE is the angle-dependent part of the energy of the molecule in the presence of the electric field, k_α is the cosine of the angle between the molecular axis α and the laboratory axis Z, and the bar indicates an average over a statistical distribution of molecular orientations. Expansion of $\exp(-\Delta E/kT)$ gives

$$\bar{\alpha}_{ZZ}=\langle\alpha\rangle_{ZZ}+\text{terms in } T . \tag{7}$$

The first term,

$$\langle\alpha\rangle_{ZZ}=(4\pi)^{-1}\int_0^{2\pi}\int_0^{\pi}\alpha_{\alpha\beta}k_\alpha k_\beta \sin\theta\, d\theta\, d\phi , \tag{8}$$

is the isotropic average, and the terms in T are identified with purely orientational effects.

The quantum-mechanical answer (Van Vleck, 1932) is that

$$\bar{\alpha}_{ZZ}(\text{total})=\bar{\alpha}_{ZZ}(\text{el})+\bar{\alpha}_{ZZ}(\text{vib})+\bar{\alpha}_{ZZ}(\text{rot}) , \tag{9}$$

where, for example, for a diatomic,

$$\bar{\alpha}_{ZZ}(\text{el})=\sum_J\sum_M \rho(v,J,M)\langle vJM|\alpha^e_{ZZ}|vJM\rangle , \tag{10}$$

and the superscript e in Eq. (10) implies the electronic polarizability and

$$\rho(v,J,M)=\frac{g_J\exp[-(E_{vJ}-E_{v0})/kT]}{\sum_J\sum_M g_J\exp[-(E_{vJ}-E_{v0})/kT]} . \tag{11}$$

In this equation $|vJM\rangle$ is the rovibrational wave function (with the usual quantum numbers v, J, and M) and E_{vJ} the corresponding energy, $\rho(vJM)$ is the distribution function for populations of the rotational states associated with the vibrational state v, and g_J is the nuclear-spin degeneracy factor and is required only for homonuclear diatomics. Summing over the rotational quantum number M and integrating over the rotational coordinates gives

$$\bar{\alpha}_{ZZ}(\text{el})=\sum_J \rho(v,J)\langle v(J)|\langle\alpha^e\rangle_{ZZ}|v(J)\rangle , \tag{12}$$

where

$$\rho(v,J)=\sum_M \rho(v,J,M) =\frac{(2J+1)g_J\exp[-(E_{vJ}-E_{v0})/kT]}{\sum_J (2J+1)g_J\exp[-(E_{vJ}-E_{v0})/kT]} , \tag{13}$$

$\langle\alpha^e\rangle_{ZZ}$ is the isotropic average given in Eq. (8), and $|v(J)\rangle$ is the vibrational wave function depending on J through centrifugal distortion. With certain approximations, to be discussed later,

$$\bar{\alpha}_{ZZ}(\text{vib})=\sum_J \rho(v,J)\langle\alpha^v\rangle_{ZZ} , \tag{14}$$

where the superscript v indicates pure vibrational polarizability. Finally, $\bar{\alpha}_{ZZ}(\text{rot})$ in Eq. (9) is the dominant T-dependent part of $\bar{\alpha}_{ZZ}(\text{total})$, but not the only one, for as we shall see in the next section, both $\bar{\alpha}_{ZZ}(\text{el})$ and $\bar{\alpha}_{ZZ}(\text{vib})$ also change slightly with T because of $\rho(v,J)$. Similar conclusions hold for the other polarizabilities, though for some the rotational contribution can be split into two parts: one that arises from the change to $\rho(v,J,M)$ caused by the field (called the distribution component), and one that does not. The distribution component is zero in the present example.

Under certain conditions, to be explored in Sec. IV, the classical orientation term (nonisotropic part) is equivalent to the quantum-mechanical rotational term—the correspondence principle, of course, demands that this be so.

C. Frequently used approximations

In order to simplify the calculations and to bring out the relations that exist between different methods of calculation, certain approximations will frequently be invoked. These often have a common thread and this is the reason we give a general synopsis at this point.

It is very common to assume that

$$\hbar\omega_e \gg \hbar\omega \gg \hbar\omega_v \gg \hbar\omega_r\,, \tag{15}$$

where ω_e, ω_v, and ω_r refer to electronic, vibrational, and rotational transition frequencies and ω is a typical laser frequency. This is a useful approximation because it often allows us to use the closure rule when summing over various quantum states. For example, if n v, and J are quantum numbers specifying electronic, vibrational, and rotational states, respectively, and Ψ_{nvJ} is the total wave function and equals $\psi_n\phi_{vJ}$, then

$$\sum_{n'\neq n}\sum_{v'}\sum_{J'}|\langle\Psi_{nvJ}|\hat{\mu}|\Psi_{n'v'J'}\rangle|^2/(E_{n'v'J'}-E_{nvJ})\cong\sum_{n'\neq n}\langle\phi_{vJ}|\mu^2_{nn'}|\phi_{vJ}\rangle/(E_{n'}-E_n)\,, \tag{16}$$

where $\mu_{nn'}=\langle\psi_n|\hat{\mu}|\psi_{n'}\rangle$. This approximation is based on the use of

$$E_{n'v'J'}-E_{nvJ}\cong E_{n'}-E_n \tag{17}$$

and

$$\sum_{v'}\sum_{J'}|\phi_{v'J'}\rangle\langle\phi_{v'J'}|=1\,. \tag{18}$$

A similar spirit is also involved in Elliott and Ward's (1984) treatment of vibrational polarizabilities, where, in certain cases, they make the approximation

$$100\omega_v\cong 10\omega\cong\omega_e\,. \tag{19}$$

In the same article they also used the concept of "enhanced terms." For example, the perturbation-theory expression for the dynamic second vibrational hyperpolarizability $\gamma^v(-\omega_\sigma;\omega_1,\omega_2,\omega_3)$ introduces terms that have different types of energy denominator, such as

$$\text{(a)}\quad \hbar^3(\omega_{mg}+\omega)(\omega_{ng}-\omega)(\omega_{pg}-\omega)\,,$$

$$\text{(b)}\quad \hbar^3(\omega_{mg}+\omega)(\omega_{ng}-\omega)(\omega_{pg})\,,$$

$$\text{(c)}\quad \hbar^3(\omega_{mg})(\omega_{ng})(\omega_{pg}+\omega)\,,$$

where ω_{mg}, etc., are vibrational transition frequencies and ω is a laser frequency; (a), (b), and (c) are called nonenhanced, singly enhanced, and doubly enhanced terms, respectively. Elliott and Ward then hypothesize that, because $\omega\gg\omega_v$, the most important contributions come from the most enhanced terms. As we shall see later, this is, in fact, not entirely justified.

For diatomics, frequent use is made of the harmonic-oscillator and rigid-rotor approximations. This means, for example, that we can write the vibrational transition matrix elements between the states $v=0$ and $v=v$ of the dipole-moment function as

$$\langle 0|\mu|v\rangle\cong\left[\frac{\hbar}{2m\omega_v}\right]^{1/2}\left[\frac{d\mu}{dR}\right]_{R_e}\,, \tag{20}$$

where m is the nuclear reduced mass, $\hbar\omega_v$ is the vibrational energy, and R is the internuclear distance. A similar approximation holds for polyatomics, with normal coordinates replacing R. In the rigid-rotor approximation, the rotational energies are given by

$$\hbar\omega_J=J(J+1)\hbar B_0\,, \tag{21}$$

where B_0 is the rotational constant and $\hbar\omega_J$ is the rotational energy of the Jth state. Moreover, at high temperatures $\hbar B_0\ll kT$, and we will be able to use

$$1-\frac{(2J+1)}{(2J+3)}\frac{\rho(J+1)}{\rho(J)}\cong\hbar(\omega_{J+1}-\omega_J)/kT\,, \tag{22}$$

$$1-\frac{(2J+1)}{(2J+5)}\frac{\rho(J+2)}{\rho(J)}\cong\hbar(\omega_{J+2}-\omega_J)/kT\,. \tag{23}$$

At room temperature, for diatomics not containing hydrogen, the most populated rotational level is $J\cong 10$, and we can take $J\gg 0$ and make approximations of the type

$$\frac{(J+1)}{(2J+1)}\frac{(J+2)}{(2J+3)}\cong\frac{1}{4}\,. \tag{24}$$

Note that Eq. (22) is used only for polar molecules, for which g_J can be ignored (as was done in deriving it), whereas Eq. (23) is quite general.

Further approximations will be (a) to ignore centrifugal distortion and thus the J dependence in the vibrational wave functions and (b) to assume that only the vibrational ground state is significantly populated and that only transitions to the fundamental vibrational levels occur in sums over the vibrational quantum number.

III. STANDARD VIBRATIONAL AND ROTATIONAL AVERAGING

It is standard procedure in quantum-mechanical calculations to follow the evaluation of molecular electronic properties at several nuclear configurations, by an averaging over the vibrational motion. If this is done for the vibrational ground state, the change in property from its equilibrium value is called the zero-point vibrational correction. For a diatomic molecule, if we allow for centrifugal distortion, the vibrational wave function will have a J dependence, and the average or expectation value of the property $P(R)$, where R is the internuclear distance, will be $\langle v(J)|P(R)|v(J)\rangle$; if we freeze the rotation, it will be $\langle v(0)|P(R)|v(0)\rangle$. Evaluation of such integrals is routinely carried out for electronic polarizabilities, but it should be recalled that this correction is quite different from the pure vibrational polarizabilities, which we shall be discussing later and which are a major part of this review.

Usually, for diatomics the potential-energy curve is available from *ab initio* calculations, and it is simple enough to use the Numerov-Cooley (Cooley, 1963; see also Cashion, 1963; Zare, 1963; LeRoy, 1986) method to obtain the vibrational wave functions $|v(J)\rangle$ and obtain the expectation values by numerical integration. If this is not so, or if one wishes to incorporate empirical data into the description of the vibrational motion, then approximate formulas are available, for example (Schlier, 1961; Buckingham, 1962b; Buckingham and Urland, 1975),

$$\langle v(J)|P(R)|v(J)\rangle = P_e + (v+\tfrac{1}{2})\left[\frac{B_e}{\omega_e}\right]\left[\frac{d^2P}{d\xi^2} - 3a\frac{dP}{d\xi}\right] + 4J(J+1)\left[\frac{B_e}{\omega_e}\right]^2\left[\frac{dP}{d\xi}\right] + \cdots , \tag{25}$$

where

$$\xi = (R - R_e)/R_e \tag{26}$$

and B_e, ω_e, and a are the rotational constant, harmonic vibrational frequency, and anharmonic constant, respectively. This equation is obtained by a Taylor-series expansion of $P(R)$ about the equilibrium e and the use of perturbation theory.

For polyatomics, necessarily, the perturbation-theory expressions are more complex, and the reader is referred to Buckingham and Urland (1975) and to an impressive series of papers by Kern and co-workers on the effect of vibrational motion on the properties of H_2O (Kern and Matcha, 1968; Ermler and Kern, 1971; Sprandel and Kern, 1972; Krohn *et al.*, 1974). Further examples will be given in the following two sections.

We have seen in Eq. (12) that, to relate calculation to experiment, it is necessary to make a thermal average of the expectation values over the rotational states; this is particularly simple for diatomics if we use Eq. (25). In the high-temperature approximation,

$$\sum_J \rho(v,J)J(J+1) \cong kT/\hbar B_e , \tag{27}$$

and with Eq. (25),

$$\sum_J \rho(v,J)\langle v(J)|P(R)|v(J)\rangle \cong \langle v(0)|P(R)|v(0)\rangle + 4\left[\frac{kB_e}{\hbar\omega_e^2}\right]\left[\frac{dP}{d\xi}\right]T , \tag{28}$$

so that there is a linear T dependence for the thermally averaged electronic polarizabilities; the correction will, however, be small and quite different from the major T dependence that comes from the rotational polarizabilities and is of the form $(kT)^{-1}$.

In the next two sections we shall look at some recent examples of polarizability averaging.

A. Vibrational averaging

Werner and Meyer (1976) were one of the earliest groups of investigators to consider zero-point vibrational corrections for electronic polarizabilities. They did this following their calculation of the α polarizability for HF, H_2O, NH_3, CH_4, and CO. They used the approximate formulas mentioned above, based on the techniques of Schlier (1961) and Kern and Matcha (1968). They estimated the corrections to α to be only a few percent (e.g., 5% for CH_4 and 2% for HF).

More recently, Malik and Dykstra (1985) calculated for LiH, using Numerov-Cooley vibrational wave functions, the effect of vibrational averaging on α, β, $\tilde{A}$, $\tilde{B}$, and $\tilde{P}_{x,xx,xx}$ (the last three being traced tensors). The electronic polarizabilities were calculated by the analytical derivative Hartree-Fock method (Dykstra and Jasien, 1984). Since the properties have a strong R dependence, with sharp changes near R_e, there are important changes in the averaged values when the vibrational state is changed; for example, the axial component of β increases by 40% [421 to 599 atomic units (a.u.)] between the $v=0$ and $v=2$ states. In general, we expect large vibrational averaging effects when the properties have a strong nonlinear dependence on R coupled with a high degree of anharmonicity in the potential-energy curve; this is apparent from Eq. (25). Pure vibrational polarizabilities were not considered by Malik and Dykstra (1985).

A recent article by Gu *et al.* (1986) investigates the α polarizability of CO_2 and, in particular, changes with vibrational state. Formulas are given for averaging over the vibrational functions.

B. Vibrational-rotational averaging

Here we look at a few examples of calculations of $\langle v(J)|P|v(J)\rangle$ rather than $\langle v(0)|P|v(0)\rangle$. Maroulis and Bishop (1986) have used Eq. (25) for the evaluation of the α polarizability of H_2, D_2, and T_2 for the $v=0, J=1$ rovibronic state. Raynes *et al.* (1988) have investigated the vibrational-rotational effects on the α polarizabilities of CH_4 and CD_4, and their article is typical of the "state of the art" for polyatomics. They compute α at 77 nuclear geometries and these are then expanded in a power series in the reduced normal coordinates (q_r). Expectation values of q_r, q_r^2, etc., are then determined from formulas developed by Fowler (1981,1984) and lead to the result that, for CH_4, for vibration (in atomic units),

$$\langle\alpha\rangle = 14.945 + 0.189(v_1+\tfrac{1}{2}) + 0.124(v_2+\tfrac{1}{2}) + 0.333(v_3+\tfrac{3}{2}) + 0.080(v_4+\tfrac{3}{2}) ,$$

and for rotation,

$$\langle \alpha \rangle_J - \langle \alpha \rangle_0 = 0.002\,467 J(J+1)\ .$$

They find the zero-point correction to be 5.6% of the equilibrium value and, after thermal averaging, the total nuclear-motion correction (at 300 K) to be 5.71%. We might note that a semi-empirical calculation [Elliott and Ward (1984)] of the pure vibrational polarizability for CH_4 is 0.04×10^{-40} $C^2m^2J^{-1}$ [not 0.04 Å^3, as Raynes *et al.* (1988) quote] and 1.6% of the total polarizability. Raynes *et al.* do not themselves calculate this term.

Mention should also be made of the "transitional" averaging requirement in the calculation of the relative intensities of the fundamental band of the vibrational-rotational Raman spectrum of H_2 and D_2. Cheung *et al.* (1981) have evaluated the needed integrals: $\langle 0(J)|\Delta\alpha(\omega)|v'(J')\rangle$ with $v'=0,1$ and $J'=J\pm 2$ and where $\Delta\alpha(\omega)$ is the frequency-dependent α polarizability anisotropy. They were found by *ab initio* calculation of $\Delta\alpha(\omega)$ followed by numerical integration using Numerov-Cooley vibrational wave functions. Hamaguchi *et al.* (1981) have tackled the same problem by expanding the vibrational wave functions as linear combinations of harmonic-oscillator eigenfunctions and $\Delta\alpha$ as a Taylor series in ξ, thereby being left with simple integrals over powers of ξ, to be evaluated in a final expression involving just $(\Delta\alpha)_e$, $d(\Delta\alpha)/d\xi$, etc., and the usual diatomic spectroscopic constants. A very complete list (many different rovibrational states) of similar integrals, calculated very precisely, for the isotopes of H_2 has been compiled by Schwartz and LeRoy (1987).

IV. POLARIZABILITY (α)

The α polarizability is the most important electrical property of a molecule after the multiple moments, and both the static property α [$\alpha(0)$ or $\alpha(0;0)$] and the dynamic one [$\alpha(\omega)$ or $\alpha(-\omega;\omega)$] are related to primary physicochemical properties, the scalar dielectric constant (ε) and the refractive index (n):

$$\varepsilon = 1 + \rho_0 \alpha / \varepsilon_0\ , \tag{29}$$

where ρ_0 is the number density and ε_0 is the permittivity of vacuum, and

$$\frac{n^2-1}{n^2+2} = \frac{\rho_0 \alpha(\omega)}{3\varepsilon_0} \tag{30}$$

or

$$n \cong 1 + \rho_0 \alpha(\omega)/2\varepsilon_0\ , \tag{31}$$

where ω is the frequency of the light. This section is concerned with contributions to α from nuclear motion that are over and beyond those discussed in the previous section; it is divided into two parts: (a) the static α and (b) the dynamic α. Furthermore, the static α is considered from (1) the clamped-nucleus point of view and (2) the sum-over-states point of view (see Sec. II.A).

The static vibrational polarizability has quite a long history, going back to 1924, when it used to be called, unfortunately, the atomic polarizability (Ebert, 1924). It should be noted that this contribution, α^v, is nonzero only, as we shall see, if the molecule is infrared active and thus, for a diatomic, only if it is polar. [A recent paper (Adamowicz, 1988a) indicates that it is only "negligible" for H_2^+, whereas it is, in fact, exactly zero.] In general, we shall consider the molecules to be in the ground electronic-vibrational state and we shall concentrate on the theory for diatomics. Many of the ideas introduced in this part will be valuable later on when we discuss hyperpolarizabilities; consequently we shall develop some of the equations to a degree higher than is strictly necessary for dealing with α.

A. Static polarizability $\alpha(0;0)$

1. Clamped-nucleus method

a. Electronic equation

From Eq. (2) it is apparent that when a molecule is placed in a static uniform electric field or fields, its electronic eigenvalues become $E = E^0 + E'$, where

$$E' = -\mu_\alpha F_\alpha - \tfrac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \tfrac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - \tfrac{1}{24}\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta - \cdots\ . \tag{32}$$

Since the subject of this review is nuclear motion, we shall take it for granted that the perturbed eigenvalues and/or electronic polarizabilities are known. They may be determined by finite-field (Cohen and Roothan, 1965), derivative Hartree-Fock (Dykstra and Jasien, 1984; Malik and Dykstra, 1985), or charge-perturbation (McLean and Yoshimine, 1967a, 1967b; Bishop and Maroulis, 1985) methods; or from perturbation-theory expressions such as

$$\alpha_{\alpha\beta} = \sum_{n' \neq n} 2 \frac{\langle n|\hat{\mu}_\alpha|n'\rangle\langle n'|\hat{\mu}_\beta|n\rangle}{(E_{n'}-E_n)}\ , \tag{33}$$

where $|n\rangle$ and $|n'\rangle$ are ground and excited electronic state wave functions and E_n and $E_{n'}$ are the corresponding energies. There is a vast literature on the evaluation of $\alpha_{\alpha\beta}$ and, to a lesser extent, on the electronic hyperpolarizabilities.

b. Rovibrational equation

(i) Electric field initially defined by molecule-fixed axes

Having assumed the electronic equation to be solved, we now turn to the rovibrational equation. We shall first consider the field as being defined with respect to the molecular axes—this is equivalent to freezing out rotation. Though this model does not represent any real physical situation, except perhaps in intermolecular interactions, we can approximate the real situation by making a classical isotropic and thermal average of the results and thereby go from the microscopic to the macroscopic. In the next section, the more realistic model of fields defined by laboratory-fixed axes is developed. There have been several methods used to solve the more limited problem but, save for certain approximations, they are all really equivalent, in spite of contrary assertions in the literature (Malik, 1988). We shall classify them as finite-field, derivative Numerov-Cooley, perturbation-theory, and force-constant methods.

Finite field. In this method, introduced by Adamowicz and Bartlett (1986), the vibrational equation is solved numerically by standard procedures (Cooley, 1963; see also Cashion, 1963; Zare, 1963; LeRoy, 1986; and Kirby-Docken and Hinze, unpublished) for different potential-energy curves (it has been applied only to diatomics). These curves have been obtained from electronic eigenvalues that incorporate the effects of different finite perturbing fields. Numerical differencing of the final eigenvalues (corresponding to the different field strengths) gives by analogy with Eq. (32) the total (electronic plus vibrational) polarizabilities. To date, in applications of this technique, only parallel polarizabilities have been determined, since it has been limited to cases in which the electronic equation has been solved by either numerical Hartree-Fock [FH, H_2^+ (Adamowicz and Bartlett, 1986)] or numerical multiconfiguration self-consistent-field (MCSCF) [H_2, HD, D_2 (Adamowicz, 1988a) and OH, OH^+, OH^- (Adamowicz, 1988b)] methods. These methods are based on partial-wave expansions in elliptical coordinates for the molecular orbitals and have been restricted to systems that are essentially two dimensional. The total (electronic and vibrational) α polarizability for FH in the $v=0$ state is 5.93 a.u., compared with the equilibrium electronic value of 5.55 a.u.—the difference, however, is not solely the pure vibrational polarizability α^v, since to determine this quantity knowledge of the vibrationally averaged electronic polarizability is required. The total value for FH ($v=0$) agrees well with that obtained from perturbation-theory expressions [6.002 a.u. (Bishop and Lam, 1987a)]. For OH, OH^+, and OH^-, several vibrational states were investigated; results for $v=0$ are given in Table II. Here, averaged electronic polarizabilities have also been found, so α^v can be deduced; it is clearly quite significant for OH^+ but less so for OH and OH^-.

Quite similar in spirit is the work of Zundel and coworkers, which has been reported in a series of papers from 1970 (Weidemann and Zundel, 1970) to the present (Eckert and Zundel, 1987, 1988). Zundel's interest has been in the vibrational polarizability of H-bonded systems, which he calls the "proton polarizability." In such systems, the potential-energy surface has a double minimum, with a symmetric ground state and a very close-lying asymmetric excited state. The perturbation ($-\mu F$; he omits $-\frac{1}{2}\alpha F^2$, etc.) is, under these circumstances, very effective. The situation is comparable, and for similar reasons, to that which leads to large values of the electronic α for H_2^+ when R is large (Bishop and Cheung, 1979a) and the phenomenon of sudden polarization in organic chemistry (Salem, 1979; see also Brooks and Schaefer, 1979). Zundel calculates vibrational wave functions for various values of the electric field and from these he determines the dipole moment of the H-bond (μ_H). He then differentiates μ_H, presumably numerically, to obtain his "proton polarizability." Since he does not do so under the limit $F \rightarrow 0$, his values, in fact, are not the pure α polarizability but include hyperpolarizability contributions; for this reason he lists them for various values of F. He has studied a great number of H-bonded systems and recently has shown that the "proton polarizability" for the $B^+H\ldots B \rightleftharpoons B\ldots H^+B$ bond within the $H_5O_2^+$ group is about two orders of magnitude larger than the usual electronic polarizability.

TABLE II. α_{zz} polarizabilities for OH, OH^+, and OH^- for $v=0$ (in a.u.). From Adamowicz (1988b).

	OH	OH^+	OH^-
$\alpha_{zz}^e(R_e)$	7.541	4.497	18.34
$\langle 0\vert\alpha_{zz}^e(R)\vert 0\rangle$	7.809	4.679	18.85
$\alpha_{zz}^{\text{total}}$	7.859	5.440	18.95

Derivative Numerov-Cooley (DNC). This technique has been formulated and implemented by Dykstra and co-workers (Dykstra and Malik, 1987; Augspurger and Dykstra, 1988; Malik, 1988). It differs from the previous method by its clever adaptation of the Numerov-Cooley method (which normally determines only the vibrational wave functions and eigenvalues) to compute directly the derivatives of the vibronic energies, and these are precisely the polarizabilities that we want. The perturbed potential-energy curve, in analytic form, is the input to the DNC program, and the output is a set of derivative values—the whole method being, therefore, semianalytic. The important fact is that this method avoids the need to choose finite fields; numerical inaccuracies occur if this choice is not judicious. It has been applied to FH (Dykstra and Malik, 1987; Malik, 1988), where the electronic problem was solved by using the derivative Hartree-Fock method (Dykstra and Jasien, 1984). In addition to the total vibronic polarizabilities for several vibrational states, the averaged values of α^e were obtained; thus the pure vibrational polarizability could be extracted, and some values are given in Table III. So far, this procedure (as with the previous one) has not been developed to take into account rotation. It has been stated (Malik, 1988) that the rotational corrections will be additive, but it is not clear that this will be the case, since rotation appears, through centrifugal distortion, in the vibrational wave functions and, as will be shown later, integrals of the form $\langle v(J)|\mu|v'(J\pm 1)\rangle$ are involved. The problem is exemplified in Table III, where a comparison with the results of Bishop *et al.* (1988), who took rotation into account, is given: the later values decrease quickly

TABLE III. Comparison of results for $\langle \alpha^v \rangle$ for *FH* (in a.u.). From Malik (1988) and Bishop *et al.* (1988).

	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$
Malik (1988)[a]	0.056	0.062	0.067	0.069	0.064
Bishop *et al.* (1988)	0.048	0.044	0.038	0.029	0.017

[a] $\langle \alpha^v \rangle = (\alpha^v_{zz} + 2\alpha^v_{xx})/3 = \alpha^v_{zz}/3$, where z is the nuclear axis; in Malik (1988) it is labeled x.

with v, whereas the former do not. The method has also been applied to H_3^+ (Augspurger and Dykstra, 1988) but considering only the pure stretch vibration; since averaged electronic values are not given, we cannot extract α^v.

Perturbation-theory expressions. Equation (32) is the perturbation to the Hamiltonian in the Schrödinger vibrational equation (we exclude rotation in this treatment). First-order perturbation theory simply averages μ_α, etc., over the unperturbed vibrational wave functions ϕ_m; second and higher orders (Hirschfelder *et al.*, 1964) lead to the vibrational polarizabilities of interest to us:

$$E^{(2)} = -\sum_k{}' V^2_{0k}/\hbar\omega_k \ , \tag{34}$$

$$E^{(3)} = \sum_k{}' \sum_l{}' V_{0k}\bar{V}_{kl}V_{l0}/\hbar^2\omega_k\omega_l \ , \tag{35}$$

$$E^{(4)} = -\sum_k{}' \sum_l{}' \sum_m{}' V_{0k}\bar{V}_{kl}\bar{V}_{lm}V_{m0}/\hbar^3\omega_k\omega_l\omega_m + \sum_k{}' V^2_{0k}/\hbar\omega_k \sum_l{}' V^2_{0l}/\hbar^2\omega_l^2 \ , \tag{36}$$

where $\hbar\omega_k$ indicates the energy difference between the kth vibrational level and the ground-state level (ϕ_0), the prime indicates omission of the vibrational ground state, $V_{0k} = \langle \phi_0 | E' | \phi_k \rangle$ and

$$\bar{V}_{kl} = \langle \phi_k | E' | \phi_l \rangle - V_{00}\delta_{kl} \ ;$$

E' is defined in Eq. (32).

By collecting terms in F^2, F^3, and F^4, we obtain the following expressions for the vibrational polarizabilities:

$$\alpha^v_{\alpha\beta} = \sum_P \sum_k{}' \hbar^{-1}\omega_k^{-1}(\mu_\alpha)_{0k}(\mu_\beta)_{0k} \ , \tag{37}$$

$$\beta^v_{\alpha\beta\gamma} = \sum_P \sum_k{}' \hbar^{-1}\omega_k^{-1}(\mu_\alpha)_{0k}(\alpha_{\beta\gamma})_{0k} + \sum_P \sum_k{}' \sum_l{}' \hbar^{-2}\omega_k^{-1}\omega_l^{-1}(\mu_\alpha)_{0k}(\mu_\beta)_{0l}(\bar{\mu}_\gamma)_{kl} \ , \tag{38}$$

$$\begin{aligned}\gamma^v_{\alpha\beta\gamma\delta} = {} & \sum_P \sum_k{}' \hbar^{-1}\omega_k^{-1}[\tfrac{1}{3}(\mu_\alpha)_{0k}(\beta_{\beta\gamma\delta})_{0k} + \tfrac{1}{4}(\alpha_{\alpha\beta})_{0k}(\alpha_{\gamma\delta})_{0k}] \\ & + \sum_P \sum_k{}' \sum_l{}' \hbar^{-2}\omega_k^{-1}\omega_l^{-1}[\tfrac{1}{2}(\mu_\alpha)_{0k}(\mu_\beta)_{0l}(\bar{\alpha}_{\gamma\delta})_{kl} + (\mu_\alpha)_{0k}(\alpha_{\beta\gamma})_{0l}(\bar{\mu}_\delta)_{kl}] \\ & + \sum_P \sum_k{}' \sum_l{}' \sum_m{}' \hbar^{-3}\omega_k^{-1}\omega_l^{-1}\omega_m^{-1}(\mu_\alpha)_{0k}(\mu_\beta)_{0m}(\bar{\mu}_\gamma)_{kl}(\bar{\mu}_\delta)_{lm} \\ & - \sum_P \sum_k{}' \sum_l{}' \hbar^{-3}\omega_k^{-1}\omega_l^{-2}(\mu_\alpha)_{0k}(\mu_\beta)_{0k}(\mu_\gamma)_{0l}(\mu_\delta)_{0l} \ ,\end{aligned} \tag{39}$$

where $\sum_P$ indicates summation over all permutations of the indices α, β, γ, and δ; $(\mu_\alpha)_{0k} = \langle \phi_0 | \mu_\alpha | \phi_k \rangle$; and μ_α and $\alpha_{\alpha\beta}$ are the dipole-moment function and electronic polarizability, respectively.

Equations (37)–(39) can be further simplified by making the summations only over the fundamental vibrational states, and for a diatomic molecule, for example, we then obtain

$$\alpha^v_{zz} = 2(\mu_z)^2_{01}/\hbar\omega_1 \ , \tag{40}$$

$$\beta^v_{zzz} = 6(\mu_z)_{01}(\alpha_{zz})_{01}/\hbar\omega_1 + 6(\mu_z)^2_{01}(\bar{\mu}_z)_{11}/\hbar^2\omega_1^2 \ , \tag{41}$$

$$\begin{aligned}\gamma^v_{zzzz} = {} & 24[(\alpha_{zz})^2_{01}/4 + (\mu_z)_{01}(\beta_{zzz})_{01}/3]/\hbar\omega_1 \\ & + 24(\mu_z)_{01}[(\mu_z)_{01}(\bar{\alpha}_{zz})_{11}/2 + (\alpha_{zz})_{01}(\bar{\mu}_z)_{11}]/\hbar^2\omega_1^2 \\ & + 24(\mu_z)^2_{01}[(\bar{\mu}_z)^2_{11} - (\mu_z)^2_{01}]/\hbar^3\omega_1^3 \ .\end{aligned} \tag{42}$$

Though our main interest in this section is Eqs. (37) and (40), we might note that if we invoke the harmonic-oscillator approximation for the vibrational transition matrix elements and ignore terms in ω_1^{-2} and ω_1^{-3}, then Eqs. (40) and (41) are the same as those of Pandey and Santry (1980), whose treatment only went as far as second-order perturbation theory. For a homonuclear diatomic, the dipole-moment matrix elements are zero and

$$\gamma^v_{zzzz} = 6(\alpha_{zz})^2_{01}/\hbar\omega_1 \ , \tag{43}$$

which is in accord with the formula of Mizrahi and Shelton (1985a). It has been pointed out by Kirtman (1990) that if the $v=2$ level is included in Eq. (42), then, at the harmonic-oscillator-level of approximation, the last term,

$-24(\mu_z)^4_{07}/\hbar^3\omega_1^3$, is exactly annulled by the additional term $24(\bar{\mu}_z)^2_{12}(\mu_z)^2_{01}/\hbar^3\omega_1^2\omega_2$ which appears; this is also true for a polyatomic molecule.

Equations (40)–(42), together with *ab initio* calculations of the transition matrix elements, have been used to calculate the polarizabilities of FH (Bishop and Lam, 1987a); it was found that $\alpha^v_{zz}=0.243$ a.u. and $\langle 0|\alpha^e|0\rangle=5.759$ a.u., giving a total polarizability of 6.002 a.u., which is in good agreement with the finite-field value of 5.93 a.u. (Adamowicz and Bartlett, 1986).

The oldest and most common method of evaluating α^v from Eq. (40) is to use the experimental infrared-intensity data to find the needed dipole-moment transition matrix elements; the method is therefore semiempirical in nature (LeFevre and Rao, 1955; see also Altshuller, 1955; Whiffen, 1958; Illinger and Smyth, 1960, 1961; Illinger, 1961; Bishop and Cheung, 1982b). For a polyatomic molecule, if g_n is the degeneracy of the nth fundamental vibrational mode, the isotropic vibrational polarizability, Eq. (52), is given by

$$\langle \alpha^v\rangle=\tfrac{2}{3}\sum_n{}' g_n(\mu)^2_{0n}/\hbar\omega_n \ , \tag{44}$$

and since the absolute integrated absorption intensities are

$$A_n=N_A\omega_n g_n(\mu)^2_{0n}/6\varepsilon_0\hbar c^2 \ , \tag{45}$$

we find

$$\begin{aligned}\langle \alpha^v\rangle&=(4\varepsilon_0c^2/N_A)\sum_n{}'(A_n/\omega_n^2)\\ &=5.285\,66\sum_n{}'\frac{(A_n/\mathrm{km\,mol^{-1}})}{(\omega_n/\mathrm{rad\,s^{-1}})^2}10^{15}\ \mathrm{C^2\,m^2\,J^{-1}}\ ,\end{aligned} \tag{46}$$

where we have taken the units of A_n and ω_n that are commonly used by experimentalists. Further relations involve the molar vibrational polarization:

$$P^v=\tfrac{4}{3}\pi N_A\left[\frac{\langle\alpha^v\rangle}{4\pi\varepsilon_0}\right] , \tag{47}$$

$$\begin{aligned}\langle\alpha^v\rangle&=3\varepsilon_0P^v/N_A\\ &=4.4108(P^v/\mathrm{cm^3\,mol^{-1}})10^{-41}\ \mathrm{C^2\,m^2\,J^{-1}}\ .\end{aligned} \tag{48}$$

Values of $\langle\alpha^v\rangle$ for some 100 or more molecules have been found in this way (Bishop and Cheung, 1982b), using known experimental data.

Rinaldi *et al.* (1986) have used the harmonic-oscillator approximation to obtain $g_n(\mu)^2_{0n}$ [see Eq. (20)]:

$$g_n(\mu)^2_{0n}=\frac{\hbar}{2\omega_n}\sum_{\xi=x,y,z}\left[\frac{\partial\mu_\xi}{\partial Q_n}\right]^2_{Q_0} , \tag{49}$$

where Q_n is the nth normal coordinate. They applied the modified neglect of diatomic overlap (MNDO) method to obtain the derivatives and investigated solvent effects on $\langle\alpha^v\rangle$ for a series of small molecules; however, compared with experiment, the results are rather poor.

Force-constant method. In this treatment, published by Duran *et al.* (1989), a specific value of the electric field is included in the electronic Hamiltonian, and the mass-weighted second derivatives (force constants) of the potential-energy surface at the equilibrium nuclear geometry (which has been optimized in the presence of the field) are found analytically. Vibrational frequencies are then obtained by diagonalization of the derivative matrix. Values were determined for CH_4 for several field strengths and orientations. The authors' intention is to predict infrared spectra in the presence of specific fields, and they do not find α^v, β^v, etc., *per se.* Nonetheless, these quantities are embedded in their results and could be extracted by fits to a power series in the field strength. Their method would then be equivalent to the application of the harmonic-oscillator approximation to the previous methods.

Classical isotropic and thermal averaging. To an extent, the polarizabilities calculated in the above manner (which neglected consideration of rotation) can be related to experiment (with space-fixed axes X, Y, and Z) by classical methods, if not by quantum-mechanical methods. Writing

$$\alpha^{ev}_{\alpha\beta}=\alpha^e_{\alpha\beta}+\alpha^v_{\alpha\beta}\ , \tag{50}$$

we find that the isotropic polarizability [see Eq. (8)] is

$$\langle\alpha\rangle_{ZZ}=(4\pi)^{-1}\int_0^{2\pi}\int_0^{\pi}\alpha^{ev}_{\alpha\beta}k_\alpha k_\beta\sin\theta\, d\theta\, d\phi\ , \tag{51}$$

where k_α is the cosine of the angle between the Z and α axes. This gives

$$\langle\alpha\rangle_{ZZ}=(\alpha^{ev}_{xx}+\alpha^{ev}_{yy}+\alpha^{ev}_{zz})/3=\alpha_{\xi\xi}/3\ . \tag{52}$$

Further, in dielectric-constant experiments, the measured quantity is

$$\bar{\alpha}=(\overline{\mu^F_Z}/F)_{F\to 0}\ , \tag{53}$$

where

$$\overline{\mu^F_Z}=\frac{\int_0^{2\pi}\int_0^{\pi}(\mu_\alpha k_\alpha+\alpha^{ev}_{\alpha\beta}k_\alpha k_\beta F+\cdots)e^{-\Delta E/kT}\sin\theta\, d\theta\, d\phi}{\int_0^{2\pi}\int_0^{\pi}e^{-\Delta E/kT}\sin\theta\, d\theta\, d\phi} \tag{54}$$

and ΔE is the angular-dependent part of the energy of the molecule in the presence of the field. If only $(kT)^{-1}$ terms are retained in the expansion of the exponential, then

$$\exp(-\Delta E/kT)=1+\mu_z k_z F/kT+\Delta\alpha k_z^2F^2/2kT+(3\beta_{zxx}k_z+\Delta\beta k_z^3)F^3/6kT+\cdots , \tag{55}$$

with $\Delta\alpha=\alpha_{zz}^{ev}-\alpha_{xx}^{ev}$, $\Delta\beta=\beta_{zzz}^{ev}-3\beta_{zxx}^{ev}$, and z is the molecular axis of symmetry. Combining Eqs. (52)–(55), we get

$$\bar{\alpha}=\langle\alpha\rangle_{ZZ}+\mu^2/3kT . \tag{56}$$

This is the same as the quantum-mechanical high-temperature result in the next section. It will generally be true that, classically, temperature dependence is coupled with a lower-order electrical property.

(ii) Electric field initially defined by space-fixed axes

In this derivation we consider the perturbation to the Hamiltonian of the Schrödinger rovibrational equation to emanate from a uniform static electric field along a space-fixed axis oriented *arbitrarily* with respect to the molecule. The derivation, for a diatomic molecule, follows that given in Bishop *et al.* (1988). Equation (32) is now replaced by

$$E'=-\mu F\cos\theta-\tfrac{1}{2}\alpha_{\|}F^2\cos^2\theta-\tfrac{1}{2}\alpha_{\perp}F^2\sin^2\theta-\cdots , \tag{57}$$

where θ is the angle between the vector separation of the nuclei and the field vector, and $\alpha_{\|}$ and $\alpha_{\perp}$ are electronic polarizability components parallel ($\alpha_{\|}=\alpha_{zz}$) and perpendicular ($\alpha_{\perp}=\alpha_{xx}$) to the nuclear axis. Second-order perturbation theory, the introduction of the rovibrational wave functions $\Phi_{vJM}=|v(J)\rangle Y_J^M(\theta,\phi)$, and integration over θ and ϕ leads to the following second-order energy:

$$E^{(2)}=-\tfrac{1}{2}\alpha(v,J,M)F^2 , \tag{58}$$

with

$$\alpha(v,J,M)=\alpha^e(v,J,M)+\alpha^v(v,J,M)+\alpha^r(v,J,M) , \tag{59}$$

where

$$\alpha^e(v,J,M)=\langle v(J)|\alpha_{\perp}|v(J)\rangle+(C_{JM}+D_{JM})\langle v(J)|\Delta\alpha|v(J)\rangle , \tag{60}$$

$$C_{JM}=\frac{(J+1)^2-M^2}{(2J+1)(2J+3)} , \tag{61}$$

$$D_{JM}=\frac{J^2-M^2}{(2J-1)(2J+1)} , \tag{62}$$

$$C_{JM}+D_{JM}=\frac{2J^2+2J-1-2M^2}{(2J+3)(2J-1)} , \tag{63}$$

and

$$\alpha^v(v,J,M)=C_{JM}X+D_{JM}Y , \tag{64}$$

with

$$X=\sum_{v'\neq v}\frac{2|\langle v(J)|\mu|v'(J+1)\rangle|^2}{E_{v',J+1}-E_{v,J}} , \tag{65}$$

$$Y=\sum_{v'\neq v}\frac{2|\langle v(J)|\mu|v'(J-1)\rangle|^2}{E_{v',J-1}-E_{v,J}} , \tag{66}$$

and

$$\alpha^r(v,J,M)=C_{JM}R+D_{JM}S , \tag{67}$$

with

$$R=2|\langle v(J)|\mu|v(J+1)\rangle|^2/(E_{v,J+1}-E_{v,J}) , \tag{68}$$

$$S=2|\langle v(J)|\mu|v(J-1)\rangle|^2/(E_{v,J-1}-E_{v,J}) . \tag{69}$$

Throughout these equations μ is the dipole-moment function and is dependent on the internuclear separation.

Assuming a Maxwell-Boltzmann distribution over the J rotational states, and summing over J and M, gives

$$\bar{\alpha}=\sum_J\rho(v,J)(2J+1)^{-1}\sum_M\alpha(v,J,M) , \tag{70}$$

$$\bar{\alpha}^e(v)=\tfrac{1}{3}\sum_J\rho(v,J)\langle v(J)|\alpha_{\|}+2\alpha_{\perp}|v(J)\rangle , \tag{71}$$

$$\bar{\alpha}^v(v)=\tfrac{1}{3}\sum_J\rho(v,J)(2J+1)^{-1}[(J+1)X+JY] , \tag{72}$$

$$\bar{\alpha}^r(v)=\tfrac{1}{3}\sum_J\rho(v,J)(2J+1)^{-1}[(J+1)R+JS] , \tag{73}$$

with $\rho(v,J)$ as defined in Eq. (13).

It is of interest, for the purposes of this review, to consider how Eqs. (72) and (73) might be approximated. We could (a) assume

$$|v'(J+1)\rangle\cong|v'(J-1)\rangle\cong|v'(J)\rangle ,$$

(b) assume

$$E_{v',J+1}\cong E_{v',J-1}\cong E_{v',J} ,$$

(c) ignore entirely the J dependence of the wave functions and energies, or (d) assume the rigid-rotor energies of Eq. (21).

Approximations (a) and (b) lead to

$$\bar{\alpha}^v(v)'=\tfrac{1}{3}\sum_J\rho(v,J)\sum_{v'\neq v}2|\langle v(J)|\mu|v'(J)\rangle|^2/(E_{v',J}-E_{v,J}) ; \tag{74}$$

alternatively, approximation (c) gives

$$\bar{\alpha}^v(v)''=\tfrac{1}{3}\sum_{v'\neq v}2|\langle v(0)|\mu|v'(0)\rangle|^2/(E_{v',0}-E_{v,0}) , \tag{75}$$

which is equivalent to Eq. (37). Approximations (a) and (d) and the high-temperature approximation for $\rho(v,J)$ lead to

$$\bar{\alpha}^r(v)'=\tfrac{1}{3}|\langle v(0)|\mu|v(0)\rangle|^2/kT , \tag{76}$$

which is the same as the classical result of Eq. (56). If, on the other hand, we do not approximate $\rho(v,J)$, we get

$$\bar{\alpha}^{r}(v)'' = \tfrac{1}{3}|\langle v(0)|\mu|v(0)\rangle|^2 \rho(v,0)/\hbar B_0$$
$$= \tfrac{1}{3}|\langle v(0)|\mu|v(0)\rangle|^2 (kT)^{-1}[1 - \tfrac{1}{3}(\hbar B_0/kT) + \tfrac{2}{45}(\hbar B_0/kT)^2 \cdots] . \tag{77}$$

This equation can be obtained by using the Euler-Maclaurin approximation or the formulas of Mulholland (1928). It necessarily applies only to polar diatomics for which nuclear spin degeneracy in $\rho(v,0)$ can be ignored.

The question now arises, how good are these approximations? This has been partially answered by Bishop *et al.* (1988), who investigated LiH and FH. For LiH, $\bar{\alpha}^{v}(v)$ and $\bar{\alpha}^{r}(v)$ and their approximants were calculated from an *ab initio* potential-energy curve and dipole-moment function of Partridge and Langhoff (1981) for several values of v; some sample results are given in Table IV. The approximations for $\bar{\alpha}^{v}(v)$ appear to deteriorate with increasing v; however, the $\bar{\alpha}^{r}(v)'$ approximation appears to be quite accurate. For FH, the same conclusions hold, and we have already seen in Table III some results for $\bar{\alpha}^{v}(v)$ compared with those of Malik (1988).

Finally, Wharton and Klemperer (1963), in an early progenitor of the work of Brieger (Brieger *et al.*, 1983; Brieger, 1984), which will be discussed in the next section, investigated electronic and vibrational effects on Stark rotational spectroscopy. They derived a formula for the vibrational contribution to a rotational-state polarizability as

$$\alpha^{v}(v,J,M) = (C_{JM} + D_{JM}) \sum_{v' \neq v} 2|\langle v|\mu|v'\rangle|^2/(E_{v'} - E_v) . \tag{78}$$

This equation is in accord with Eq. (64) when approximation (c) is invoked.

2. Sum-over-states method

The most detailed and comprehensive analysis of the α polarizability of a diatomic molecule has been formulated by Brieger (Brieger *et al.*, 1983; Brieger, 1984). His particular interest was the Stark splitting of the $A\,{}^1\Sigma^+, v'=5, J'=1$ level of ^{7}LiH, but his treatment is of quite general utility. He uses the sum-over-states method [see Sec. II.A], and the field is held along an arbitrary space-fixed axis; this introduces $3j$ symbols from the necessary Eulerian transformation. Since the field is considered to perturb the molecule as a whole, the Schrödinger equation is in principle not separated into electronic and rovibrational parts. Use of perturbation theory leads to an expression for the second-order perturbation energy or α, which involves the complete unperturbed rovibronic excited-state wave functions $|n'v'J'\rangle$ and energies $E_{n'v'J'}$; unprimed labels will specify the state for which α is being calculated. This expression is then partitioned into four terms: (a) an "electronic" term, where the intermediate states involve electronic states of Σ symmetry different from that of interest: $n \neq n'$; (b) a second "electronic" term, where the intermediate states involve electronic states of Π symmetry: $n \neq n'$; (c) a "vibrational" term, where $n = n'$, but the intermediate vibrational states are different from that of the state of interest: $n = n'$, $v \neq v'$; (d) a "rotational" term, where the intermediate states are different from the state of interest only in their rotational motion: $n = n'$, $v = v'$. Another way of expressing this is that (a) and (b) account for interaction with adjacent rovibrational levels of other Σ- and Π-symmetry electronic states, (c) accounts for the interaction with rovibrational levels of the same Σ electronic state, and (d) accounts for the interaction with adjacent rotational states.

The following equation results:

$$E^{(2)} = -\tfrac{1}{2}F^2 \sum_{J'} (2J'+1)(2J+1) \begin{bmatrix} J' & J & 1 \\ M & -M & 0 \end{bmatrix}^2 \left\{ \begin{bmatrix} J' & J & 1 \\ 0 & 0 & 0 \end{bmatrix}^2 [\alpha_{\parallel}^{e}(J,J') + \alpha_{\parallel}^{v}(J,J') + \alpha_{\parallel}^{r}(J,J')] + \begin{bmatrix} J' & J & 1 \\ -1 & 0 & 1 \end{bmatrix}^2 2\alpha_{\perp}^{e}(J,J') \right\} , \tag{79}$$

with the electronic, vibrational, and rotational branch polarizabilities (Brieger, 1984)

$$\alpha_{\parallel}^{e}(J,J') = -\sum_{n' \neq n} \sum_{v'} \frac{2|\langle nv(J)|\mu_0^{M}|n'v'(J')\rangle|^2}{E_{nvJ} - E_{n'v'J'}} \quad (n' = \Sigma) , \tag{80}$$

TABLE IV. Calculations of vibrational and rotational polarizabilities for LiH at $T=22\,^{\circ}\mathrm{C}$ (in a.u.). From Bishop *et al.* (1988).

	$v=0$	$v=2$	$v=5$
$\bar{\alpha}^{v}(v)$	0.923	0.726	0.148
$\bar{\alpha}^{v}(v)'$	0.941	1.099	1.158
$\bar{\alpha}^{v}(v)''$	0.930	1.089	1.154
$\bar{\alpha}^{r}(v)$	1898	2040	2248
$\bar{\alpha}^{r}(v)'$	1914	2056	2264

$$\alpha_{\perp}^{e}(J,J')=-\sum_{n'\neq n}\sum_{v'}\frac{|\langle nv(J)|\mu_{-1}^{M}|n'v'(J')\rangle|^2}{E_{nvJ}-E_{n'v'J'}}\quad(n'=\Pi)\ , \tag{81}$$

$$\alpha_{\parallel}^{v}(J,J')=-\sum_{v'\neq v}\frac{2|\langle nv(J)|\mu_{0}^{M}|nv'(J')\rangle|^2}{E_{nvJ}-E_{nv'J'}}\ , \tag{82}$$

$$\alpha_{\parallel}^{r}(J,J')=-2\frac{|\langle nv(J)|\mu_{0}^{M}|nv(J')\rangle|^2}{E_{nvJ}-E_{nvJ'}}\ , \tag{83}$$

where μ_g^M is the spherical vector component of the dipole-moment operator, e.g., $\mu_0^M=\hat{\mu}_z$.

It is instructive to see how certain approximations will bring these expressions into line with those of the clamped-nucleus method in Sec. IV.A.1.b.(ii). If we ignore the negligible "electronic-branch-polarizability" differences with respect to different J', then the electronic contribution is

$$E_{\mathrm{el}}^{(2)}\cong-\tfrac{1}{2}F^2\left[\bar{\alpha}(J)-\tfrac{2}{3}\Delta\alpha(J)\frac{3M^2-J(J+1)}{(2J-1)(2J+3)}\right]\ , \tag{84}$$

with

$$\bar{\alpha}(J)=\tfrac{1}{3}[\alpha_{\parallel}(J)+2\alpha_{\perp}(J)]\ , \tag{85}$$

$$\Delta\alpha(J)=\alpha_{\parallel}(J)-\alpha_{\perp}(J)\ , \tag{86}$$

$$\alpha_{\parallel}(J)=\tfrac{1}{2}[\alpha_{\parallel}(J,J-1)+\alpha_{\parallel}(J,J+1)]\ , \tag{87}$$

$$\alpha_{\perp}(J)=\tfrac{1}{3}[\alpha_{\perp}(J,J-1)+\alpha_{\perp}(J,J)+\alpha_{\perp}(J,J+1)]\ . \tag{88}$$

If we equate the polarizabilities $\alpha_{\parallel}(J)$ and $\alpha_{\perp}(J)$ with the vibrationally averaged values in Eq. (60), the latter equation can be shown to be equivalent to Eq. (84). However, this is an approximation, and it has been noted before (Bishop *et al.*, 1980) that the $\alpha_{\parallel}(J,J)$ etc. given above are intrinsically different from those of Eq. (60). Among other things, the former have denominators that are differences of total energies of rovibronic *states*, while the latter, vibrationally averaged standard electronic polarizabilities, have embedded energy differences between electronic states at fixed internuclear separations. Even if one neglects the vibrational-rotational energy in the denominator of Eq. (80) and uses closure over v', this problem remains. Fortunately, it appears (Bishop *et al.*, 1980) that the quantitative consequencies are very small.

For the vibrational and rotational components, the two methods are equivalent: combining Eqs. (79) and (82) will lead to Eq. (64), and combining Eqs. (79) and (83) will lead to Eq. (67). In the latter case, the rigid-rotor approximation coupled with

$$|v(J+1)\rangle\cong|v(J-1)\cong|v(J)\rangle$$

gives

$$E_{\mathrm{rot}}^{(2)}\cong\frac{(\mu)_{v(J)}^2}{2B_vJ(J+1)}\frac{J(J+1)-3M^2}{(2J-1)(2J+3)}F^2\quad(J\neq0)\ , \tag{89}$$

$$E_{\mathrm{rot}}^{(2)}\cong\frac{-(\mu)_v^2}{6B_v}F^2\quad(J=0)\ , \tag{90}$$

and Eq. (89) is the same as that in Wharton and Klemperer (1963). However, Brieger cautions against the second approximation.

His example, the $A\,{}^1\Sigma^+$ state of LiH, though not necessarily typical (the dipole-moment function changes sign at 5.8 Å), does emphasize the importance of considering all terms in rotational Stark spectroscopy and not just Eqs. (83) or (89). Using the limited theoretical data of Vidal and Stwalley (1982) and Partridge *et al.* (1981), he finds the field-reduced level shift for $v'=5$, $J=1$, $M=0$ to be

$$\begin{aligned}E^{(2)}/F^2&=2.436(\mathrm{rot})-20.654(\mathrm{vib})\\&\quad+16.918(\mathrm{el}-\parallel)-0.139(\mathrm{el}-\perp)\\&=-1.439\ \mathrm{kHz/(kV/cm)^2}\ .\end{aligned} \tag{91}$$

Hence there is almost complete cancellation of the first three terms. His estimate of the $M=0\rightarrow M=\pm1$ splitting is only one-half of the experimental value, but whether this is due to inadequate theoretical data or inaccurate experimentation is not really known. However, the smallness of this splitting puts great demands on both theory and experiment.

B. Dynamic polarizability $\alpha(-\omega;\omega)$

The dynamic α polarizability is directly related to a material's refractive index [see Eq. (30)]. To be consistent with the notation used later for the dynamic hyperpolarizabilities, we should write it as $\alpha_{\alpha\beta}(-\omega_\sigma;\omega_1)$ or $\alpha_{\alpha\beta}(-\omega;\omega)$, though $\alpha_{\alpha\beta}(\omega)$ is more frequently employed in the literature. Using time-dependent perturbation theory (Langhoff *et al.*, 1972) and the formalism of Orr and Ward (1971), we have

$$\alpha_{\alpha\beta}(-\omega_\sigma;\omega_1)=\sum_P\sum_{n'v'J'}{}'\frac{\langle nvJ|\hat{\mu}_\alpha|n'v'J\rangle\langle n'v'J'|\hat{\mu}_\beta|nvJ\rangle}{E_{n'v'J'}-E_{nvJ}-\hbar\omega_\sigma}\ , \tag{92}$$

where $\sum_P$ indicates permutation of the pairs $(\hat{\mu}_\alpha/-\omega_\sigma)$ and $(\hat{\mu}_\beta/\omega_1)$ and the prime on the second summation means exclusion of the state of interest, whose energy is E_{nvJ} and whose rovibronic wave function is $|nvJ\rangle$. This expression has been partitioned into electronic, vibrational, and rotational components, using the usual energy approximations and closure techniques of Sec. II.C, by Bishop and Cheung (1980, 1982a). The results were applied to H_2 and HeH^+. In that work the dipole-moment operators $\hat{\mu}_\alpha$ were defined with respect to molecular axes, and classical isotropic and thermal averaging was carried out.

A more rigorous and realistic treatment is to use space-fixed axes for the electric field and to follow the methodology in Sec. IV.A.1.b.(ii). We then obtain, for a diatomic molecule,

$$\bar{\alpha}(-\omega;\omega)=\bar{\alpha}^{e}+\bar{\alpha}^{v}+\bar{\alpha}^{r}\,, \tag{93}$$

where the electronic component is given by

$$\bar{\alpha}^{e}=\tfrac{1}{3}\sum_{J}\rho(v,J)\langle v(J)|\alpha_{\parallel}+2\alpha_{\perp}|v(J)\rangle \tag{94}$$

and

$$\alpha_{\parallel}=\sum_{P}\sum_{n'\neq n}\frac{|\langle n|\mu_0^{M}|n'\rangle|^2}{E_{n'}-E_{n}-\hbar\omega_{\sigma}}\,, \tag{95}$$

or the more familiar

$$\alpha_{\parallel}=\sum_{n'\neq n}\frac{2(E_{n'}-E_{n})}{(E_{n'}-E_{n})^2-(\hbar\omega)^2}|\langle n|\mu_0^{M}|n'\rangle|^2\,, \tag{96}$$

where $|n'\rangle$ is the electronic wave function of an excited state and $E_{n'}$ is the corresponding energy (both depend on the internuclear separation).

For the vibrational component

$$\bar{\alpha}^{v}=\tfrac{1}{3}\sum_{J}\rho(v,J)(2J+1)^{-1}[(J+1)X+JY]\,, \tag{97}$$

where

$$X=\sum_{P}\sum_{v'\neq v}\frac{|\langle v(J)|\langle n|\mu_0^{M}|n\rangle|v'(J+1)\rangle|^2}{E_{v',J+1}-E_{v,J}-\hbar\omega_{\sigma}}\,, \tag{98}$$

$$Y=\sum_{P}\sum_{v'\neq v}\frac{|\langle v(J)|\langle n|\mu_0^{M}|n\rangle|v'(J-1)\rangle|^2}{E_{v',J-1}-E_{v,J}-\hbar\omega_{\sigma}}\,, \tag{99}$$

and $E_{v,J}$ and $|v(J)\rangle$ are rovibrational energies and vibrational wave functions for the nth electronic state. Or, approximately,

$$\bar{\alpha}^{v}\cong\tfrac{1}{3}\sum_{P}\sum_{v'\neq v}\frac{|\langle v(0)|\langle n|\mu_0^{M}|n\rangle|v'(0)\rangle|^2}{E_{v',0}-E_{v,0}-\hbar\omega_{\sigma}}\,. \tag{100}$$

For the rotational component

$$\bar{\alpha}^{r}=\tfrac{1}{3}\sum_{J}\rho(v,J)(2J+1)^{-1}[(J+1)R+JS]\,, \tag{101}$$

where

$$R=\sum_{P}\frac{|\langle v(J)|\langle n|\mu_0^{M}|n\rangle|v(J+1)\rangle|^2}{E_{v,J+1}-E_{v,J}-\hbar\omega_{\sigma}}\,, \tag{102}$$

$$S=\sum_{P}\frac{|\langle v(J)|\langle n|\mu_0^{M}|n\rangle|v(J-1)\rangle|^2}{E_{v,J-1}-E_{v,J}-\hbar\omega_{\sigma}}\,. \tag{103}$$

If we assume, as is often the case, $\hbar\omega\gg 0$ for all ω, then $\bar{\alpha}^{r}=0$; that is, in classical terms, there is no orienting effect for an oscillating electric field. On the other hand, if $\infty>\hbar\omega>\tilde{\Omega}$ (where $\tilde{\Omega}$ is a mean rotational-energy-level separation), then

$$\bar{\alpha}^{r}\cong-\frac{4}{3}\frac{B_v}{(\hbar\omega)^2}\mu_0^2\,. \tag{104}$$

Finally, we can get the classical result $\bar{\alpha}^{r}=\mu_0^2/3kT$ by setting $\hbar\omega=0$.

Alternatively, using the rigid-rotor approximation, defining $\Omega_{J,J'}$ as the energy separation between the J and J' rotational levels, and approximating

$$R\cong 2\mu^2\frac{\Omega_{J+1,J}}{\Omega_{J+1,J}^2-(\hbar\omega)^2}\,, \tag{105}$$

$$S\cong 2\mu^2\frac{\Omega_{J-1,J}}{\Omega_{J-1,J}^2-(\hbar\omega)^2}\,, \tag{106}$$

where μ is a mean vibrational value of the dipole moment, then

$$\bar{\alpha}^{r}\cong\tfrac{1}{3}\mu^2\sum_{J}\frac{\rho(v,J)}{(2J+1)B_v}\frac{\Omega_{J+1,J}^2}{\Omega_{J+1,J}^2-(\hbar\omega)^2}\times\left[1-\frac{(2J+1)\rho(v,J+1)}{(2J+3)\rho(v,J)}\right]\,, \tag{107}$$

and with the approximation of Eq. (22), appropriate for a heteronuclear (polar) diatomic molecule, this leads to

$$\bar{\alpha}^{r}\cong\frac{1}{3}\frac{\mu^2}{kT}\sum_{J}\rho(v,J)\left[\frac{(2J+2)}{(2J+1)}\frac{\Omega_{J+1,J}^2}{\Omega_{J+1,J}^2-(\hbar\omega)^2}\right] \tag{108}$$

$$=\frac{1}{3}\frac{\mu^2}{kT}\left\langle\frac{(2J+2)}{(2J+1)}\frac{\Omega_{J+1,J}^2}{\Omega_{J+1,J}^2-(\hbar\omega)^2}\right\rangle\,, \tag{109}$$

where $\langle\ \rangle$ indicates an average over the thermally populated rotational states. Equation (109) is equivalent to Eq. (177) in Debye's (1929) book.

For common laser frequencies $\bar{\alpha}^{v}(-\omega;\omega)$ is negligible, and if the temperature-dependent $\bar{\alpha}^{r}(-\omega;\omega)$ component has been extracted from the experimental values of $\bar{\alpha}(-\omega;\omega)$, then an extrapolation to $\omega=0$ of these values for these frequencies will give $\bar{\alpha}^{e}(0;0)$; if, as well, the temperature-independent part of $\bar{\alpha}(0,0)$ is known from static-field experiments, we will have an experimental means of determining $\bar{\alpha}^{v}(0;0)$; that is, in these circumstances:

$$\bar{\alpha}^{v}(0;0)=\bar{\alpha}(0;0)-\lim_{\omega\to 0}\bar{\alpha}(-\omega;\omega)\,. \tag{110}$$

This is a simple example of how, from different processes, here dynamic and static, we can extract the different contributions to the total polarizability. Elliott and Ward (1984) have used this method and compared experimental $\bar{\alpha}^{v}(0;0)$ values with those found by semiempirical means by way of Eq. (46). Typical of the kind of agreement they find is for CF_4 $\bar{\alpha}^{v}(\text{expt.})=1.13\times10^{-40}$ $C^2\,m^2\,J^{-1}$ and $\bar{\alpha}^{v}(\text{semiempirical})=1.02\times10^{-40}$ $C^2\,m^2\,J^{-1}$. Recently, it has been noted by Lu and Shelton (1987) that for CF_4 $\bar{\alpha}^{v}(0;0)$ must be of the same order as $\bar{\alpha}^{e}(0;0)$, i.e., 3.14×10^{-40} $C^2\,m^2\,J^{-1}$. The simple reason is that with mean values ($\tilde{A}$) for the transition energies and transition matrix elements, both electronic (e) and vibrational (v), $\tilde{\Omega}_e\cong100\tilde{\Omega}_v$ and $|\tilde{\mu}_e|\cong10|\tilde{\mu}_v|$ and hence $|\tilde{\mu}_e|^2/\tilde{\Omega}_e\cong|\tilde{\mu}_v|^2/\tilde{\Omega}_v$; see Eqs. (33) and (40).

Cai *et al.* (1987) have used Eq. (110) for studies on three vibrational states of CO_2. They compared their results from this equation, using their own experimental Rayleigh scattering data for $\bar{\alpha}(-\omega;\omega)$, with those obtained by using Eq. (46) and infrared intensities. The difference between the two methods for $\Delta\alpha^v$ was about 20%. It is likely that this discrepancy can be explained by the lack of quality in some of the infrared-intensity data.

V. HYPERPOLARIZABILITIES (β,γ)

Much of the theory and many of the techniques for calculating the effects of vibration and rotation on the polarizability α may be extended to the hyperpolarizabilities β and γ. We shall therefore organize this section in the same way as we did in Sec. IV for α.

A. Static hyperpolarizabilities $\beta(0;0,0)$ and $\gamma(0;0,0,0)$

Commonly written simply as β,γ or $\beta(0),\gamma(0)$, the notation $\beta(0;0,0)$, $\gamma(0;0,0,0)$ is consistent with that required for delineating the dynamic hyperpolarizabilities. The static hyperpolarizabilities are usually determined experimentally from the dynamic quantities (which mediate nonlinear optical processes) by extrapolation of the values to zero optical frequency. Again, our focus is on the effect of vibrational and rotational motion.

1. Clamped-nucleus method

a. Electric field initially defined by molecule-fixed axes

Finite field. This technique, which we have already discussed in connection with α, is readily extended to β and γ by using higher-order numerical differencing on the field-perturbed vibronic energies. Adamowicz (1988b) has used it for OH, OH^+, and OH^- and for a variety of vibrational states. The results for OH^- were not as numerically stable as those for OH and OH^+. In Table V we give his values for OH and OH^+ for $v=0$. It is apparent that the vibrational polarizability is very significant for these species. Since the numerical MCSCF method, which was used in determining the electronic wave functions, is limited to systems with axial symmetry, only the molecular axial (z) components were determined. Adamowicz (1988a) has also carried out the same procedure for H_2, HD, and D_2 for the three lowest vibrational states, and his value for the vibronic γ_{zzzz} component of H_2 for $v=0$ is 1088 a.u., which is in line with other methods in this section (see Table VI) [e.g., Bishop and Lam (1987b)], although greater than the thermal value based on spaced-fixed axes (Bishop and Lam, 1988a; Bishop *et al.*, 1990), which is discussed in Sec. V.B.3.b. Since the value of $\gamma_{zzzz}(R_e)$ is on the order of 600 a.u., the vibrational contribution is of about equal size. The β hyperpolarizability is exactly zero for homonuclear diatomics.

TABLE V. Values of $\beta_{zzz}(0;0,0)$ and $\gamma_{zzzz}(0;0,0,0)$ for OH and OH^+ for $v=0$ (in a.u.). From Adamowicz (1988b).

		At R_e	Vibrational average	Total
OH	β_{zzz}	−11.83	−13.43	−6.72
	γ_{zzzz}	582	630	905
OH^+	β_{zzz}	−7.51	−8.61	16.88
	γ_{zzzz}	128	139	597

The $H_2{}^+$ ion was one of the first cases in which it was discovered that vibrational effects could enormously influence the hyperpolarizabilities (Bishop and Solunac, 1985; Adamowicz and Bartlett, 1986). Adamowicz and Bartlett found the vibronic γ_{zzzz} component to be 2.3×10^3 a.u., two orders of magnitude greater than the electronic value at R_e, and in agreement with the results of perturbation theory (Bishop *et al.*, 1986; Bishop and Lam, 1987b); see Table VII. Adamowicz (1988a) showed that this value increases with vibrational quantum number and for $v=4$ becomes 41.6×10^3 a.u. The method has been applied to FH by Adamowicz and Bartlett (1986) and Bishop and Lam (1987a), and results are given in Table VIII. There is a radical change to β_{zzz} when vibration is taken into account and γ_{zzzz} is increased by about 50%. These two sets of calculation are in good agreement with each other if one bears in mind that different procedures were used to determine the electronic wave functions.

Derivative Numerov-Cooley (DNC). This method determines *directly*, from an adaptation of the Numerov-Cooley method, and without the need for fitting or differencing procedures, the polarizabilities from the field-perturbed potential-energy curve. Dykstra and Malik (1987) and Malik (1988) have applied it to FH, and the results for the axial β component ($v=0$) are given in Table VIII; the value of β^v (10.041 a.u.) agrees reasonably well with other treatments, e.g., Bishop and Lam (1987a); the total (vibronic) value is, however, somewhat smaller. β^v increases to 32.52 a.u. for $v=4$. In Dykstra and Malik

TABLE VI. Values of the total (electronic and vibrational) second hyperpolarizability calculated by different methods for H_2 ($v=0$) (in a.u.).

Method	Reference[a]	Property	Value
Finite field	A	γ_{zzzz}	1088
Derivative	AD	γ_{zzzz}	1086
Perturbation theory	BL	γ_{zzzz}	1099[b]
Exact[c]	BPR	γ_{ZZZZ}	854.5

[a] A=Adamowicz (1988a); AD=Augspurger and Dykstra (1988); BL=Bishop and Lam (1987b); BPR=Bishop *et al.* (1990).

[b] The calculated value of γ^v_{zzzz} is 416, to which has been added γ_{zzzz} (at R_e) [taken from Maroulis and Bishop (1986)].

[c] This value is a thermal average and with respect to space-fixed axes [see Sec. V.B.3.b and Bishop *et al.* (1990)].

TABLE VII. Values of the axial component of the second hyperpolarizability of H_2^+ for $v=0$ (in a.u.).

	Finite field	Perturbation theory	
	AB[a]	Eq. (111)[b]	Eq. (114)[c]
$\gamma(R_e)$		-40.9	
$\gamma^{e\,d}$		-193	-193
γ^{v}		2390	1695
Total	2.3×10^3	2197	1502

[a] Adamowicz and Bartlett (1986).

[b] From Bishop and Lam (1987b).

[c] From Bishop *et al.* (1986).

[d] Averaged over the vibrational ground state.

(1987) the observation is made that β^v will be small if $\mu(R)$ and $\alpha(R)$ change slowly with internuclear distance (R); this is transparent if one considers Eqs. (41) and (20). Augspurger and Dykstra (1988) have also looked at H_2 and H_3^+ (one of the few cases of a polyatomic, although limited to the pure symmetric-stretch vibrational mode). Their value for H_2 for the axial vibronic γ $(v=0)$ agrees well with the other values in Table VI. For the vibrational ground state of H_3^+, they find the axial vibronic β to be 241.63 a.u., once again a value very different from the value at R_e $(-58.744$ a.u.).

Perturbation-theory expressions. Bishop and Lam (1987b), following the theory in Bishop (1987a), have calculated the independent components of γ^v for H_2^+, H_2, and N_2 for $v=0$. For homonuclear diatomics the equations they used, which follow from Eq. (39), are

$$\gamma^{v}_{zzzz}=6\sum_{k}{}'(\alpha_{zz})^2_{0k}/\hbar\omega_k\ , \tag{111}$$

$$\gamma^{v}_{xxxx}=6\sum_{k}{}'(\alpha_{xx})^2_{0k}/\hbar\omega_k\ , \tag{112}$$

$$\gamma^{v}_{xxzz}=2\sum_{k}{}'(\alpha_{xx})_{0k}(\alpha_{zz})_{0k}/\hbar\omega_k\ , \tag{113}$$

TABLE VIII. Values of the axial hyperpolarizabilities of FH for $v=0$ (in a.u.).

	Finite field		DNC	Perturbation theory	
Reference[a]	AB	BL	M	BL[b]	LRZ[c]
$\beta(R_e)$	-7.6	-8.02	-9.139	-8.02	-8.42
$\beta^{e\,d}$			-10.505	-8.47	
β^{v}			10.041	10.99	10.5
Total	1.6	2.35	-0.464	2.5	
$\gamma(R_e)$	230	229		229	
$\gamma^{e\,d}$				235.3	
γ^{v}				139.3	
Total	362	382		374	

[a] AB=Adamowicz and Bartlett (1986); BL=Bishop and Lam (1987a); M=Malik (1988); LRZ=Lazzeretti *et al.* (1981).

[b] Equations (41) and (42).

[c] Equation (41), but only the first term and the harmonic-oscillator approximation.

[d] Averaged over the vibrational ground state.

where $(\alpha)_{0k}$ indicates a vibrational transition matrix element for the ground vibrational state to the kth excited vibrational state of the electronic polarizability. The values for H_2^+ and H_2 for the axial component are given in Tables VI and VII and have already been referred to. The same authors (1987a) have also used Eqs. (41) and (42) to obtain β^v_{zzz} and γ^v_{zzzz} for FH; the results are to be found in Table VIII.

Equation (41), but with the second term missing and the harmonic-oscillator approximation assumed, i.e., the formula given in Pandey and Santry (1980), has been used by Lazzeretti *et al.* (1981) to find β^v_{zzz} for FH (10.5 a.u.) and HCl (21.6 a.u.). Finally, Eq. (42) in the harmonic-oscillator approximation [see Eq. (20)] becomes

$$\gamma^{v}_{zzzz}=\frac{3}{m\omega^2}\left[\frac{\partial\alpha_{zz}}{\partial R}\right]^2_{R_e} \tag{114}$$

for a homonuclear diatomic; here m is the reduced nuclear mass and ω is the fundamental vibrational frequency. For H_2^+ this gives 1695 a.u., which, when compared with the other values in Table VII, shows that the approximation is rather severe.

Classical isotropic averaging. The previous methods for calculating β^v and γ^v may be used in conjunction with isotropic averaging (Bishop, 1987b). If k_α is the cosine of the angle between space-fixed axis Z and molecular axis α, then

$$\begin{aligned}\langle\gamma\rangle_{ZZZZ}&=(4\pi)^{-1}\int_0^{2\pi}\int_0^{\pi}\gamma_{\alpha\beta\gamma\delta}k_\alpha k_\beta k_\gamma k_\delta\sin\theta\,d\theta\,d\phi\\&=\tfrac{1}{5}\gamma_{\xi\xi\eta\eta}(0;0,0,0)\ .\end{aligned} \tag{115}$$

A similar prescription for β leads to $\langle\beta\rangle_{ZZZ}=0$; however, a mean value is defined in the literature that is relevant to nonlinear optical processes. It comes from classical thermal averaging. Using Eq. (55) and the equivalent of Eqs. (53) and (54) but with μ^F_Z replaced by

$$\beta^F_{ZZZ}=\beta_{\alpha\beta\gamma}k_\alpha k_\beta k_\gamma+\gamma_{\alpha\beta\gamma\delta}k_\alpha k_\beta k_\gamma k_\delta F+\cdots\ , \tag{116}$$

we obtain

$$\bar{\gamma}=(\overline{\beta^F_{ZZZ}/F})_{F\to0}=\langle\gamma\rangle_{ZZZZ}+\frac{\mu\bar{\beta}}{3kT}\ , \tag{117}$$

where

$$\bar{\beta}=\tfrac{3}{5}\beta_{z\xi\xi}(0;0,0)\ . \tag{118}$$

For a diatomic molecule, the symmetry allows for simplification and

$$\bar{\beta}=\tfrac{3}{5}(\beta_{zzz}+2\beta_{zxx}) \tag{119}$$

and

$$\langle\gamma\rangle_{ZZZZ}=\tfrac{1}{15}(3\gamma_{zzzz}+12\gamma_{xxzz}+8\gamma_{xxxx})\ , \tag{120}$$

where z is the bond axis; here use has been made of the relation

$$\gamma_{xxxx}=3\gamma_{xxyy}\ , \tag{121}$$

which is found by isotropic averaging over the equivalent x and y axes. Expressions for $\langle\gamma\rangle$ for the other combinations of space-fixed axes will be given in Sec. V.B.2, where they relate to the dynamic hyperpolarizabilities.

b. Electric field initially defined by space-fixed axes

The theory in Sec. IV.A.1.b.(ii) for determining α for a diatomic molecule when the electric field is placed arbitrarily in space can be extended to the hyperpolarizabilities. The perturbation to the Hamiltonian in the rovibrational Schrödinger equation now includes higher terms:

$$\begin{aligned} E' = &-[\mu P_1(\cos\theta)]F - \tfrac{1}{2}[\bar{\alpha} + \tfrac{2}{3}\Delta\alpha P_2(\cos\theta)]F^2 \\ &- \tfrac{1}{6}[\bar{\beta}P_1(\cos\theta) + \tfrac{2}{5}\Delta\beta P_3(\cos\theta)]F^3 - \cdots , \end{aligned} \tag{122}$$

where $\bar{\alpha}=(\alpha_{zz}+2\alpha_{xx})/3$, $\Delta\alpha=(\alpha_{zz}-\alpha_{xx})$, $\bar{\beta}=3(\beta_{zzz}+2\beta_{zxx})/5$, $\Delta\beta=(\beta_{zzz}-3\beta_{zxx})$, θ is the angle between the space-fixed axis Z and the bond axis z, and P_k are the usual Legendre polynomials.

Using standard perturbation theory, the second-, third-, and fourth-order perturbation energies are

$$\begin{aligned} E^{(2)} = &-\sum_k{}' |\langle 0|\mu P_1|k\rangle|^2 F^2/\hbar\omega_k - \sum_k{}' \langle 0|\bar{\alpha}+\tfrac{2}{3}\Delta\alpha P_2|k\rangle\langle k|\mu P_1|0\rangle F^3/\hbar\omega_k \\ &-\tfrac{1}{3}\sum_k{}' \langle 0|\mu P_1|k\rangle\langle k|\bar{\beta}P_1+\tfrac{2}{5}\Delta\beta P_3|0\rangle F^4/\hbar\omega_k - \tfrac{1}{4}\sum_k{}' \langle 0|\bar{\alpha}+\tfrac{2}{3}\Delta\alpha P_2|k\rangle\langle k|\bar{\alpha}+\tfrac{2}{3}\Delta\alpha P_2|0\rangle F^4/\hbar\omega_k , \end{aligned} \tag{123}$$

$$\begin{aligned} E^{(3)} = &-\sum_k{}'\sum_l{}' \langle 0|\mu P_1|k\rangle\langle \overline{k|\mu P_1|l}\rangle\langle l|\mu P_1|0\rangle F^3/\hbar^2\omega_k\omega_l - \sum_k{}'\sum_l{}' \langle 0|\mu P_1|k\rangle\langle k|\mu P_1|l\rangle\langle l|\bar{\alpha}+\tfrac{2}{3}\Delta\alpha P_2|0\rangle F^4/\hbar^2\omega_k\omega_l \\ &-\sum_k{}'\sum_l{}' \langle 0|\mu P_1|k\rangle\langle \overline{k|\bar{\alpha}+\tfrac{2}{3}\Delta\alpha P_2|l}\rangle\langle l|\mu P_1|0\rangle F^4/\hbar^2\omega_k\omega_l , \end{aligned} \tag{124}$$

$$\begin{aligned} E^{(4)} = &-\sum_k{}'\sum_l{}'\sum_m{}' \langle 0|\mu P_1|k\rangle\langle \overline{k|\mu P_1|l}\rangle\langle \overline{l|\mu P_1|m}\rangle\langle m|\mu P_1|0\rangle F^4/\hbar^3\omega_k\omega_l\omega_m \\ &+\sum_k{}'\sum_l{}' |\langle 0|\mu P_1|k\rangle|^2|\langle 0|\mu P_1|l\rangle|^2 F^4/\hbar^3\omega_k\omega_l^2 , \end{aligned} \tag{125}$$

where, for the sake of brevity, we have used a very simplified notation for the rovibrational wave functions and energies of the unperturbed system: $|k\rangle$ and $\hbar\omega_k$; the bar indicates $\langle k|A|l\rangle-\langle 0|A|0\rangle\delta_{kl}$; and the prime on the sums indicates omission of the rovibrational ground state $|0\rangle$ or the state for which the polarizability is being determined, $|vJM\rangle$.

Collecting terms in F^4, integrating over the rotational angles θ and ϕ, summing over the rotational quantum number M, and taking a Maxwell-Boltzmann distribution for the population of the rotational states [$\rho(v,J)$ in Eq. (13)] gives, after some tedious algebra,

$$\begin{aligned} \gamma^v_{ZZZZ} = \sum_v\sum_J\sum_{v'\neq v} \Bigg[&\frac{8}{3}\left[\frac{(J+1)}{(2J+1)}\rho(v,J)\mu_{vJ,v'J+1}\bar{\beta}_{v'J+1,vJ}/\hbar\omega_{v'J+1,vJ} + \frac{(J+1)}{(2J+3)}\rho(v,J+1)\mu_{vJ+1,v'J}\bar{\beta}_{v'J,vJ+1}/\hbar\omega_{v'J,vJ+1}\right] \\ &+6\Bigg\{\rho(v,J)\alpha^2_{vJ,v'J}/\hbar\omega_{v'J,vJ} + \frac{2}{15}\frac{(J+1)(J+2)}{(2J+1)(2J+3)}\rho(v,J)\Delta\alpha^2_{vJ,v'J+2}/\hbar\omega_{v'J+2,vJ} \\ &+\frac{4}{45}\frac{J(J+1)}{(2J+3)(2J-1)}\rho(v,J)\Delta\alpha^2_{vJ,v'J}/\hbar\omega_{v'J,vJ} \\ &+\frac{2}{15}\frac{(J+2)(J+1)}{(2J+3)(2J+5)}\rho(v,J+2)\Delta\alpha^2_{vJ+2,v'J}/\hbar\omega_{v'J,vJ+2}\Bigg]\Bigg] . \end{aligned} \tag{126}$$

These are the leading terms; other exist, with denominators of ω^2 and ω^3, which we shall not give (they are very cumbersome and, in perturbation terms, of less significance)—they will be zero for a nonpolar diatomic. In Eq. (126) $\mu_{vJ,v'J+1}$ is $\langle v(J)|\mu|v'(J+1)\rangle$ etc., and $\hbar\omega_{v'J+1,vJ}$ is the transition energy between the two states $(v',J+1)$ and (v,J). If only the $v=0$ vibrational state is populated, then the first summation is dropped, and we can write $\rho(v,J)$ as $\rho(0,J)=\rho(J)$.

γ^r_{ZZZZ} emanates from the same procedure and is composed of those terms with $v'=v$ [which are excluded in Eq. (126)] and for which the denominator is nonzero. Thus

$$\begin{aligned} \gamma^r_{ZZZZ} = \sum_J \Bigg[&\frac{8}{3}\frac{(J+1)}{(2J+1)}\mu_{vJ,vJ+1}\bar{\beta}_{vJ,vJ+1}\left\{\rho(v,J)-\frac{(2J+1)}{(2J+3)}\rho(v,J+1)\right]\Big/\hbar\omega_{vJ+1,vJ} \\ &+\frac{4}{5}\frac{(J+1)(J+2)}{(2J+1)(2J+3)}\Delta\alpha^2_{vJ,vJ+2}\left\{\rho(v,J)-\frac{(2J+1)}{(2J+5)}\rho(v,J+2)\right]\Big/\hbar\omega_{vJ+2,vJ}\Bigg] , \end{aligned} \tag{127}$$

where $\hbar\omega_{vJ+1,vJ}$ is a rotational-energy separation in the vibrational state v.

We can, if we wish, approximate Eq. (126) by dropping the J dependence in the vibrational wave functions and assuming the high-temperature approximation ($J \gg 0$). This leads to

$$\gamma^{v}_{ZZZZ}=\sum_{v'\neq v}\left[\tfrac{8}{3}\mu_{vv'}\bar{\beta}_{v'v}+6\bar{\alpha}^{2}_{vv'}+\tfrac{8}{15}\Delta\alpha^{2}_{vv'}\right]\Big/\hbar\omega_{v'v}\ , \tag{128}$$

which is identical to the molecule-fixed-axis result, which follows after isotropic averaging.

The same approximations for γ^{r}_{ZZZZ} and using Eqs. (22) and (23) give

$$\gamma^{r}_{ZZZZ}=(kT)^{-1}(\tfrac{4}{3}\mu_{vv}\bar{\beta}_{vv}+\tfrac{1}{5}\Delta\alpha^{2}_{vv})\ . \tag{129}$$

Equations (128) and (129), as well as (126) and (127), are only the leading terms, though complete for a homonuclear diatomic, where of course the $\mu\bar{\beta}$ contributions are zero.

So far, we have not taken into account the fact that the distribution function $\rho(v,J)$ or $\rho(J)$ will also be affected by the field and thus may contribute terms to certain electric-field-related properties. The only important example is the Kerr effect (Bishop and Shelton, 1988). Here what is being measured is the field-perturbed α polarizability. We start with Eq. (84) and reexpress it as

$$\alpha_{ZZ}(J,M)=\bar{\alpha}_{vv}+\tfrac{2}{3}B\,\Delta\alpha_{vv}\ ,$$
$$B=\frac{J^{2}+J-3M^{2}}{(2J-1)(2J+3)}\ , \tag{130}$$

and

$$\sum_{M=-J}^{+J}B=0\ . \tag{131}$$

We now express α_{ZZ} pertrubed by the field as

$$\alpha^{F}_{ZZ}(J,M)=\alpha_{ZZ}(J,M)+\tfrac{1}{2}\gamma_{ZZZZ}(J,M)F^{2} \tag{132}$$

and the field-perturbed distributions as

$$\rho^{F}(J,M)=\frac{g_{J}\exp(-E^{F}_{JM}/kT)}{\sum_{J}\sum_{M}g_{J}\exp(-E^{F}_{JM}/kT)}\ . \tag{133}$$

Assuming the diatomic is nonpolar,

$$E^{F}_{JM}=E^{0}_{J}-\tfrac{1}{2}\alpha_{ZZ}(J,M)F^{2}-\cdots \tag{134}$$

and

$$\rho^{F}(J,M)=\frac{g_{J}\exp(-E^{0}_{J}/kT)[1+\tfrac{1}{3}B\,\Delta\alpha F^{2}/kT+\cdots]}{\sum_{J}g_{J}(2J+1)\exp(-E^{0}_{J}/kT)}\ , \tag{135}$$

where we have made use of Eq. (131). The property to be measured is of the form

$$\begin{aligned}(\overline{\alpha^{F}_{ZZ}}/F^{2})_{F\to 0}&=\left[\sum_{J}\sum_{M}\rho^{F}(J,M)\alpha^{F}_{ZZ}(J,M)/F^{2}\right]_{F\to 0}\\&=\tfrac{1}{2}\gamma_{ZZZZ}+\sum_{J}\sum_{M}(\tfrac{2}{3}B\,\Delta\alpha_{vv})(\tfrac{1}{3}B\,\Delta\alpha_{vv})(2J+1)^{-1}(kT)^{-1}\rho(J)\ .\end{aligned} \tag{136}$$

We therefore define the distribution component as

$$\begin{aligned}\gamma^{\text{dist}}_{ZZZZ}&=\sum_{J}\tfrac{4}{9}\rho(J)\Delta\alpha^{2}_{vv}(kT)^{-1}(2J+1)^{-1}\sum_{M}B^{2}\\&=\sum_{J}\frac{4}{45}\frac{J(J+1)}{(2J-1)(2J+3)}\rho(J)(kT)^{-1}\Delta\alpha^{2}_{vv}\ ,\end{aligned} \tag{137}$$

or, with the high-temperature approximation,

$$\gamma^{\text{dist}}_{ZZZZ}=\tfrac{1}{45}(kT)^{-1}\Delta\alpha^{2}_{vv}\ . \tag{138}$$

Adding this to γ^{r}_{ZZZZ}, we find that the total rotational γ for this experiment in the limiting static case is

$$\gamma^{r}_{ZZZZ}=(kT)^{-1}(\tfrac{4}{3}\mu_{vv}\bar{\beta}_{vv}+\tfrac{2}{9}\Delta\alpha^{2}_{vv})\ . \tag{139}$$

The same approximate result can be found by classical thermal averaging. In reality, in the Kerr experiment both a dynamic and a static field are present, and Eq. (139) is modified; this will be discussed in Sec. V.B.5.

Equations (126) and (127) have been used (Bishop and Lam, 1988b) to calculate the γ vibrational and rotational contributions to the states $v=0$ and $J=0,1,\ldots,10$ for H_2^+ (i.e., the sums over v and J are not made). These intermediate results are useful for analysis of high-angular-momentum states of H_2. For γ^{v}_{ZZZZ} ($v=0$), if the sum over the eleven rotational states is made, one obtains 585 a.u., and the equivalent electronic property is γ^{e}_{ZZZZ} ($v=0$)=28 a.u. As we have seen before, the vibrational contribution by far outweighs the electronic contribution for γ_{zzzz}; we now have the same situation for the space-fixed-field quantities. These *ab initio* calculations used essentially exact electronic and vibrational wave functions and energies, something possible only for a system as simple as H_2^+. In Bishop and Lam (1988c) a comparison has been made for H_2^+ and for H_2 of the exact expressions, Eqs. (126) and (127), and the approximate ones, Eqs. (128) and (129). To Eqs. (127) and (129), a distribution term was added which for a measurement based on the induced dipole moment, is three times[1] the term for the Kerr experiment given in Eqs. (137) and (138). Consequently,

$$\sum_J \frac{4}{15}\frac{J(J+1)}{(2J-1)(2J+3)}\rho(J)(kT)^{-1}\Delta\alpha^2$$

was added to Eq. (127) and $\frac{1}{15}(kT)^{-1}\Delta\alpha^2$ to Eq. (129). Results were given for the $v=0$ to $v=5$ vibrational states for $H_2{}^+$. At 295 K for $v=0$, γ^v_{ZZZZ} is 584 a.u. and unchanged by the approximations, but for $v=5$ the exact and approximate values are 18 704 and 21 179, respectively. So, once again, the approximation deteriorates with the higher vibrational levels. For H_2, only the $v=0$ level was considered, and both expressions gave the same γ^v_{ZZZZ} value: ~183 a.u. The approximations for rotation for both $H_2{}^+$ and H_2 were seen to be acceptable only at high temperature; at 295 K for $v=0$, the error is 10% for $H_2{}^+$ and 30% for H_2, this difference reflecting the larger rotational constant for H_2.

2. Sum-over-states method

A complete and rigorous derivation using the sum-over-states approach, such as Brieger (1984) gave for α, has not yet been accomplished for β and γ. What follows is a sketch of how this could be done. We start with the perturbation expressions for the electronic static hyperpolarizabilities

$$\beta_{\alpha\beta\gamma}=\hbar^{-2}\sum_{p}\sum_{m\neq g}\sum_{n\neq g}\frac{\langle g|\hat{\mu}_\alpha|m\rangle\langle \overline{m|\hat{\mu}_\gamma|n}\rangle\langle n|\hat{\mu}_\beta|g\rangle}{\omega_{mg}\omega_{ng}}\,, \tag{140}$$

$$\gamma_{\alpha\beta\gamma\delta}=\hbar^{3}\sum_{P}\left[\sum_{m\neq g}\sum_{n\neq g}\sum_{p\neq g}\frac{\langle g|\hat{\mu}_\alpha|m\rangle\langle \overline{m|\hat{\mu}_\delta|n}\rangle\langle \overline{n|\hat{\mu}_\gamma|p}\rangle\langle\,|\hat{\mu}_\beta|g\rangle}{\omega_{mg}\omega_{ng}\omega_{pg}} - \sum_{m\neq g}\sum_{n\neq g}\frac{\langle g|\hat{\mu}_\alpha|m\rangle\langle m|\hat{\mu}_\delta|g\rangle\langle g|\hat{\mu}_\gamma|n\rangle\langle n|\hat{\mu}_\beta|g\rangle}{\omega_{mg}\omega_{ng}^2}\right], \tag{141}$$

where $|g\rangle$ and $|m\rangle$ are ground- and excited-state electronic wave functions and $\hbar\omega_{mg}$ is the energy difference between the two, $\sum_P$ indicates the summation over all permutations of $\hat{\mu}_\alpha$, $\hat{\mu}_\beta$, $\hat{\mu}_\gamma$, and $\hat{\mu}_\delta$, and the bar means $\langle \overline{m|\hat{\mu}_\delta|n}\rangle=\langle m|\hat{\mu}_\delta|n\rangle-\langle g|\hat{\mu}_\delta|g\rangle\delta_{mn}$. These expressions can then be generalized so that the wave functions and energies are the total rovibronic ones and the sums are carried out over all electronic, vibrational, and rotational quantum numbers; the dipole-moment operators are understood to be defined with respect to laboratory axes.

The resulting expressions can be partitioned into three types of terms: (a) rotational (those involving a pure rotational state of the electronic ground state as an intermediate), (b) vibrational (those involving a rovibrational state of the electronic ground state), and (c) electronic (all the rest). Use of the approximation $\omega_e>\omega_v>\omega_r$ for the electronic, vibrational, and rotational transition frequencies, followed by closure and summing over the free-rotor states with thermal averaging, will give results equivalent to those in the previous section.

Let us, as an example, consider γ^v for a homonuclear diatomic molecule. Since $\langle g|\hat{\mu}_\alpha|m\rangle=0$ for transitions to states within the rovibrational manifold of the ground electronic state, we need take only contributions where $|n\rangle$, the middle intermediate state, belongs to the ground electronic state manifold:

$$\gamma^v_{\alpha\beta\gamma\delta}=\hbar^{-3}\sum_P\sum_{n\neq g}\omega_{ng}^{-1}\left[\sum_{m\neq g}\frac{\langle g|\hat{\mu}_\alpha|m\rangle\langle m|\hat{\mu}_\delta|n\rangle}{\omega_{mg}}\right]\left[\sum_{p\neq g}\frac{\langle n|\hat{\mu}_\gamma|p\rangle\langle p|\hat{\mu}_\beta|g\rangle}{\omega_{pg}}\right], \tag{142}$$

with $|g\rangle=|e,v,J,M\rangle$, $|m\rangle$ or $|p\rangle=|e'',v'',J'',M''\rangle$ and $e''\neq e$, $|n\rangle=|e,v',J',M'\rangle$ and $v'\neq v$. This can be rewritten as

$$\gamma^v_{\alpha\beta\gamma\delta}=\sum_P\sum_{n\neq g}\tfrac{1}{4}(\alpha_{\alpha\delta})_{gn}(\alpha_{\gamma\beta})_{ng}/\hbar\omega_{ng}\,, \tag{143}$$

where

$$(\alpha_{\alpha\delta})_{gn}=\sum_{m\neq g}2\langle g|\hat{\mu}_\alpha|m\rangle\langle m|\hat{\mu}_\delta|n\rangle/\hbar\omega_{mg} \tag{144}$$

and

$$(\alpha_{\gamma\beta})_{ng}=\sum_{p\neq g}2\langle n|\hat{\mu}_\gamma|p\rangle\langle p|\hat{\mu}_\beta|g\rangle/\hbar\omega_{pg}\,. \tag{145}$$

The expression in Eq. (143) can then be evaluated by taking a statistical distribution over rotational states and summing over the rotational quantum numbers. This we shall leave until the next section, in which we shall con-

---

[1] The factor of three is really a question of defining γ with respect to a particular experiment. Here the assumption is made that the experiment involves measurement of the induced dipole moment, and γ is extracted from the coefficient of F^3 in the expansion of this moment.

sider dynamic hyperpolarizabilities and use the procedure of Shelton (1987a). Closure and the usual approximations concerning rotation allow us to write Eq. (143) as

$$\gamma^{v}_{\alpha\beta\gamma\delta}=\sum_{P}\sum_{v'\neq v}\tfrac{1}{4}\langle v|\alpha_{\alpha\delta}|v'\rangle\langle v'|\alpha_{\gamma\beta}|v\rangle/\hbar\omega_{vv'}\ , \tag{146}$$

where the integrals and energies are for vibrational transitions and $\alpha_{\alpha\delta}$ is the electronic polarizability.

B. Dynamic hyperpolarizabilities $\beta(-\omega_\sigma;\omega_1,\omega_2)$ and $\gamma(-\omega_\sigma;\omega_1,\omega_2,\omega_3)$

1. Introduction

As was stated in Sec. I, the importance of the dynamic hyperpolarizabilities lies in their relation to the science of nonlinear optics. Again, we are concerned with the effects of vibration and rotation, and here much less progress has been made than was the case for the static quantities; most of the investigations have been carried out by just three groups, those of Ward, Shelton, and Bishop and their co-workers. Except for H_2^+ and H_2, the numerical results achieved have been based on the use of empirical data for the required matrix elements and energies, and these have been taken from infrared, Raman, and hyper-Raman intensities and frequencies. Because these data are often approximate and usually the signs of the matrix elements are unknown, the final results are more qualitative than quantitative. The experimental quantities obtained from nonlinear optical processes, and with which we want to make a comparison, are usually decomposed into a temperature-dependent and a temperature-independent part, so that, if we ignore the small temperature dependence that comes from standard vibrational averaging (see Sec. III), the temperature-independent part can approximately be assumed to encompass the pure vibrational contributions, and this is where most of the theoretical effort has been placed. We shall, for the sake of clarity, concentrate on just two processes: the Kerr effect and electric-field-induced second-harmonic generation (ESHG).

The formulas for the dynamic hyperpolarizabilities, which are the counterparts to Eqs. (140) and (141), have been given by Orr and Ward (1971), they are

$$\beta_{\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2)=\hbar^{-2}\sum_{P}\sum_{m,n\neq g}\frac{\langle g|\bar{\mu}_\alpha|m\rangle\overline{\langle m|\bar{\mu}_\gamma|n\rangle}\langle n|\bar{\mu}_\beta|g\rangle}{(\omega_{mg}-\omega_\sigma)(\omega_{ng}-\omega_1)}\ , \tag{147}$$

$$\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)=\hbar^{-3}\sum_{P}\left[\sum_{m,n,p\neq g}\frac{\langle g|\bar{\mu}_\alpha|m\rangle\overline{\langle m|\bar{\mu}_\delta|n\rangle}\,\overline{\langle n|\bar{\mu}_\gamma|p\rangle}\langle p|\bar{\mu}_\beta|g\rangle}{(\omega_{mg}-\omega_\sigma)(\omega_{ng}-\omega_1-\omega_2)(\omega_{pg}-\omega_1)}-\sum_{m,n\neq g}\frac{\langle g|\bar{\mu}_\alpha|m\rangle\langle m|\bar{\mu}_\delta|g\rangle\langle g|\bar{\mu}_\gamma|n\rangle\langle n|\bar{\mu}_\beta|g\rangle}{(\omega_{mg}-\omega_\sigma)(\omega_{ng}-\omega_1)(\omega_{ng}+\omega_2)}\right]\ , \tag{148}$$

where $\sum_P$ now means the sum over all permutations of the *pairs*: $(\bar{\mu}_\alpha/-\omega_\sigma),(\bar{\mu}_\beta/\omega_1)$, $(\bar{\mu}_\gamma/\omega_2),(\bar{\mu}_\delta/\omega_3)$. The reader is reminded that our definitions of β and γ give values that are twice and six times as great, respectively, as those of Ward and co-workers. Equations (147) and (148) will be the basis for our discussion. For the Kerr effect we shall also give an alternative formulation. The generalization of Eqs. (147) and (148) and subsequent decomposition into electronic, vibrational, and rotational contributions will follow as in the preceding section.

2. Classical isotropic averaging

Our initial discussion will assume that rotation is frozen and that connection to experiment is to be made through classical isotropic averaging. To this end the following relations are employed (Bogaard and Orr, 1975; Shelton, 1986c):

$$\langle\gamma\rangle_{ZZZZ}=\tfrac{1}{15}(\gamma_{\xi\xi\eta\eta}+\gamma_{\xi\eta\xi\eta}+\gamma_{\xi\eta\eta\xi})\ , \tag{149}$$

$$\langle\gamma\rangle_{ZZXX}=\tfrac{1}{30}(4\gamma_{\xi\xi\eta\eta}-\gamma_{\xi\eta\xi\eta}-\gamma_{\xi\eta\eta\xi})\ , \tag{150}$$

$$\langle\gamma\rangle_{ZXZX}=\tfrac{1}{30}(4\gamma_{\xi\eta\xi\eta}-\gamma_{\xi\eta\eta\xi}-\gamma_{\xi\xi\eta\eta})\ , \tag{151}$$

$$\langle\gamma\rangle_{ZXXZ}=\tfrac{1}{30}(4\gamma_{\xi\eta\eta\xi}-\gamma_{\xi\xi\eta\eta}-\gamma_{\xi\eta\xi\eta})\ , \tag{152}$$

where the laboratory axes X, Z, etc., follow the sequence of the frequencies ω_σ, ω_1, ω_2, and ω_3. Also, for a diatomic molecule, isotropic averaging over the equivalent x and y axes gives

$$\gamma_{xxxx}=\gamma_{xxyy}+\gamma_{xyxy}+\gamma_{xyyx}\ . \tag{153}$$

For the Kerr effect (K), we have

$$\begin{aligned}\beta^K_{\parallel}&=\langle\beta\rangle^K_{ZZZ}\\&=\tfrac{1}{5}[\beta_{\xi\xi z}(-\omega;\omega,0)+2\beta_{\xi z\xi}(-\omega;\omega,0)]\ ,\\\beta^K_{\perp}&=\langle\beta\rangle^K_{XXZ}\\&=\tfrac{1}{5}[2\beta_{\xi\xi z}(-\omega;\omega,0)-\beta_{\xi z\xi}(-\omega;\omega,0)]\ ,\end{aligned} \tag{154}$$

$$\beta^K = \tfrac{3}{2}(\beta_{\parallel}^K - \beta_{\perp}^K)$$

$$= \tfrac{3}{10}[3\beta_{\xi z\xi}(-\omega;\omega,0) - \beta_{\xi\xi z}(-\omega;\omega,0)] \,, \tag{155}$$

$$\gamma_{\parallel}^K = \langle \gamma \rangle_{ZZZZ}^K$$

$$= \tfrac{1}{15}[\gamma_{\xi\xi\eta\eta}(-\omega;\omega,0,0) + 2\gamma_{\xi\eta\xi\eta}(-\omega;\omega,0,0)] \,, \tag{156}$$

$$\gamma_{\perp}^K = \langle \gamma \rangle_{XXZZ}^K$$

$$= \tfrac{1}{15}[2\gamma_{\xi\xi\eta\eta}(-\omega;\omega,0,0) - \gamma_{\xi\eta\xi\eta}(-\omega;\omega,0,0)] \,, \tag{157}$$

$$\gamma^K = \tfrac{3}{2}(\gamma_{\parallel}^K - \gamma_{\perp}^K)$$

$$= \tfrac{1}{10}[3\gamma_{\xi\eta\xi\eta}(-\omega;\omega,0,0) - \gamma_{\xi\xi\eta\eta}(-\omega;\omega,0,0)] \,. \tag{158}$$

For the ESHG process (E),

$$\beta_{\parallel}^E = \langle \beta \rangle_{ZZZ}^E = \tfrac{1}{5}[2\beta_{\xi\xi z}(-2\omega;\omega,\omega) + \beta_{z\xi\xi}(-2\omega;\omega,\omega)] \,, \tag{159}$$

$$\beta_{\perp}^E = \langle \beta \rangle_{ZXX}^E = \tfrac{3}{5}[2\beta_{z\xi\xi}(-2\omega;\omega,\omega) - \beta_{\xi\xi z}(-2\omega;\omega,\omega)] \,, \tag{160}$$

$$\gamma_{\parallel}^E = \langle \gamma \rangle_{ZZZZ}^E = \tfrac{1}{15}[2\gamma_{\xi\xi\eta\eta}(-2\omega;\omega,\omega,0) + \gamma_{\xi\eta\eta\xi}(-2\omega;\omega,\omega,0)] \,, \tag{161}$$

$$\gamma_{\perp}^E = \langle \gamma \rangle_{ZXXZ}^E = \tfrac{1}{15}[2\gamma_{\xi\eta\eta\xi}(-2\omega;\omega,\omega,0) - \gamma_{\xi\xi\eta\eta}(-2\omega;\omega,\omega,0)] \,. \tag{162}$$

In the above equations z denotes the molecule-fixed electric dipole axis.

3. Vibrational component

a. Classical averaging

For the present we ignore (or freeze) rotation and use Eqs. (147) and (148) and the procedure of Sec. V.A.2. This leads (Bishop, 1987a) to the following molecular-axis-defined vibrational polarizabilities (only terms up to second order are given explicitly):

$$\beta_{\alpha\beta\gamma}^v(-\omega_\sigma;\omega_1,\omega_2) = \hbar^{-1} \sum_k{}' \{(\mu_\alpha)_{0k}(\alpha_{\beta\gamma})_{0k}[(\omega_k-\omega_\sigma)^{-1} + (\omega_k+\omega_\sigma)^{-1}] + (\mu_\beta)_{0k}(\alpha_{\alpha\gamma})_{0k}[(\omega_k-\omega_1)^{-1} + (\omega_k+\omega_1)^{-1}]$$
$$+ (\mu_\gamma)_{0k}(\alpha_{\alpha\beta})_{0k}[(\omega_k-\omega_2)^{-1} + (\omega_k+\omega_2)^{-1}]\} + \text{terms in } (\mu_\alpha)(\mu_\beta)(\mu_\gamma) \,, \tag{163}$$

$$\gamma_{\alpha\beta\gamma\delta}^v(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \hbar^{-1} \sum_k{}' \{(\alpha_{\alpha\beta})_{0k}(\alpha_{\gamma\delta})_{0k}[(\omega_k-\omega_2-\omega_3)^{-1} + (\omega_k+\omega_2+\omega_3)^{-1}]$$
$$+ (\alpha_{\alpha\gamma})_{0k}(\alpha_{\beta\delta})_{0k}[(\omega_k-\omega_1-\omega_3)^{-1} + (\omega_k+\omega_1+\omega_3)^{-1}]$$
$$+ (\alpha_{\alpha\delta})_{0k}(\alpha_{\beta\gamma})_{0k}[(\omega_k-\omega_1-\omega_2)^{-1} + (\omega_k+\omega_1+\omega_2)^{-1}]$$
$$+ (\mu_\alpha)_{0k}(\beta_{\beta\gamma\delta})_{0k}[(\omega_k-\omega_\sigma)^{-1} + (\omega_k+\omega_\sigma)^{-1}]$$
$$+ (\mu_\beta)_{0k}(\beta_{\alpha\gamma\delta})_{0k}[(\omega_k-\omega_1)^{-1} + (\omega_k+\omega_1)^{-1}]$$
$$+ (\mu_\gamma)_{0k}(\beta_{\alpha\beta\delta})_{0k}[(\omega_k-\omega_2)^{-1} + (\omega_k+\omega_2)^{-1}]$$
$$+ (\mu_\delta)_{0k}(\beta_{\alpha\beta\gamma})_{0k}[(\omega_k-\omega_3)^{-1} + (\omega_k+\omega_3)^{-1}]\}$$
$$+ \text{terms in } (\mu_\alpha)(\mu_\beta)(\alpha_{\gamma\delta}) \text{ and } (\mu_\alpha)(\mu_\beta)(\mu_\gamma)(\mu_\delta) \,, \tag{164}$$

where ω_k are the vibrational frequencies and, for example, $(\alpha_{\alpha\beta})_{0k}$ is a vibrational transition matrix element of the $\alpha_{\alpha\beta}$ electronic polarizability component; the prime indicates omission of the vibrational ground state (0) in the summation. For the Kerr effect the axial components are

$$\beta_{zzz}^v(-\omega;\omega,0) = \hbar^{-1} \sum_k{}' 2(\mu_z)_{0k}(\alpha_{zz})_{0k}[(\omega_k+\omega)^{-1} + \omega_k^{-1} + (\omega_k-\omega)^{-1}] + \cdots \,, \tag{165}$$

$$\gamma_{zzzz}^v(-\omega;\omega,0,0) = \hbar^{-1} \sum_k{}' \{2(\alpha_{zz})_{0k}^2[(\omega_k+\omega)^{-1} + \omega_k^{-1} + (\omega_k-\omega)^{-1}]$$
$$+ 2(\mu_z)_{0k}(\beta_{zzz})_{0k}[(\omega_k+\omega)^{-1} + 2\omega_k^{-1} + (\omega_k-\omega)^{-1}]\} + \cdots \,, \tag{166}$$

and for ESHG they are

$$\beta^{v}_{zzz}(-2\omega;\omega,\omega)=\hbar^{-1}\sum_{k}{}'(\mu_z)_{0k}(\alpha_{zz})_{0k}[(\omega_k+2\omega)^{-1}+2(\omega_k+\omega)^{-1}+2(\omega_k-\omega)^{-1}+(\omega_k-2\omega)^{-1}]+\cdots\ , \qquad (167)$$

$$\begin{aligned}\gamma^{v}_{zzzz}(-2\omega;\omega,\omega,0)=\hbar^{-1}\sum_{k}{}'\{&(\alpha_{zz})^2_{0k}[(\omega_k+2\omega)^{-1}+2(\omega_k+\omega)^{-1}+2(\omega_k-\omega)^{-1}+(\omega_k-2\omega)^{-1}]\\&+(\mu_z)_{0k}(\beta_{zzz})_{0k}[(\omega_k+2\omega)^{-1}+2(\omega_k+\omega)^{-1}+2\omega_k^{-1}+2(\omega_k-\omega)^{-1}+(\omega_k-2\omega)^{-1}]\}+\cdots\ .\end{aligned} \qquad (168)$$

After classical isotropic averaging, we obtain for an axially symmetric molecule the following leading terms for γ:

$$\gamma^{v}_{\parallel}(K)=\sum_{k}{}'(\hbar\omega_k)^{-1}\left[\tfrac{4}{3}(\mu)_{0k}(\bar{\beta})_{0k}\left[1+\frac{1}{1-x^2}\right]+\tfrac{8}{45}(\Delta\alpha)^2_{0k}\left[1+\frac{2}{1-x^2}\right]+2(\bar{\alpha})^2_{0k}\left[1+\frac{2}{1-x^2}\right]\right]\ , \qquad (169)$$

$$\gamma^{v}_{\perp}(K)=\sum_{k}{}'(\hbar\omega_k)^{-1}\left[\tfrac{4}{9}(\mu)_{0k}(\bar{\beta})_{0k}\left[1+\frac{1}{1-x^2}\right]+\tfrac{4}{45}(\Delta\alpha)^2_{0k}\left[\frac{3}{1-x^2}-1\right]+2(\bar{\alpha})^2_{0k}\right]\ , \qquad (170)$$

$$\begin{aligned}\gamma^{v}_{\parallel}(E)=\sum_{k}{}'(\hbar\omega_k)^{-1}\Bigg[&\tfrac{2}{3}(\mu)_{0k}(\bar{\beta})_{0k}\left[1+\frac{2}{1-x^2}+\frac{1}{1-4x^2}\right]+\tfrac{8}{45}(\Delta\alpha)^2_{0k}\left[\frac{1}{1-4x^2}+\frac{2}{1-x^2}\right]\\&+2(\bar{\alpha})^2_{0k}\left[\frac{1}{1-4x^2}+\frac{2}{1-x^2}\right]\Bigg]\ ,\end{aligned} \qquad (171)$$

$$\gamma^{v}_{\perp}(E)=\sum_{k}{}'(\hbar\omega_k)^{-1}\left[\tfrac{2}{9}(\mu)_{0k}(\bar{\beta})_{0k}\left[1+\frac{2}{1-x^2}+\frac{1}{1-4x^2}\right]+\tfrac{4}{45}(\Delta\alpha)^2_{0k}\left[\frac{3}{1-x^2}-\frac{1}{1-4x^2}\right]+2(\bar{\alpha})^2_{0k}\left[\frac{1}{1-4x^2}\right]\right]\ , \qquad (172)$$

where $x=\omega/\omega_k$.

Equations (169) and (171) have been used by Bishop and Lam (1987c) to obtain the vibrational polarizabilities for these processes for $H_2{}^+$. Values were reported for the laser wavelengths $\lambda=4880$, 6328, and 6943 Å.

Elliott and Ward (1984) investigated vibrational hyperpolarizabilities for CH_4, SF_6, and the fluorinated methanes. Their strategy was based on retaining only the enhanced terms [see Sec. II.C] in the generalization of Eqs. (147) and (148). For example, in third-harmonic generation their $\gamma^{v}(-3\omega;\omega,\omega,\omega)$ would be zero, since there are no enhanced terms, as all the denominators contain the laser frequency ω. They did not explicitly carry out isotropic averaging, since their formulas were directly related to empirical data. Because of the lack of such information (particularly with respect to the signs of the matrix elements), their results, overall, were not conclusive. Nonetheless, they did show that vibrational contributions to second hyperpolarizabilities are significant in certain cases, as for example in the Kerr effect for the fluorinated molecules, where they are comparable with the experimental γ values. However, this conclusion was based on an equation (17′ in their paper) that, because of the "enhanced term" procedure, ignores the lowest-order terms (in a perturbation sense), which are precisely those given explicitly in Eq. (166). They retain only terms of the type $(\alpha)(\mu)^2/\omega_k^2$—the doubly enhanced ones. This would seem to be a doubtful procedure. In other respects their working equations for $\beta^{v}(K)$ and $\gamma^{v}(E)$ are consistent with those we have given. It should be stressed that their formulas necessarily will not be correct in the limit $\omega\to 0$.

Mizrahi and Shelton (1958a, 1958b) have used Eq. (171), without the $(\mu)(\beta)$ term (which is zero for a homonuclear diatomic), to evaluate $\gamma^{v}_{\parallel}(E)$ for H_2 and D_2. Taking *ab initio* theoretical values for $(\Delta\alpha)_{01}$ and $(\bar{\alpha})_{01}$ and summing only over the fundamental vibration, they found (Mizrahi and Shelton, 1985b) that at $\omega=0$, $\gamma^{v}_{\parallel}(E)=184$ and 178 a.u. for H_2 and D_2, respectively. These values agree with those of Bishop *et al.* (1990) and may be compared with $\gamma^{e}_{\parallel}(E)=671$ and 652 a.u. They also subtracted vibrational polarizabilities, calculated at nonzero frequencies, from their experimental data for H_2 and extrapolated the results to $\omega=0$. They did this in order to be able to make a comparison with theoretical estimates of the static $\gamma^{e}_{\parallel}(E)$; their resulting value is 2.7% higher than it would have been by extrapolation of the raw experimental data, thus showing the importance of the vibrational polarizability correction. Similarly, the H_2:D_2 ratio for $\gamma_{\parallel}(E)$ was changed by 1.2% at $\omega=0$, when the vibrational corrections were made to the experimental results, and is thereby closer to the theoretically estimated ratio. They showed (Mizrahi and Shelton, 1985a) that for H_2 and $\lambda=5145$ Å, $\gamma^{v}_{\parallel}(E)\cong\gamma^{e}_{\parallel}(E)/100$, again in line with Bishop *et al.* (1990): Equation (171) shows that as $\omega\to\infty$, so does x, and hence the vibrational γ polarizability for ESHG experiments drops to zero.

In some recent papers by Shelton and co-workers on the vibrational hyperpolarizabilities γ^{v} for different nonlinear optical processes for CO_2 (Shelton, 1986a), CH_4 (Shelton, 1986b), CF_4 (Lu and Shelton, 1987), and SF_6 (Shelton and Ulivi, 1988), Shelton follows much more the spirit of Elliott and Ward (1984). This is necessitated by the fact that for polyatomic molecules, the expressions for γ^v are very complex—one need only look at Eqs. (5)–(8) in Shelton and Ulivi (1988). Shelton uses the "enhancement" approximation and takes the needed integrals from experiment as well as using, as with all the results in this section, the classical isotropic averaging procedure. For CO_2 he concludes that $\gamma^v(E)$ is insignificant, and for $\gamma^v(K)$, where he only seriously accounts for the doubly enhanced terms, he finds $0\pm2\times10^{-63}$ $C^4m^4J^{-3}$. Singly enhanced terms such as $(\alpha)^2/\hbar\omega_k$ contribute 0.4×10^{-63} $C^4m^4J^{-3}$, and those such as $(\mu)(\beta)/\hbar\omega_k$ contribute 2×10^{-63} $C^4m^4J^{-3}$. The doubly enhanced ones contribute -1.1×10^{-63} $C^4m^4J^{-3}$ (assuming all matrix elements are positive). The electronic contribution to $\gamma(K)$ is on the order of 73×10^{-63} $C^4m^4J^{-3}$ at 6328 Å. For CH_4 he makes no specific calculations but uses the principle that different processes will have different preponderances of the vibrational contribution; this is made limpid by comparing, for example, Eqs. (169) and (171). If values of γ for different processes plotted against $\omega_L^2==\omega_\sigma^2+\omega_1^2+\omega_2^2+\omega_3^2$ fall on the same line, then one can assume that the vibrational contribution is negligible, since it can be shown (Bishop, 1989) that γ^e is approximately linear in ω_L^2. This is true for CH_4, and the obvious conclusion is drawn. Previously, Elliott and Ward (1984) had estimated $\gamma^v(K)$ for CH_4 to be about 3% of the electronic hyperpolarizability and $\gamma^v(E)$ to be about a tenth of this. For CF_4, considering only doubly and singly enhanced terms for the Kerr and ESHG processes, respectively, Lu and Shelton (1987) have found significant vibrational contributions: 30–40% for the Kerr process and 5% for ESHG. For SF_6, Shelton and Ulivi (1988) do not make the "enhancement assumption," and all terms are retained. Though the empirical data that are incorporated are often sketchy, they find the dramatic result that for $\omega=0$, $\gamma^v\cong20\gamma^e$. At optical frequencies for the three processes, Kerr, ESHG, and third-harmonic generation, the two components are still comparable in magnitude, though γ^v is now smaller.

b. Quantum-mechanical averaging

For simplicity and clarity, we shall confine our discussion of quantum-mechanical averaging to a homonuclear diatomic molecule and to the second vibrational hyperpolarizability. Following Shelton (1987a), we start with Eq. (148), make the same energy approximations that led to Eq. (143) in the static case, and, to simplify the isotropic averaging, express the result in terms of irreducible spherical tensors. We can then multiply by the population distribution $\rho(J)$ and sum over the free-rotor states after rotational-angle integration has been achieved. The vibrational component is then given by

$$\begin{aligned}\gamma^v=\sum_J\sum_{v\neq0}[&A_0\langle0(J)|\bar{\alpha}|v(J)\rangle^2\\&+A_1\langle0(J)|\Delta\alpha|v(J+2)\rangle^2\\&+A_2\langle0(J)|\Delta\alpha|v(J)\rangle^2\\&+A_3\langle0(J+2)|\Delta\alpha|v(J)\rangle^2]\ .\end{aligned}\tag{173}$$

We have assumed that all the molecules are in the lowest vibrational state $|0\rangle$ and the constants A_i are

$$A_0=\rho(J)f(E_{v,J}-E_{0,J})\ ,\tag{174}$$

$$\begin{aligned}A_1=&[(J+1)(J+2)/(2J+1)(2J+3)]\\&\times\rho(J)f'(E_{v,J+2}-E_{0,J})\ ,\end{aligned}\tag{175}$$

$$\begin{aligned}A_2=&[2J(J+1)/3(2J+3)(2J-1)]\\&\times\rho(J)f'(E_{v,J}-E_{0,J})\ ,\end{aligned}\tag{176}$$

$$\begin{aligned}A_3=&[(J+1)(J+2)/(2J+3)(2J+5)]\\&\times\rho(J)f'(E_{v,J}-E_{0,J+2})\ ;\end{aligned}\tag{177}$$

the frequency factors $f(E_{v,J}-E_{0,J})$, etc., are given in Table IX.

Bishop and Lam (1988a) and Bishop *et al.* (1990) have used these equations in a study on H_2 and D_2 for the Kerr and ESHG processes. Some sample results are given in Table X for H_2; the static value was previously referred to in Table VI. As expected (see Table IX), the vibrational component compared with the electronic component is less significant at optical frequencies and only ~1% for ESHG, as was the case with classical averaging.

For $\omega=0$, Eq. (173) is, of course, compatible with Eq. (126), and we may consider the same approximations as we did for that equation, i.e., neglecting the J dependence of the vibrational wave functions, ignoring the rotational contribution to the energies, and taking the sums only over the fundamental vibrational levels. The resulting expressions are equivalent to the classically averaged ones of Eqs. (169)–(172). Shelton (1987a) has investigated these approximations and found them to be important only for the Kerr effect, for which at 6328 Å the vibrational γ^K [see Eq. (158)] changed after the approximations from -0.041 to -0.032 for H_2 (in units of 10^{-62} $C^4m^4J^{-3}$) and from 0.001 to 0.007 for D_2. For the other molecules he considered (N_2 and O_2), there was no change. The approximate (classical) formula was used for the same four molecules for evaluating γ^v for several other nonlinear optical processes.

4. Rotational component

The rotational dynamic hyperpolarizabilities may, in the manner used before, be found from Eq. (173) by taking the $v=0$ term (excluded from that equation) and dropping the terms in A_0 and A_2. This was first done by Shelton (1987b). Here we give an extension of that result by including the leading $(\mu)(\beta)$ term, which arises for a heteronuclear diatomic molecule:

TABLE IX. Frequency factors for Eqs. (174)–(177) with $z=\hbar\omega/x$.

$f(x)$	Kerr-∥	$2[1+2(1-z^2)^{-1}]/x$
	Kerr-⊥	$2/x$
	ESHG-∥	$2[(1-4z^2)^{-1}+2(1-z^2)^{-1}]/x$
	ESHG-⊥	$2(1-4z^2)^{-1}/x$
$f'(x)$	Kerr-∥	$4[1+2(1-z^2)^{-1}]/15x$
	Kerr-⊥	$2[3(1-z^2)^{-1}-1]/15x$
	ESHG-∥	$4[(1-4z^2)^{-1}+2(1-z^2)^{-1}]/15x$
	ESHG-⊥	$2[3(1-z^2)^{-1}-(1-4z^2)^{-1}]/15x$

TABLE XI. Frequency factors for Eq. (178). For $f(x)$: $x=\omega_{J+1,J}$ and $y=\omega/\omega_{J+1,J}$; for $f'(x)$: $x=\omega_{J+2,J}$ and $y=\omega/\omega_{J+2,J}$.

$f(x)$	Kerr-∥	$(12/x)[1+(1-y^2)^{-1}]$
	Kerr-⊥	$(4/x)[1+(1-y^2)^{-1}]$
	ESHG-∥	$(6/x)[1+2(1-y^2)^{-1}+(1-4y^2)^{-1}]$
	ESHG-⊥	$(2/x)[1+2(1-y^2)^{-1}+(1-4y^2)^{-1}]$
$f(x)$	Kerr-∥	$(8/x)[1+2(1-y^2)^{-1}]$
	Kerr-⊥	$(4/x)[3(1-y^2)^{-1}-1]$
	ESHG-∥	$(8/x)[2(1-y^2)^{-1}+(1-4y^2)^{-1}]$
	ESHG-⊥	$(4/x)[3(1-y^2)^{-1}-(1-4y^2)^{-1}]$

$$\gamma^r=\tfrac{1}{9}\hbar^{-1}\sum_J f(\omega_{J+1,J})(\mu)_{J+1,J}(\bar{\beta})_{J+1,J}\rho(J)\frac{(J+1)}{(2J+1)}\left[1-\frac{(2J+1)}{(2J+3)}\frac{\rho(J+1)}{\rho(J)}\right]$$
$$+\tfrac{1}{30}\hbar^{-1}\sum_J f'(\omega_{J+2,J})(\Delta\alpha)^2_{J+2,J}\rho(J)\frac{(J+1)(J+2)}{(2J+1)(2J+3)}\left[1-\frac{(2J+1)}{(2J+5)}\frac{\rho(J+1)}{\rho(J)}\right]. \tag{178}$$

The frequency factors f and f' for the Kerr and ESHG processes are given in Table XI. As we have noted previously, to this expression a distribution term γ^{dist}, neglected by Shelton (1987b), must be added for the Kerr experiment (Bishop and Shelton, 1988). This is to account for the fact that the electric field changes the distribution of populated rotational states and contributes an additional factor for this particular nonlinear optical process.

We now make the high-temperature approximation ($\hbar B_0 \ll kT$) and use Eqs. (22) and (23) for the terms in square brackets in Eq. (178). This gives

$$kT\gamma^r_\parallel(K)=\tfrac{2}{3}(\mu)(\bar{\beta})(1+a)+\tfrac{1}{15}(\Delta\alpha)^2(1+2b)+kT\gamma^{\text{dist}}_\parallel\ , \tag{179}$$

where

$$kT\gamma^{\text{dist}}_\parallel=(\Delta\alpha)^2/45 \tag{180}$$

[see Eq. (138)],

$$kT\gamma^r_\perp(K)=\tfrac{2}{9}(\mu)(\bar{\beta})(1+a)+\tfrac{1}{30}(\Delta\alpha)^2(3b-1)+kT\gamma^{\text{dist}}_\perp\ , \tag{181}$$

where

$$kT\gamma^{\text{dist}}_\perp=-(\Delta\alpha)^2/90\ , \tag{182}$$

$$kT\gamma^r_\parallel(E)=\tfrac{1}{3}(\mu)(\bar{\beta})(1+2a+c)+\tfrac{1}{15}(\Delta\alpha)^2(2b+d)\ , \tag{183}$$

and

$$kT\gamma^r_\perp(E)=\tfrac{1}{9}(\mu)(\bar{\beta})(1+2a+c)+\tfrac{1}{30}(\Delta\alpha)^2(3b-d)\ . \tag{184}$$

In these equations

$$a=[1-(\omega/\bar{\omega}_{J+1,J})^2]^{-1}\ , \tag{185}$$

$$b=[1-(\omega/\bar{\omega}_{J+2,J})^2]^{-1}\ , \tag{186}$$

$$c=[1-4(\omega/\bar{\omega}_{J+1,J})^2]^{-1}\ , \tag{187}$$

$$d=[1-4(\omega/\bar{\omega}_{J+2,J})^2]^{-1}\ , \tag{188}$$

where the bar indicates a mean rotational-energy separation. These expressions will be used in the next section, where we give an analysis of two earlier theoretical treatments of the Kerr effect.

TABLE X. Electronic and vibrational hyperpolarizabilities (γ) for H_2 (in a.u.). From Bishop *et al.* (1990).

λ/Å	$\gamma^e_\parallel$	$\gamma^v_\parallel$	$\gamma^e_\perp$	$\gamma^v_\perp$
∞	670.8	183.7	223.6	61.2
4880-Kerr	753.4	63.5	247.8	64.2
4880-ESHG	969.1	−6.8	337.8	−0.9

5. More on the Kerr effect

The original treatment (Buckingham and Pople, 1955; Buckingham, 1962a; Buckingham and Orr, 1968), for obtaining useful expressions for γ^K was inspired directly by the experiment itself, namely, to consider the effect of a uniform static electric field F on the optical polarizability $\alpha(\omega)$ in directions parallel (Z) and perpendicular (X) to the field. The standard formula for $\alpha(\omega)$ was then adapted by changing all the wave functions and energies therein to field-perturbed values:

$$\alpha^F=\hbar^{-1}\sum_{n\neq g}\frac{2\omega_{ng}^F|\langle g^F|\hat{\mu}|n^F\rangle|^2}{(\omega_{ng}^F)^2-\omega^2}\ . \tag{189}$$

The F^2 term in $\alpha_{ZZ}^F-\alpha_{XX}^F$, which leads to γ^K, was then extracted by employing perturbation-theory expressions for the wave functions and energies. The results of this treatment are exactly equivalent to those we have previously derived, although this is not always obvious. One apparent difficulty in making the equivalence is that the perturbation expansions introduce energy differences between *two* excited states (say, $\hbar\omega_{mn}$), and such differences do not appear in Eqs. (140) and (141), for example, where all energies are with respect to the ground state. The trick for conversion is best demonstrated by considering the following steps, starting with a term in the original method and ending with a term in Eq. (141); A_{nk} is an integral product symmetric in n and k, and the prime denotes ground-state omission:

$$\begin{aligned}
&\sum_n{}' \sum_{k\neq n}{}' A_{nk}\omega_{ng}^{-2}\omega_{kn}^{-1}\\
&\quad=\tfrac{1}{2}\sum_n{}' \sum_{k\neq n}{}' A_{nk}(\omega_{ng}^{-2}\omega_{kn}^{-1}+\omega_{kg}^{-2}\omega_{nk}^{-1})\\
&\quad=\tfrac{1}{2}\sum_n{}' \sum_{k\neq n}{}' A_{nk}(\omega_{ng}^{-2}-\omega_{kg}^{-2})\omega_{kn}^{-1}\\
&\quad=\tfrac{1}{2}\sum_n{}' \sum_{k\neq n}{}' A_{nk}(\omega_{kg}^{2}-\omega_{ng}^{2})(\omega_{kg}-\omega_{ng})^{-1}/\omega_{ng}^{2}\omega_{kg}^{2}\\
&\quad=\tfrac{1}{2}\sum_n{}' \sum_{k\neq n}{}' A_{nk}(\omega_{ng}^{-2}\omega_{kg}^{-1}+\omega_{ng}^{-1}\omega_{kg}^{2})\ ,
\end{aligned}\tag{190}$$

which is a term in Eq. (141).

The original approach was used in 1981 to estimate vibrational effects in Kerr measurements of the symmetric tops $CHCl_3$ and CHF_3 (Bishop, 1981). It is instructive to rederive these results with the methods detailed in this review and make a comparison. A number of approximations were originally made: (a) classical thermal averaging, (b) truncation of the perturbation expressions so that no terms of order higher than ω_n^{-1} appeared (ω_n is the vibrational energy), and (c) the assumption that the optical frequency $\omega\gg0$ for all ω. We shall also use (a); we shall use (b) insofar as we shall consider only what we have been calling "leading terms," but we shall not introduce (c). We shall give results up to $(kT)^{-1}$, though $(kT)^{-2}$ terms were included in the original work.

From Eqs. (154)–(158) and (179)–(182), we obtain

$$kT\gamma_r^K=\tfrac{2}{3}(\mu)(\bar{\beta})(1+a)+\tfrac{1}{20}(\Delta\alpha)^2(3+b)+kT\gamma_{\text{dist}}^K\ , \tag{191}$$

with

$$kT\gamma_{\text{dist}}^K=\tfrac{1}{20}(\Delta\alpha)^2\ . \tag{192}$$

Hence, for $\omega=0$ ($a=b=1$),

$$kT\gamma_r^K=\tfrac{4}{3}(\mu)(\beta^K)+\tfrac{1}{4}(\Delta\alpha)^2\ , \tag{193}$$

and for $\omega\gg0$ ($a=b=0$),

$$kT\gamma_r^K=\tfrac{2}{3}(\mu)(\beta^K)+\tfrac{1}{5}(\Delta\alpha)^2\ . \tag{194}$$

(β^K) is the value of β^K, as defined in Eq. (155), after averaging over the vibrational ground state and ignoring centrifugal distortion; similarly for (μ) and $(\Delta\alpha)$.

From Eqs. (169) and (170),

$$\begin{aligned}
\gamma_v^K=\sum_n{}'(\hbar\omega_n)^{-1}g_n\Bigg[&\tfrac{4}{3}(\mu)_{0n}(\beta^K)_{0n}\left[1+\frac{1}{1-x^2}\right]\\
&+\tfrac{2}{15}(\Delta\alpha)_{0n}^2\left[3+\frac{1}{1-x^2}\right]\\
&+6(\bar{\alpha})_{0n}^2\left[\frac{1}{1-x^2}\right]\Bigg]\ ,
\end{aligned}\tag{195}$$

where x signifies (ω/ω_n) and $|n\rangle$ signifies the fundamental vibrational-mode wave functions of degeneracy g_n of the symmetric top. The previous formulas have been simply adapted to the symmetric-top case by interpreting $(\mu)_{0n}$, $(\beta^K)_{0n}$, etc., as the appropriate moment or polarizability component(s) with x, y, or z symmetry to go with the same-symmetry normal-mode vibration $|n\rangle$; for example, Eq. (155) specifies the z symmetry β^K. Only fundamental levels are included in the vibrational sum. For $\omega\gg0$ for all ω,

$$\gamma_v^K=\sum_n{}'(\hbar\omega_n)^{-1}g_n[\tfrac{4}{3}(\mu)_{0n}(\beta^K)_{0n}+\tfrac{2}{5}(\Delta\alpha)_{0n}^2]\ . \tag{196}$$

We now assume that the vibrational component of $\Delta\alpha$ is included in $\Delta\alpha$ in Eq. (194), but that the vibrational component of β^K is not. There is therefore an additional term:

$$kT\gamma_{v/r}^K=\tfrac{2}{3}(\mu)(\beta_v^K)\ , \tag{197}$$

with

$$\begin{aligned}
\beta_v^K=\sum_n{}'(\hbar\omega_n)^{-1}g_n(\mu)_{0n}\Bigg[&6(\bar{\alpha})_{0n}\left[\frac{1}{1-x^2}\right]\\
&+\tfrac{2}{5}(\Delta\alpha)_{0n}\left[3+\frac{1}{1-x^2}\right]\Bigg]\ .
\end{aligned}\tag{198}$$

This result has been derived from Eqs. (163) and (155). Alternatively, we could have collected vibrational-rotational terms from the partitioning of the generalized version of Eq. (148).

If we look at Eqs. (37) and (38) of Bishop (1981) for γ^K, we see that Eq. (194) is present but Eq. (195) is represented only by the first term—the second was not present because Eq. (9) of that work was not sufficiently complete for a full delineation of γ^K. Equation (198) is present in Eqs. (39), (41), and (42) of Bishop (1981). To obtain the terms eliminated in Eq. (191) by the restriction $\omega\gg0$ would require adding to the original field-perturbed optical polarizability the terms $\alpha_{ZZ}^{r,F}$, $\alpha_{XX}^{r,F}$, which are field-perturbed versions of the rotational dynamic polarizability of Eq. (109).

Use of empirical data for the matrix elements and energies showed $\beta_v^K/\beta^K \cong 25\%$ for $CHCl_3$ and 37% for CHF_3.

This method had been used earlier by Buckingham and Orr (1968) for diatomics in general and H_2 in particular. They ignored the influence of vibration (except for zero-point motion) and handled rotation by quantum-mechanical methods—a necessity when dealing with H_2, for which the classical approximation $\hbar B_0 \gg kT$ is especially inappropriate. They found

$$kT\gamma_r^K = \tfrac{2}{3}(\mu)(\beta^K)(1-\tfrac{1}{3}\sigma_0+\tfrac{2}{45}\sigma_0^2+\cdots) + \tfrac{1}{5}(\Delta\alpha)^2(1-\sigma_0+\tfrac{8}{15}\sigma_0^2+\cdots)\,, \tag{199}$$

which can be compared with Eq. (194), or, for a nonpolar diatomic,

$$kT\gamma_r^K = \tfrac{1}{5}(\Delta\alpha)^2(1-\sigma_0+\tfrac{8}{15}\sigma_0^2+\cdots)\,, \tag{200}$$

where $\sigma_0 = \hbar B_0/kT$. The bracketed expression in Eq. (200) is 0.76 for H_2 at 300 K and, except for a few hydrides, is normally not significantly different from unity. Equation (199) can also be derived from Eqs. (137) and (178).

Again, it was implicitly assumed that the optical frequency ω is much greater than zero. If this were not so, terms such as

$$(\alpha_{ZZ}^{r,F}/F^2)_{F\to 0} = \sum_{J'} 2(\hbar\omega_{J,J'})^{-1}(1-z^2)^{-1}(2J+1)^{-1} \times \sum_M |\langle JM|\alpha_{ZZ}|J'M\rangle|^2 \tag{201}$$

would have to be incorporated, and this would lead to

$$kT\gamma_r^K = \tfrac{1}{20}(\Delta\alpha)^2\left[4+\frac{1}{1-z^2}\right](1-\sigma_0+\tfrac{8}{15}\sigma_0^2+\cdots) \tag{202}$$

for H_2, where $z = \omega/\overline{\omega}_{J,J+2}$.

VI. FIELD-GRADIENT POLARIZABILITIES (A,B,C)

A. Definitions

So far, we have dealt only with uniform electric fields; however, it is also of interest to consider the nonuniform ones, which arise, for example, when a molecule is in the presence of a set of external charges. The perturbed Hamiltonian, Eq. (1), then contains $-\frac{1}{3}\hat{\Theta}_{\alpha\beta}F_{\alpha\beta}$, where $F_{\alpha\beta}$ is a field-gradient tensor. The energy is changed by [see Eq. (2)]

$$-\tfrac{1}{3}\Theta_{\alpha\beta}F_{\alpha\beta} - \tfrac{1}{3}A_{\gamma,\alpha\beta}F_\gamma F_{\alpha\beta} - \tfrac{1}{6}B_{\alpha\beta,\gamma\delta}F_\alpha F_\beta F_{\gamma\delta} - \tfrac{1}{6}C_{\alpha\beta,\gamma\delta}F_{\alpha\beta}F_{\gamma\delta} - \cdots\,,$$

where A, B, and C are field-gradient polarizabilities (dipole-quadrupole, dipole-dipole-quadrupole, and quadrupole-quadrupole, respectively).

We shall consider $\hat{\Theta}_{\alpha\beta}$ to be the traceless operators

$$\hat{\Theta}_{\alpha\beta} = \sum_i q_i(\tfrac{3}{2}r_{i\alpha}r_{i\beta} - \tfrac{1}{2}r_i^2\delta_{\alpha\beta})\,, \tag{203}$$

where q_i is the charge on the ith particle at $\underline{r}_i$. However, recently, definitions of A,B, and C have been used that are based on the traced operators (Applequist, 1983, 1984; Liu and Dykstra, 1987; Augspurger and Dykstra, 1988)

$$\hat{Q}_{\alpha\beta} = \sum_i q_i r_{i\alpha} r_{i\beta}\,. \tag{204}$$

We shall distinguish these by a tilde: $\widetilde{A}$, $\widetilde{B}$, and $\widetilde{C}$. Relations exist between the traced and traceless properties and have been given in Jameson and Fowler (1986), Liu and Dykstra (1987; see their footnote 50), Augspurger and Dykstra (1988) (though the footnote to Table II is in error), and Maroulis and Thakkar (1988):

$$A_{\alpha,\beta\gamma} = \tfrac{1}{2}(3\widetilde{A}_{\alpha,\beta\gamma} - \delta_{\beta\gamma}\widetilde{A}_{\alpha,\mu\mu})\,, \tag{205}$$

$$B_{\alpha\beta,\gamma\delta} = \tfrac{1}{2}(3\widetilde{B}_{\alpha\beta,\gamma\delta} - \delta_{\gamma\delta}\widetilde{B}_{\alpha\beta,\mu\mu})\,, \tag{206}$$

$$C_{\alpha\beta,\gamma\delta} = \tfrac{1}{4}(3\widetilde{C}_{\alpha\beta,\gamma\delta} - \delta_{\alpha\beta}\widetilde{C}_{\mu\mu,\gamma\delta} - \delta_{\gamma\delta}\widetilde{C}_{\alpha\beta,\mu\mu} + \tfrac{1}{3}\delta_{\alpha\beta}\delta_{\gamma\delta}\widetilde{C}_{\mu\mu,\nu\nu})\,. \tag{207}$$

More recently, Dykstra and co-workers (Liu and Dykstra, 1987; Augspurger and Dykstra, 1988) have used a factor of $\frac{1}{2}$ in Eq. (204). When this is done, the factors of $\frac{1}{2}$ and $\frac{1}{4}$ do not appear in Eqs. (205)–(207); moreover, the properties they calculate are frequently given the opposite sign to the usual convention.

Following the formalism of Orr and Ward (1971), the perturbation-theory expressions for the dynamic field-gradient polarizabilities are

$$A_{\alpha,\beta\gamma}(-\omega_\sigma;\omega_1) = \hbar^{-1}\sum_P \sum_{m\neq g} \frac{\langle g|\hat{\mu}_\alpha|m\rangle\langle m|\hat{\Theta}_{\beta\gamma}|g\rangle}{(\omega_{mg}-\omega_\sigma)}\,, \tag{208}$$

where $\sum_P$ is the sum over the permutation of the pairs $(-\omega_\sigma/\hat{\mu}_\alpha)$ and $(\omega_1/\hat{\Theta}_{\beta\gamma})$,

$$B_{\alpha\beta,\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2) = \hbar^{-2}\sum_P \sum_{m\neq g}\sum_{n\neq g} \frac{\langle g|\hat{\mu}_\alpha|m\rangle\langle \overline{m|\hat{\mu}_\beta|n}\rangle\langle n|\hat{\Theta}_{\gamma\delta}|g\rangle}{(\omega_{mg}-\omega_\sigma)(\omega_{ng}-\omega_2)}\,, \tag{209}$$

and $\sum_P$ is the sum over the permutations of the pairs $(-\omega_\sigma/\hat{\mu}_\alpha)$,$(\omega_1/\hat{\mu}_\beta)$, and $(\omega_2/\hat{\Theta}_{\gamma\delta})$, and

$$C_{\alpha\beta,\gamma\delta}(-\omega_\sigma;\omega_1) = \tfrac{1}{3}\hbar^{-1}\sum_P \sum_{m\neq g} \frac{\langle g|\hat{\Theta}_{\alpha\beta}|m\rangle\langle m|\hat{\Theta}_{\gamma\delta}|g\rangle}{(\omega_{mg}-\omega_\sigma)} \tag{210}$$

where $\sum_P$ is the sum over the permutation of the pairs

$(-\omega_\sigma/\hat{\Theta}_{\alpha\beta})$ and $(\omega_1/\hat{\Theta}_{\gamma\delta})$. These expressions are such that, in the static limit (all frequencies zero), we retrieve Eqs. (13) and (14) of Buckingham (1967). Equivalent, but not identical expressions have been given by Buckingham and Longuet-Higgins (1968) for $B_{\alpha\beta,\gamma\delta}(-\omega;\omega,0)$ and $B_{\alpha\beta,\gamma\delta}(-\omega;0,\omega)$. Identical expressions for $A_{\alpha,\beta\gamma}(-\omega;\omega)$ and $C_{\alpha\beta,\gamma\delta}(-\omega;\omega)$ are to be found in Eqs. (20c) and (20g), respectively, of Buckingham (1967).

For atoms, the static field-gradient polarizability C requires some further discussion, since slightly different definitions (by a numerical factor) are often used. For example, for $C_{zz,zz}$ Eq. (210) leads to

$$C_{zz,zz}=\tfrac{2}{3}\hbar^{-1}\sum_{m\neq g}|\langle g|\hat{\Theta}_{zz}|m\rangle|^2/\omega_{mg}\ , \tag{211}$$

whereas Sternheimer (1954), Dalgarno (1962), and recently Thakkar (1981) define a quadrupole polarizability, in analogy with the α (dipole) polarizability, as

$$\alpha_q=2\hbar^{-1}\sum_{m\neq g}|\langle g|\hat{\Theta}_{zz}|m\rangle|^2/\omega_{mg}=3C_{zz,zz}\ . \tag{212}$$

Buckingham (1967), in Eqs. (7d) and (8a), uses an average, for an atom, which he defines as

$$C=\tfrac{1}{5}C_{\alpha\beta,\alpha\beta}=\tfrac{3}{2}C_{zz,zz}\ . \tag{213}$$

For diatomic molecules the isotropic average static polarizabilities, using

$$\langle P\rangle_{ZZZZ}=\tfrac{1}{15}(P_{\xi\xi\eta\eta}+P_{\xi\eta\xi\eta}+P_{\xi\eta\eta\xi})\ , \tag{214}$$

are

$$\langle B\rangle_{ZZZZ}=\tfrac{2}{15}(B_{zz,zz}+4B_{xz,xz}+B_{xx,zz}+4B_{xx,xx})\ , \tag{2.15}$$

$$\langle C\rangle_{ZZZZ}=\tfrac{1}{15}(C_{zz,zz}+8C_{xz,xz}+8C_{xx,xx})\ . \tag{216}$$

TABLE XII. Comparison of electronic and vibrational field-gradient polarizabilities for $H_2{}^+$ and H_2 (in a.u.). From Bishop and Lam (1987b).

		$B_{zz,zz}$	$B_{xx,zz}$	$C_{zz,zz}$
$H_2{}^+$	Electronic[a]	−54.24	8.28	2.18
	Vibrational	136.13	18.08	7.86
H_2	Electronic[b]	−90.3	34.4	5.98
	Vibrational	10.67	5.01	0.27

[a] Vibrationally averaged.
[b] At $R_e=1.4a_0$ [from Bishop *et al.* (1990)].

B. Results

Until recently, only static values of A, B, and C have been determined. If rotation is ignored, then perturbation-theory expressions for the vibrational field-gradient polarizabilities of a homonuclear diatomic molecule are readily found in the manner used for α^v in Sec. IV.A.1.b or γ^v in Sec. V.A.1.a:

$$B^v_{zz,zz}=2\hbar^{-1}\sum_{k\neq 0}(\alpha_{zz})_{0k}(\Theta_{zz})_{0k}/\omega_k\ , \tag{217}$$

$$B^v_{xx,zz}=2\hbar^{-1}\sum_{k\neq 0}(\alpha_{xx})_{0k}(\Theta_{zz})_{0k}/\omega_k\ , \tag{218}$$

$$C^v_{zz,zz}=\tfrac{2}{3}\hbar^{-1}\sum_{k\neq 0}(\Theta_{zz})^2_{0k}/\omega_k\ , \tag{219}$$

where z is the bond axis. The other components are either zero or simply related by definition, e.g., $B_{xx,xx}=-\frac{1}{2}B_{xx,zz}, C_{xx,xx}=\frac{1}{4}C_{zz,zz}$.

Bishop and Lam (1987b) have evaluated these components for $H_2{}^+$, H_2, and N_2. As can be seen in Table XII, where a comparison is made with the corresponding electronic components, vibrational field-gradient polarizabilities are apparently quite significant.

Later, the same authors (1988b, c) made more realistic calculations for $H_2{}^+$ and H_2 by using space-fixed axes, in the manner of Sec. V.A.1.b. The perturbation to the rovibrational Schrödinger equation was taken as

$$E'=-\tfrac{1}{2}\alpha_{ZZ}F_Z^2-\tfrac{1}{3}\Theta_{ZZ}F_{ZZ}\ , \tag{220}$$

with

$$\alpha_{ZZ}=\bar{\alpha}+\tfrac{2}{3}\Delta\alpha P_2(\cos\theta) \tag{221}$$

and

$$\Theta_{ZZ}=\Theta P_2(\cos\theta)\ , \tag{222}$$

where $\Theta=\Theta_{zz}$ and θ is the angle between the laboratory (Z) and bond (z) axes. This led, after introducing a distribution over populated rotational states, to the following polarizabilities for the vibrational state v:

$$B^v_{ZZZZ}=\tfrac{2}{15}\sum_J\sum_{v'\neq v}[A_1\langle v(J)|\Theta|v'(J+2)\rangle\langle v(J)|\Delta\alpha|v'(J+2)\rangle+A_2\langle v(J)|\Theta|v'(J)\rangle\langle v(J)|\Delta\alpha|v'(J)\rangle$$
$$+A_3\langle v(J+2)|\Theta|v'(J)\rangle\langle v(J+2)|\Delta\alpha|v'(J)\rangle] \tag{223}$$

and

$$C^v_{ZZZZ}=\tfrac{1}{15}\sum_J\sum_{v'\neq v}[A_1|\langle v(J)|\Theta|v'(J+2)\rangle|^2+A_2|\langle v(J)|\Theta|v'(J)\rangle|^2+A_3|\langle v(J+2)|\Theta|v'(J)\rangle|^2]\ , \tag{224}$$

TABLE XIII. Comparison of exact and approximate field-gradient polarizabilities for H_2^+ and H_2 (in a.u.); $v=0$ and $T=295$ K. From Bishop and Lam (1988c).

		Vibration		Rotation	
		Exact	Approximate	Exact	Approximate
H_2^+	B_{zzzz}	13.84	15.74	841	936
	C_{zzzz}	1.33	1.57	170	191
H_2	B_{zzzz}	1.21	1.51	213	279
	C_{zzzz}	0.17	0.22	51	67

where

$$A_1=3\frac{(J+1)(J+2)}{(2J+1)(2J+3)}\rho(v,J)(E_{v',J+2}-E_{v,J})^{-1} , \tag{225}$$

$$A_2=2\frac{J(J+1)}{(2J+1)(2J-1)}\rho(v,J)(E_{v',J}-E_{v,J})^{-1} , \tag{226}$$

$$A_3=3\frac{(J+1)(J+2)}{(2J+3)(2J+5)}\rho(v,J+2)(E_{v',J}-E_{v,J+2})^{-1} . \tag{227}$$

The rotational polarizabilities were found by letting $v'=v$ in Eqs. (223) and (224) (having excluded terms in A_2) and adding the following distribution terms:

$$B^{\text{dist}}_{ZZZZ}=\tfrac{2}{15}\sum_J \frac{J(J+1)}{(2J-1)(2J+3)}\,\frac{\rho(v,J)}{kT} \times\langle v(J)|\Theta|v(J)\rangle\langle v(J)|\Delta\alpha|v(J)\rangle , \tag{228}$$

$$C^{\text{dist}}_{ZZZZ}=\tfrac{1}{15}\sum_J \frac{J(J+1)}{(2J-1)(2J+3)}\,\frac{\rho(v,J)}{kT} \times|\langle v(J)|\Theta|v(J)\rangle|^2 . \tag{229}$$

Approximations to these equations were made by ignoring centrifugal distortion and the rotational energy when $v'\neq v$, and, assuming $kT \gg \hbar B_0$, this gave

$$B^{v}_{ZZZZ}=\tfrac{4}{15}\sum_{v'\neq v}\frac{\langle v(0)|\Theta|v'(0)\rangle\langle v(0)|\Delta\alpha|v'(0)\rangle}{E_{v',0}-E_{v,0}} , \tag{230}$$

$$C^{v}_{ZZZZ}=\tfrac{2}{15}\sum_{v'\neq v}\frac{|\langle v(0)|\Theta|v'(0)\rangle|^2}{E_{v',0}-E_{v,0}} , \tag{231}$$

$$B^{r}_{ZZZZ}=2\langle v(0)|\Theta|v(0)\rangle\langle v(0)|\Delta\alpha|v(0)\rangle/15kT , \tag{232}$$

$$C^{r}_{ZZZZ}=|\langle v(0)|\Theta|v(0)\rangle|^2/15kT . \tag{233}$$

Classical averaging of the molecule-fixed axis components would lead to the same approximate expressions. Some sample results, shown in Table XIII, indicate that these approximations are more acute than they were for γ_{zzzz}.

Malik (1988), using the derivative Numerov-Cooley method, has calculated the vibrational components of the $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$ tensors of FH. Rotation was ignored and no classical averaging was carried out. However, several vibrational states were investigated and some of his results for the ground state are given in Table XIV for the bond-axial components. In this table we compare the vibrationally averaged electronic component with the total vibronic component, i.e., vibrational polarizability included. It is clear that the vibrational polarizability makes an important contribution to the $\tilde{B}$ and $\tilde{C}$ tensors.

Augspurger and Dykstra (1988) have used the same method (frozen rotation) and numerical technique (DNC) to compute the vibronic $\tilde{A}$ and $\tilde{C}$ tensors for H_3^+. Only the dominant symmetric-stretch vibration was considered. Their values for $v=0$, 1,2 were compared with the equilibrium electronic ones (not the vibrationally averaged ones), so that one cannot extract the pure vibrational polarizability. This is the first time that vibrational effects on these properties have been calculated for a polyatomic molecule. It was found that, in general, they increased with vibrational excitation. Similar calculations were made for H_2, but they may not be very accurate, since the basis set used gave, using Eq. (207), $C^{e}_{xx,xx}(R_e)=5.355$ a.u. (x is the bond axis), compared with a richer basis set, which gave $C^{e}_{xx,xx}(R_e)=5.936$ a.u. This latter result is close to the very accurate value of 5.97 a.u. (Bishop and Cheung, 1979b).

VII. NON-BORN-OPPENHEIMER METHOD

Only one polarizability calculation (Bishop and Solunac, 1985) has been attempted that does not incorporate the separation of the wave function into electronic and nonelectronic parts, and even then it was only for the simplest molecule H_2^+ (and its isotopes) and with the electric field aligned with the bond axis. To that extent, it is only a model calculation, since we cannot reproduce such a condition in the laboratory. To the complete Hamiltonian, the perturbation $-\hat{\mu}F=zF$ was added. In fact, if one takes the total dipole-moment operator and excludes the center-of-mass component, the proper perturbation for this study would be (Wu, 1952; see also

TABLE XIV. Comparison of vibrationally averaged axial-electronic polarizabilities with the total values for FH, $v=0$ (in a.u.). From Malik (1988).

	Averaged electronic	Total
$\tilde{A}$	−2.269	−2.646
$\tilde{B}$	36.54	22.50
$\tilde{C}$	4.612	5.448

Bishop, 1974) $z(1+m_e/M)F$, where M is the total molecular mass; the results in Bishop and Solunac (1985) were later corrected (Bishop *et al.*, 1986) to account for this: notably, the γ values must be multiplied by $(1+m_e/M)^4$.

A variational calculation was made for a series of small finite fields using the following wave function:

$$\Psi=\sum_{i=0}^{9}\sum_{j=0}^{14}\sum_{k=0}^{15}C_{ijk}\phi_{ijk} , \tag{234}$$

with basis functions ϕ_{ijk} excluded if $i+j+k>17$ and j is even, or if $i+j+k>15$ and j is odd. This gave an 888-term function with 888 linear coefficients. The ϕ_{ijk} were defined by

$$\phi_{ijk}(\xi,\eta,R)=\exp(-\alpha\xi)\cosh(\beta\eta)\xi^i\eta^iR^{-3/2} \times\exp(-x^2/2)H_k(x) , \tag{235}$$

where ξ and η are the usual elliptical coordinates of the electron, R is the internuclear separation, $x=\gamma(R-\delta)$, $H_k(x)$ are the Hermite polynomials, and α, β, γ, and δ are optimized nonlinear parameters.

The most interesting final result was for γ_{zzzz}, which was extracted from a polynomial fit of the perturbed energies, and which necessarily includes the full effects of vibrational motion. The value for the lowest quantum state of H_2^+ was 2.19×10^3 a.u. A more precise value, which avoids the fitting procedure but uses the same variational wave function and integrals, can be found from the perturbational-variational Rayleigh-Ritz method (Silverman *et al.*, 1986). This value is 2.19309×10^3 a.u. The fact that, using the results in Bishop and Lam (1987b), the addition of a vibrationally averaged Born-Oppenheimer γ^e_{zzzz} and a perturbation-theory-calculated γ^v_{zzzz} gives 2.202×10^3 a.u. (if an adiabatic potential curve is employed for finding the vibrational wave functions) or 2.197×10^3 a.u. (with a Born-Oppenheimer curve) shows that the errors incurred by the Born-Oppenheimer approximation must be extremely small.

VIII. CONCLUSIONS AND PROSPECTS

The study of the effect of an electric field on electronic motion is "old hat," as is to a certain extent, its effect on rotational motion ("orientation") and vibrational motion ("atomic polarizabilities"). In the past, however, these studies have been compartmentalized—the electronicists, vibrationalists, and rotationalists have kept to their respective lasts. But a molecule is a whole, and all its motions are going on at the same time. Consequently, it behooves us to consider the "grey" areas of vibration in electronic calculations or vibration and electronic motions in rotation experiments. Sometimes these "grey" areas become "black," as witness the dramatic examples given in the Introduction. Even if we feel safe in ignoring one kind of motion, it is obvious that accurate results will be achieved only if we consider everything. Even when we suspect these effects are small, we cannot be sure until they are calculated. Differences between theory and experiment are left in limbo until we have asked, is the experiment in error or is neglect of vibration (for example) in the theory the problem? This sort of question was recently raised (Dudley and Ward, 1985; Sekino and Bartlett, 1986) by the discrepancy between theory and experiment for the hyperpolarizabilities (β and γ) for hydrogen fluoride. In fact, it appears that vibrational effects are not the cause of the problem, though this was not known *a priori,* and it is more likely that the experimental results are in error from contamination by hydrogen fluoride dimers. An earlier example of this sort of dispute was the difference between the β hyperpolarizabilities of halogenated methanes extracted from different nonlinear optical experiments (Bishop, 1981).

To resolve these questions, there have been, broadly speaking, three types of theoretical investigation: (a) *ab initio* calculations that ignore rotation and are largely restricted to diatomic molecules and static polarizabilities; (b) *ab initio* calculations that do not ignore rotation (e.g., sum-over-states method) but that so far have been restricted to the smallest of diatomics, though both static and dynamic properties have been studied; (c) semiempirical calculations, which again ignore rotation but have been applied to much larger molecules for both static and dynamic properties.

Under (a), the methods used have been extensions of those developed for electronic motion alone: the electronic finite field becomes a vibronic finite field, derivative Hartree-Fock becomes derivative Numerov-Cooley, perturbation-theory expressions for α^e, β^e, γ^e become similar expressions for α^v, β^v, γ^v. Probably the most progress will be made here (with rotation ignored) by methods that were successful in pure vibrational spectroscopy—where, slowly, numerical methods have been superseded by analytical ones. Certainly, the study of large molecules, where unperturbed potential surfaces are now becoming available, will be most easily accomplished by straightforward production of perturbed surfaces for various field strengths, followed by vibrational analysis as before. The work of Duran *et al.* (1989) is a step in this direction, but it needs to be extended so that the α,β,γ, with which we are familiar, are extracted. In this way, we can build on the knowledge so painstakingly acquired about pure unperturbed vibrational motion.

Under (b), it is likely that for some time we shall be limited to very simple species; but work in this area is important both for benchmark calculations and for identifying the influence of rotation on vibrational polarizabilities. Getting from the molecule to the laboratory, other than by classical averaging, is largely an unresolved problem for lack of any *simple* technique. The type of theory in (b) that comes from extension of the electronic formulas of Orr and Ward (1971) can be applied to dynamic polarizabilities, whereas type (a) calculations cannot, and this is of great use.

Under (c), semiempirical calculations for polyatomics will probably be with us for a while, particularly for the dynamic polarizabilities, though, for these, the extraction of rotation from the experimental data by T-dependent studies, the use of "enhancement" techniques, and the comparison of different nonlinear optical processes may make life easier. The basic perturbation-theory expressions for polyatomics are very unwieldy, and further approximations need to be explored.

An ultimate goal would be to carry out polarizability calculations for the whole molecule for arbitrarily oriented space-fixed fields without using the Born-Oppenheimer approximation.

As was said at the beginning, the subject is in its infancy, and we are a long way from routine "black box" calculations—there is still much to be done and much room for innovation.

ACKNOWLEDGMENTS

I thank Professor C. E. Dykstra and Professor D. P. Shelton for their useful advice and J. D. Mertl for his constructive criticism, as well as the Natural Sciences and Engineering Research Council of Canada for their financial support.

REFERENCES

Adamowicz, L., 1988a, Mol. Phys. **65**, 1047.

Adamowicz, L., 1988b, J. Chem. Phys. **89**, 6305.

Adamowicz, L., and R. J. Bartlett, 1986, J. Chem. Phys. **84**, 4988; **86**, 7250(E).

Altshuller, A. P., 1955, J. Chem. Phys. **23**, 256.

Applequist, J., 1983, J. Math. Phys. **24**, 736.

Applequist, J., 1984, Chem. Phys. **85**, 279.

Augspurger, J. D., and C. E. Dykstra, 1988, J. Chem. Phys. **88**, 3817; **91**, 1384(E).

Bishop, D. M., 1974, J. Chem. Phys. **60**, 2360.

Bishop, D. M., 1981, Mol. Phys. **42**, 1219.

Bishop, D. M., 1987a, J. Chem. Phys. **86**, 5613.

Bishop, D. M., 1987b, Chem. Phys. Lett. **135**, 594.

Bishop, D. M., 1989, J. Chem. Phys. **90**, 3192.

Bishop, D. M., and L. M. Cheung, 1979a, Chem. Phys. Lett. **66**, 467.

Bishop, D. M., and L. M. Cheung, 1979b, Phys. Rev. A **20**, 1310.

Bishop, D. M., and L. M. Cheung, 1980, J. Chem. Phys. **72**, 5125.

Bishop, D. M., and L. M. Cheung, 1982a, J. Chem. Phys. **76**, 2492.

Bishop, D. M., and L. M. Cheung, 1982b, J. Phys. Chem. Ref. Data **11**, 119.

Bishop, D. M., L. M. Cheung, and A. D. Buckingham, 1980, Mol. Phys. **41**, 1225.

Bishop, D. M., and B. Lam, 1987a, unpublished results.

Bishop, D. M., and B. Lam, 1987b, Chem. Phys. Lett. **134**, 283.

Bishop, D. M., and B. Lam, 1987c, Mol. Phys. **62**, 721.

Bishop, D. M., and B. Lam, 1988a, J. Chem. Phys. **89**, 1571.

Bishop, D. M., and B. Lam, 1988b, Mol. Phys. **65**, 679.

Bishop, D. M., and B. Lam, 1988c, Chem. Phys. Lett. **143**, 151.

Bishop, D. M., B. Lam, and S. T. Epstein, 1988, J. Chem. Phys. **88**, 337.

Bishop, D. M., and G. Maroulis, 1985, J. Chem. Phys. **82**, 2380.

Bishop, D. M., J. Pipin, and M. Rérat, 1990, J. Chem. Phys. **92**, 1902.

Bishop, D. M., J. Pipin, and J. N. Silverman, 1986, Mol .Phys. **59**, 165.

Bishop, D. M., and D. P. Shelton, 1988, Phys. Rev. A **38**, 1656.

Bishop, D. M., and S. A. Solunac, 1985, Phys. Rev. Lett. **55**, 1986; **55**, 2627(E).

Bogaard, M. P., and B. J. Orr, 1975, in *MTP International Review of Science, Physical Chemistry,* Ser. 2, Vol. 2, edited by A. D. Buckingham (Butterworths, London), p. 149.

Brieger, M., 1984, Chem. Phys. **89**, 275.

Brieger, M., A. Renn, A. Sodeik, and A. Hese, 1983, Chem. Phys. **75**, 1.

Brooks, B. R., and H. F. Schaefer III, 1979, J. Am. Chem. Soc. **101**, 307.

Buckingham, A. D., 1962a, Proc. R. Soc. London Ser. A **267**, 271.

Buckingham, A. D., 1962b, J. Chem. Phys. **36**, 3096.

Buckingham, A. D., 1967, Adv. Chem.Phys. **12**, 107.

Buckingham, A. D., 1970, in *Physical Chemistry: An Advanced Treatise,* Vol. 4, edited by D. Henderson (Academic, New York), p. 349.

Buckingham, A. D., 1972, in *MTP International Review of Science, Physical Chemistry,* Ser. 1, Vol. 3, edited by D. A. Ramsey (Butterworths, London), p. 73.

Buckingham, A. D., and H. C. Longuet-Higgins, 1968, Mol. Phys. **14**, 63.

Buckingham, A. D., and B. J. Orr, 1968, Proc. R. Soc. London Ser. A **305**, 259.

Buckingham, A. D., and J. A. Pople, 1955, Proc. Phys. Soc. London Sect. A **68**, 905.

Buckingham, A. D., and W. Urland, 1975, Chem. Rev. **75**, 113.

Cai, W. Q., T. E. Gough, X. J. Gu, N. R. Isenor, and G. Scoles, 1987, Phys. Rev. A **36**, 4722.

Cashion, J. K., 1963, J. Chem. Phys. **39**, 1872.

Chemla, D. S., and J. Zyss, 1987, *Nonlinear Optical Properties of Organic Molecules and Crystals* (Academic, Orlando), Vols. I and II.

Cheung, L. M., D. M. Bishop, D. L. Drapcho, and G. M. Rosenblatt, 1981, Chem. Phys. Lett. **80**, 445.

Cohen, E. R., and B. N. Taylor, 1987, Rev. Mod. Phys. **59**, 1221.

Cohen, H. D., and C. C. J. Roothaan, 1965, J. Chem. Phys. **43**, S34.

Cooley, J. W., 1963, Math. Computations **15**, 363.

Coulson, C. A., A. Macoll, and L. E. Sutton, 1952, Trans. Faraday Soc. **48**, 106.

Dalgarno, A., 1962, Adv. Phys. **11**, 281.

Debye, P., 1912, Phys. Z **13**, 97.

Debye, P., 1929, *Polar Molecules* (Dover, New York).

Dudley, J. W., II, and J. F. Ward, 1985, J. Chem. Phys. **82**, 4673.

Duran, M., J. L. Andrés, A. Lledós, and J. Bertrán, 1989, J. Chem. Phys. **90**, 328.

Dykstra, C. E., and P. G. Jasien, 1984, Chem. Phys. Lett. **109**, 388.

Dykstra, C. E., S.-Y. Liu, and D. J. Malik, 1990, Adv. Chem. Phys. **75**.

Dykstra, C. E., and D. J. Malik, 1987, J. Chem. Phys. **87**, 2806.

Ebert, L., 1924, Z. Phys. Chem. **113**, 1.
Eckert, M., and G. Zundel, 1987, J. Phys. Chem. **91**, 5170.
Eckert, M., and G. Zundel, 1988, J. Phys. Chem. **92**, 7016.
Elliott, D. S., and J. F. Ward, 1984, Mol. Phys. **51**, 45.
Ermler, W. C., and C. W. Kern, 1971, J. Chem. Phys. **55**, 4851.
Fowler, P. W., 1981, Mol. Phys. **43**, 591.
Fowler, P. W., 1984, Mol. Phys. **51**, 1423 [misprint in Eq. (23): the power of (B/ω_1) should be 3/2].
Gu, X. J., N. R. Isenor, and G. Scoles, 1986, Phys. Rev. A **39**, 413.
Hamaguchi, H., I. Suzuki, and A. D. Buckingham, 1981, Mol. Phys. **43**, 963.
Hanna, D. C., M. A. Yuratich, and D. Cotter, 1979, *Nonlinear Optics of Free Atoms and Molecules* (Springer, Berlin).
Hirschfelder, J. O., W. Byers Brown, and S. T. Epstein, 1964, Adv. Quantum Chem. **1**, 255.
Illinger, K. H., 1961, J. Chem. Phys. **35**, 409.
Illinger, K. H., and C. P. Smyth, 1960, J. Chem. Phys. **32**, 787.
Illinger, K. H., and C. P. Smyth, 1961, J. Chem. Phys. **35**, 397.
Jameson, C. J., and P. W. Fowler, 1986, J. Chem. Phys. **85**, 3432.
Kang, M. H., K. M. Chung, and M. F. Becker, 1976, J. Appl. Phys. **47**, 4944.
Kern, C. W., and R. L. Matcha, 1968, J. Chem. Phys. **49**, 2081.
Kirby-Docken, K., and J. Hinze, DVIBRO, a rovibrational eigenvalue program (unpublished).
Kirtman, B., 1990, private communication.
Krohn, B. J., W. C. Ermler, and C. W. Kern, 1974, J. Chem. Phys. **60**, 22.
Langhoff, P. W., S. T. Epstein, and M. Karplus, 1972, Rev. Mod. Phys. **44**, 602.
Lazzeretti, P., E. Rossi, and R. Zanasi, 1981, J. Phys. B **14**, L269.
LeFevre, R. J. W., and D. A. A. S. N. Rao, 1955, Aust. J. Chem. **8**, 39.
LeRoy, R. J., 1986, Univ. of Waterloo Chemical Physics Res. Rept. CP230R.
Levenson, M. D., 1982, *Introduction to Nonlinear Laser Spectroscopy* (Academic, New York).
Liu, S.-Y., and C. E. Dykstra, 1987, J. Phys. Chem. **91**, 1749.
Logan, D. E., 1982, Mol. Phys. **46**, 271.
Lu, Z., and D. P. Shelton, 1987, J. Chem. Phys. **87**, 1967 [Equations (18) and (23) are corrected in Shelton and Ulivi (1988)].
Malik, D. J., 1988, J. Chem. Phys. **88**, 2624.
Malik, D. J., and C. E. Dykstra, 1985, J. Chem. Phys. **83**, 6307.
Maroulis, G., and D. M. Bishop, 1986, Chem. Phys. Lett. **128**, 462.
Maroulis, G., and A. J. Thakkar, 1988, J. Chem. Phys. **88**, 7623.
McLean, A. D., and M. Yoshimine, 1967a, J. Chem. Phys. **46**, 3682.
McLean, A. D., and M. Yoshimine, 1967b, J. Chem. Phys. **47**, 3256.
Mills, I., 1988, *Quantities, Units and Symbols in Physical Chemistry* (IUPAC, Blackwell Sci. Publ., Oxford).
Mizrahi, V., and D. P. Shelton, 1985a, Phys. Rev. A **31**, 3145.
Mizrahi, V., and D. P. Shelton, 1985b, Phys. Rev. A **32**, 3454.
Mulholland, H. P., 1928, Proc. Cambridge Philos. Soc. **24**, 280.
Orr, B. J., and J. F. Ward, 1971, Mol. Phys. **20**, 513.
Pandey, P. K. K., and D. P. Santry, 1980, J. Chem. Phys. **73**, 2899.
Partridge, H., and S. R. Langhoff, 1981, J. Chem. Phys. **74**, 2361.
Partridge, H., S. R. Langhoff, W. C. Stwalley, and W. T. Zemke, 1981, J. Chem. Phys. **75**, 2299.
Raynes, W. T., P. Lazzeretti, and R. Zanasi, 1988, Mol. Phys. **64**, 1061.
Rinaldi, D., M. F. Ruiz-Lopez, M. T. C. Martins Costa, and J.-L. Rivail, 1986, Chem. Phys. Lett. **128**, 177.
Salem, L., 1979, Acc. Chem. Res. **12**, 87.
Schlier, C., 1961, Fortschr. Phys. **9**, 455.
Schwartz, C., and R. J. LeRoy, 1987, J. Mol. Spectrosc. **121**, 420.
Sekino, H., and R. J. Bartlett, 1986, J. Chem. Phys. **84**, 2726.
Shelton, D. P., 1986a, J. Chem. Phys. **85**, 4234.
Shelton, D. P., 1986b, Phys. Rev. A **34**, 304.
Shelton, D. P., 1986c, private communication.
Shelton, D. P., 1987a, Mol. Phys. **60**, 65 [corrections to Table 4 are to be found in Shelton (1987b)].
Shelton, D. P., 1987b, Phys. Rev. A **36**, 3461.
Shelton, D. P., and L. Ulivi, 1988, J. Chem. Phys. **89**, 149.
Shen, Y. R., 1984, *Principles of Nonlinear Optics* (Wiley, New York).
Silverman, J. N., D. M. Bishop, and J. Pipin, 1986, Phys. Rev. Lett. **56**, 1358.
Smyth, C. P., 1955, *Dielectric Behavior and Structure* (McGraw-Hill, New York).
Sprandel, L. L., and C. W. Kern, 1972, Mol. Phys. **24**, 1383.
Sternheimer, R. M., 1954, Phys. Rev. **96**, 951.
Thakkar, A. J., 1981, J. Chem. Phys. **75**, 4496.
Van Vleck, J. H., 1932, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University, London), especially Chapter 7.
Vidal, C. R., and W. C. Stwalley, 1982, J. Chem. Phys. **77**, 883.
Weidemann, E. G., and G. Zundel, 1970, Z. Naturforsch. **25**, 627.
Werner, H.-J., and W. Meyer, 1976, Mol. Phys. **31**, 855.
Wharton, L., and W. Klemperer, 1963, J. Chem.Phys. **39**, 1881.
Whiffen, D. H., 1958, Trans. Faraday Soc. **54**, 327.
Wu, T.-Y., 1952, Can. J. Phys. **30**, 291.
Zare, R. N., 1963, Univ. of California Lawrence Radiation Lab. Report No. UCRL-10925.