Vibrational Stark Spectroscopy. 1. Basic Theory and Application to the CO Stretch

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The effects of uniform electric fields on equilibrium interatomic separations, vibrational energy levels, and infrared transition moments are summarized for diatomic molecules in a matrix in which random orientation is maintained in both ground and excited states. The dependence of each property on field strength F can be expressed as a function of a linear and a quadratic term in the field strength. For vibrational energy levels, these terms are conventionally but imprecisely described as the vibrational dipole moment change and the vibrational polarizability change, respectively, accompanying excitation to a given vibrational excited state; for the dipole moment gradient, which determines the intensity, the analogous terms correspond to the transition polarizability and transition hyperpolarizability, respectively. Parameters describing the electric field response can be defined in terms of the quadratic and cubic force constants, and the first, second, and third gradients of the dipole moment, polarizability, and first hyperpolarizability of the molecule considered. This develops the earlier work of Hush and Williams (1974), Gready, Bacskay and Hush (1977–8), Lambert (1983–91), and the more recent work of Bishop *et al.* (1993–). The electric field response can, in principle, be measured in a manner analogous to that of electronic transitions in electroabsorption spectroscopy. The general form of this, based on the analysis of Liptay for the Stark effect on electronic transitions, is outlined for the corresponding vibrational case, and computational strategies are discussed. Stark vibrational spectral parameters for CO calculated at different levels of quantum calculation and by different strategies for analysis of the electric field perturbation data are presented.

1. Introduction

The perturbation of vibrational properties of molecules by electric fields is clearly a subject of wide-ranging importance, particularly in inorganic and biological contexts. However, it has received only intermittent theoretical treatment in the last 20 years or so. The first quantum-chemical analyses were made by Hush and Williams[1] and by Gready, Bacskay, and Hush.[2–6] In those works, finite electric field theory in which the Hamiltonian H is expressed as

$$\mathbf{H} = \mathbf{H}_0 - \boldsymbol{\mu} \cdot \mathbf{F} \qquad (1)$$

where $\mathbf{H}_0$ is the field-free Hamiltonian for the molecule considered, $\boldsymbol{\mu}$ is its dipole moment, and $\mathbf{F}$ is the uniform electric field, was employed to determine molecular vibrational response functions. This was on analogous lines to that of previous work on electronic response functions (e.g. polarizabilities and hyperpolarizabilities[7–10]). In addition, the vibrational responses were analyzed in terms of perturbation theory, which enabled them to be related to fundamental molecular parameters.

The first molecule to be studied was CO, at the CNDO approximate self-consistent field (SCF) level of computation[1] (the species N_2, H_2, NO, O_2, CN^-, and O_2^- were also studied at this level[11]). It was found that the vibrational frequency ν could be expressed as the sum of a linear and a quadratic term in the field strength, and this assumption is used herein. It is usual to refer to these terms as the *vibrational dipole moment change* $\Delta\mu$ and *vibrational polarizability* change $\Delta\alpha$ respectively, i.e.

$$h\delta\nu = h\nu(\mathbf{F}) - h\nu(0) = -\Delta\boldsymbol{\mu} \cdot \mathbf{F} - \tfrac{1}{2}\mathbf{F} \cdot \Delta\boldsymbol{\alpha} \cdot \mathbf{F} \qquad (2)$$

where h is Planck's constant; this language is misleading,

however, as they are *not* exactly equivalent to the changes in the expectation values of the dipole and polarizability operators, respectively, induced by the vibrational transition; however, for simplicity, we retain the notation. The first term, $-\Delta\mu$, is actually the Stark tuning rate: it is a quantity which has been measured for orientated CO, for example at interfaces, either physisorbed (as, for example, in zeolites) or chemisorbed (as, for example on Au or Pt surfaces at the vacuum/metal or metal/electrolyte interface). Calculations of the Stark tuning rate for the free molecule can be used in discussing observed shifts in the former but not the latter case. For example, the Stark shifts of CO physisorbed in X- and Y-zeolites were found[1] to correlate well with a reasonable estimate of the field strength variation at the point of attachment. This suggests that the estimate of $-\Delta\mu$ obtained by this approximate SCF calculation,[1] ca. 0.0070 au (1 atomic unit (au) = 42.6784 cm^{-1} (MV/cm)$^{-1}$ so this corresponds to 0.30 cm^{-1} (MV/cm)$^{-1}$), is reasonably accurate; a later *ab initio* calculation with allowance for electron correlation by the CASSCF method[12] yielded 0.0089 au, in acceptable agreement with this.

Detailed calculations at the *ab initio* SCF level, and in part at the configuration interaction (CI) level, of the perturbation of vibrational properties by a parallel electric field were carried out for LiH.[2] In this work, frequencies of the lowest three vibrational transitions as a function of field strength were calculated. The SCF-predicted energy level shifts were quite large (e.g., −506.8 and 306.4 cm^{-1} for the vibrational level n = 3 at field strengths of ±0.01 au, respectively), as were the shifts of intensity. These were analyzed in terms of perturbation theory. A point of interest is that the first anharmonic constant in the vibrational potential energy expression was found also to exhibit a linear plus quadratic dependence on the field intensity. According to the analytic theory[2] (and *vide infra*), these depend respectively on nonvanishing of the third deriva-

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tives of the dipole moment and axial polarizability with respect to interatomic separation; this indicates that a general analytic theory should include terms up to this order of expansion.

This reasonable agreement for CO for estimation of the Stark tuning rate between an approximate SCF and a correlated *ab initio* approach should not be taken to imply that SCF methods will, in general, be adequate for calculation of the vibrational response functions. Indeed, when the approximate SCF calculation for CO was followed by an *ab initio* SCF study,[5] a value of $-\Delta\mu = 0.016$ au was obtained for the tuning rate; this high value results mainly from the overestimate at the SCF level of the derivative of the dipole moment with respect to bond length. The value of this derivative obtained from CASSCF calculations[12] is the most accurate value so far available and is 0.0089 au. The *ab initio* SCF value[5] is thus 50% too large; more recent SCF calculations[13,14] give overestimates ranging from 60 to 70%. Inclusion of configuration interaction is clearly necessary in *ab initio* calculations of this type. The reasonable CNDO result must really be regarded as due to fortuitous cancelation of errors arising from approximations to the SCF limit and from neglect of electron correlation; we return to the comparison of *approximate* SCF (in this case AM1) and correlated *ab initio* calculations in section 4.

In this paper, we set out a general theory of the vibrational Stark effect for the special case of a molecule which retains a fixed random orientation when a field is applied, such as will be found in solution in a low-temperature glass (the so-called "infinite temperature" approximation); this is the experimental situation employed to good effect by Oh and Boxer in studying the electronic Stark effect[15,16] and more recently by Chattopadhyay and Boxer in a pioneering experimental study of the vibrational Stark effect[17] for molecules in bulk phases. A consequence of the use of an isotropic sample is that no linear response is observed in eq 2 as contributions from a molecule with one orientation are canceled by those from another; instead, the linear and quadratic responses are convolved into a new quadratic response, as shown below.

The basic approach to interpretation of observed field-dependent spectra for isotropic samples is that devoloped by Liptay.[18,19] We assume that the absorption envelope corresponds to a single molecular vibrational transition. A perturbing electric field is applied, such that the vector internal field at the molecular site is **F**; the relation between the internal field **F** and the external field $\mathbf{F}_{app}$ is assumed to be

$$\mathbf{F} = f\mathbf{F}_{app} \qquad (3)$$

A reliable estimate for f is not yet generally available; however, it is likely[15] to be in the range $1 \leq f \leq 1.3$. This imposes a limit on the accuracy of derived quantities. Recent work by Creutz et al.,[20] however, proposes an experimental method for determination of the proportionality constant which, if generally applicable, will remove this uncertainty.

It is assumed that the shape of the absorption band remains invariant on application of the field (this most likely will not apply if the absorption corresponds to more than one vibrational absorption process). The effect of the field is thus limited to changes of the transition absorption frequency and to modifications of the transition moment. For each molecule in the sample, the individual absorption frequency is taken to vary in accord with eq 2, while the transition moment vector is taken to vary according to

$$\mathbf{M}(F) = \mathbf{M} + \mathbf{A}\cdot\mathbf{F} + \mathbf{F}\cdot\mathbf{B}\cdot\mathbf{F} \qquad (4)$$

where **A** and **B** are respectively the transition polarizability

(second-rank) and transition hyperpolarizability (third-rank) tensors.

We further assume an experimental situation in which linearly polarized light passes through a sample held between two electrodes in a configuration such that the propagation vector of the light is normal to the field direction, with the polarization vector **e** making an angle χ with the field direction. If the angle between the vectors **M** and $\Delta\mu$ is ζ, a sensitivity function $R(\chi)$ is defined as

$$R(\chi) = {}^{1}/_{15}[5 + (3\cos^2\zeta - 1)(3\cos^2\chi - 1)] \qquad (5)$$

While a general solution for the vibrational spectroelectric effect in terms of all the tensor components of **M**, **A**, **B**, $\Delta\mu$, and $\Delta\alpha$ is easily obtained, we assume that only one component M_z, A_{zz}, B_{zzz}, $\Delta\mu_z$, and $\Delta\alpha_{zz}$, respectively, of each of these tensors is important; this component is written as M, A, B, $\Delta\mu$, and $\Delta\alpha$, respectively, and as a consequence we have $\zeta = 0$. For a molecule AB, the z direction is taken to be that from A to B; this convention determines the sign of M, A, and $\Delta\mu$.

With these assumptions, the lowest order isotropic-averaged perturbation to the absorption band is expressed as

$$\frac{1}{F^2 R(\chi)}\left[\frac{\epsilon}{\nu}(F) - \frac{\epsilon}{\nu}(0)\right] = D_e\frac{\epsilon}{\nu}(0) + F_e\frac{d}{h\,d\nu}\frac{\epsilon}{\nu}(0) +$$
$$H_e\frac{d^2}{2h^2\,d\nu^2}\frac{\epsilon}{\nu}(0) \qquad (6)$$

where ϵ is the absorption intensity, $F = |\mathbf{F}|$, and the expansion coefficients are given by

$$D_e = \frac{A^2}{M^2} + \frac{2B}{M},\ F_e = \frac{2A\delta\mu}{M} + \frac{\Delta\alpha}{2},\ \text{and}\ H_e = (\Delta\mu)^2 \qquad (7)$$

These coefficients represent contributions to the electroabsorption signal whose shapes are proportional to the absorption band contour (ϵ/ν) and its first and second frequency derivatives, respectively. As an illustration, the electroabsorption response predicted for CO (see section 4) and these three separate contributions are shown in Figure 1. The first term, D_e, has the shape of the unperturbed absorption envelope; as in the corresponding perturbation of an electronic transition, this is referred to as the "constant" term. If the transition moment hyperpolarizability B is 0 but the transition moment polarizability is finite ($A \neq 0$), the constant term is positive (proportional to the square of the ratio of transition polarizability to transition moment). However, when $B \neq 0$, the constant term may be either positive or negative. The second term in the perturbation, F_e, has the shape of the first derivative of the unperturbed absorption envelope. If the change of dipole moment $\Delta\mu$ accompanying excitation is 0, this term may be either positive or negative and is a measure of the polarizability change $\Delta\alpha$; examples of both positive and negative $\Delta\alpha$ are found in the electric field perturbation of charge-transfer transitions in metal complexes.[15,16,21,22] In general, we anticipate that $\Delta\alpha$ would be swamped by $2A\Delta\mu/M$, however. The third term, H_e, has the shape of the second derivative of the absorption spectrum and is simply proportional to $(\Delta\mu)^2$; it thus yields unambiguously the absolute value of $\Delta\mu$ when the proportionality factor f is known. Unfortunately, no general unique solution

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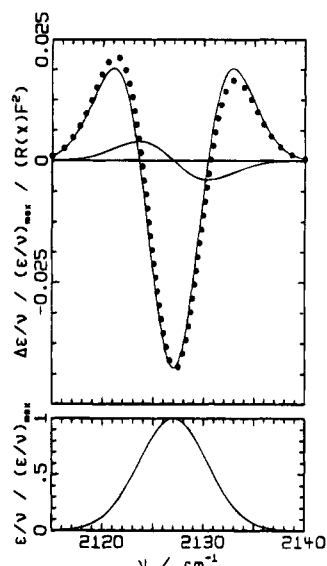
Figure 1. Model CO thin-film absorption spectrum (Gaussian band with a half-width at half-maximum of 4 cm^{-1}) (bottom) and the predicted electroabsorption response from eq 6, where $\Delta\epsilon/\nu = (\epsilon(F) - \epsilon(0))/\nu$, in au (top). There, the solid lines show the contributions from the constant, first-derivative, and second-derivative terms, while the points indicate the total response.

for the other three molecular properties, $\Delta\alpha$, A, and B, is available from the remaining two experimental observables, D_e and F_e.

In analyzing the electric field perturbation of electronic transitions in metal complexes, the question of deviation from the classical Liptay expressions has been considered.[22] In bis-metal complexes, for example, it is found that the band shape is not necessarily independent of the applied field strength. The possibility of deviation from this assumption in certain cases of perturbation of vibrational transitions must be borne in mind. A situation which is difficult to analyze occurs when a second weak absorption occurs in the vicinity of the band of interest: although this band has, by assumption, a relatively small value of ϵ/ν, both $d^2/d\nu^2(\epsilon/\nu)$ and $\Delta\mu$ for this band may be significant. Alternatively, it could be said that vibrational electroabsorption spectroscopy offers the possibility of detecting or resolving infrared transitions that are otherwise obscured.

Primarily, we are concerned with the significance and interpretation of the spectroelectric response parameters $\Delta\mu$, $\Delta\alpha$, A, and B. Since the original treatments of Hush et al.,[1,2,5] some or all of these properties have been considered in more detail by other authors,[23-30] with some of these being compared and contrasted with the most sophisticated treatment presented thus far, that of Martí and Bishop.[14,31] We adopt a finite-field approach, as this method readily allows for the provision of energy transfer between the chromophore and its environment, a key feature of the physical process. In an analytical approach, we include all terms in the expansion of the potential energy and other functions of up to third order and describe electro-absorption responses up to order F^2 (cf. eq 6). At the simplest level of theory, we isolate both terms which are well-known[14,31] and terms which are previously undescribed; at a more sophisticated level, we produce, for the first time, an analysis which treats the mechanical anharmonicity consistently throughout. The basic theory is developed in section 2, possible computational strategies are considered in section 3, an application to CO is developed in section 4, and extensions of the formalism to include polyatomic molecules with possibly more than one electroabsorption-active vibrational mode and overtone or combination transitions are considered in section

5. Atomic units are used throughout; conversion factors to other commonly used units include

1 au =	0.529177 Å	(length r)
	27.2107 eV	(energy V)
	219 477 cm^{-1}	(wavenumber ν)
	5142.57 MV/cm	(electric field F)
	42.6784 cm^{-1} (MV/cm)$^{-1}$	(Stark tuning rate)
	2.54156 D	(dipole moment μ, m)
	0.148 185 Å^3	(polarizability α)
	8.65710 × 10^{-33} esu	(hyperpolarizability β)

2. Interpretation of the Response Functions

To interpret the meaning of the molecular electroabsorption response parameters $\Delta\mu$, $\Delta\alpha$, A, and B, the molecular potential energy V, dipole moment μ, polarizability α, and first hyper-polarizability β are expanded field-free about the equilibrium bond length r_e as

$$V = V_0 + a_1(r - r_e)^2 + a_2(r - r_e)^3$$

$$\mu = m_0 + m_1(r - r_e) + m_2(r - r_e)^2 + m_3(r - r_e)^3 \quad (8)$$

$$\alpha = \alpha_0 + \alpha_1(r - r_e) + \alpha_2(r - r_e)^2 + \alpha_3(r - r_e)^3$$

$$\beta = \beta_0 + \beta_1(r - r_e) + \beta_2(r - r_e)^2 + \beta_3(r - r_e)^3$$

In the presence of an applied electric field of magnitude F applied parallel to the vectors **M** and $\Delta\mu$, etc., the energy and dipole moment become

$$V(F) = V - \mu F - \alpha F^2/2 - \beta F^3/6$$

$$\mu(F) = \mu + \alpha F + \beta F^2/2 \quad (9)$$

$$\alpha(F) = \alpha + \beta F$$

The electric field thus modifies the ratio of the second and third derivatives of the energy, and hence the equilibrium bond length shifts to

$$r_e(F) = r_e + F\frac{m_1}{2a_1} + F^2\left(\frac{\alpha_1}{4a_1} + \frac{m_1 m_2}{2a_1^2} - \frac{3m_1^2 a_2}{8a_1^3}\right) \quad (10)$$

where here and subsequently only field effects of order F^2 are considered. We assume that any temporal variation in F is slow compared to energy relaxation times and thus that the sample re-equilibrates with its environment; the importance of this step has been stressed by Martí and Bishop.[31] At this new bond length, the molecular properties can be re-expanded and the energy can be expressed as

$$V(F) = a_1(F)[r - r_e(F)]^2 + a_2(F)[r - r_e(F)]^3 \quad (11)$$

where

$$a_1(F) = a_1 + F\left(-m_2 + \frac{3m_1 a_2}{2a_1}\right) +$$

$$F^2\left[-\frac{\alpha_2}{2} + \frac{3(a_2\alpha_1 - 2m_1 m_3)}{4a_1} + \frac{3m_1 m_2 a_2}{2a_1^2} - \frac{9m_1^2 a_2^2}{8a_1^3}\right] \quad (12)$$

and

$$a_2(F) = a_2 - Fm_3 - F^2\alpha_3/2 \quad (13)$$

From $a_1(F)$ the harmonic vibration frequency $\nu_H(F)$ can be

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extracted and expressed as

$$h\nu_H(F) = h\nu_H - \Delta\mu_H F - \Delta\alpha_H F^2/2 \quad (14)$$

where ν_H is the field-free harmonic vibration frequency and

$$\Delta\mu_H = \frac{h\nu_H}{4a_1^2}(2m_2 a_1 - 3m_1 a_2)$$

and

$$\Delta\alpha_H = \Delta\alpha'_H + \Delta\alpha''_H \quad (15)$$

where

$$\Delta\alpha'_H = \frac{3h\nu_H}{16a_1^4}(3a_2 m_1 - 2a_1 m_2)^2$$

and

$$\Delta\alpha''_H = \frac{h\nu_H}{4a_1^2}(2a_1\alpha_2 - 3a_2\alpha_1 - 2m_2^2 + 6m_1 m_3)$$

Other than for the contribution from the high-order component m_3, these expressions are well-known[14,31] (note,[32] however, that while eq 20 from Martí and Bishop[31] is correct, eq 19 (for α-(curv) $= \Delta\alpha_H/2$) contains a misprint and there should be a factor of 4 preceding its $a_{21}^2 a_{20}^2$ term).

In the preceding analysis, the inclusion of the anharmonicity a_2 is an essential feature; it is not included in a consistent fashion, however, as a_2 is taken to be nonzero, yet $a_2(F)$ is assumed to be 0, inconsistent with eq 13. To minimize this effect, an improved estimate of the actual $0 \rightarrow 1$ transition frequency ν can be obtained by applying first-order perturbation theory to the harmonic energy levels in order to incorporate the effects of the anharmonicity $a_2(F)$. This produces

$$\nu_P(F) = \nu_H(F)\left(1 - \frac{15a_2^2(F)}{16a_1^3(F)}h\nu_H(F)\right) \quad (16)$$

The correction factor is typically small as, in au for say a CO or CN stretch, $a_1 \sim |a_2| \sim 0.6$, while $h\nu_H \sim 0.01$, making the correction on the order of 1.5% of the harmonic frequency. The vibrational transition energy can thus be written as

$$h\nu_P(F) = h\nu_P - \Delta\mu_P F - \Delta\alpha_P F^2/2 \quad (17)$$

where

$$\Delta\mu_P = \Delta\mu_H\left(1 + \frac{15a_2^2}{4a_1^3}h\nu_H\right) - \frac{15a_2 m_3}{8a_1^3}(h\nu_H)^2$$

and

$$\Delta\alpha_P = \Delta\alpha'_P + \Delta\alpha''_P +$$
$$\frac{15}{8a_1^3}\left(m_3^2 - \alpha_3 a_2 - \frac{4m_2 m_3 a_2}{a_1} + \frac{6m_1 m_3 a_2^2}{a_1^2}\right)(h\nu_H)^2 \quad (18)$$

where

$$\Delta\alpha'_P = \Delta\alpha'_H\left(1 + \frac{10a_2^2}{a_1^3}h\nu_H\right)$$

and

$$\Delta\alpha''_P = \Delta\alpha''_H\left(1 + \frac{15a_2^2}{4a_1^3}h\nu_H\right)$$

We see that inclusion of the anharmonicity correction to the field-free vibration frequency results in additional contributions to the frequency shift and provides multiplicative factors for the existing terms. The additional terms involve the (usually small) high-order expansion parameters m_3 and α_3 and are also second order in the expansion parameter $h\nu$; their effect should thus be small in most cases. The multiplicative factors, however, modify the electric field response functions by 4–8 times that which the original anharmonicity correction modifies the harmonic vibration frequency. As an example, for a CN or CO stretch, the anharmonic shift is ca. 1% of the harmonic frequency, and so the contributions to $\Delta\mu_H$ and $\Delta\alpha_H$ will each be increased by ca. 4–8%. There may be a profound effect for $\Delta\alpha_P$ if the two contributions $\Delta\alpha'_H$ and $\Delta\alpha''_H$ to $\Delta\alpha_H$ are of similar magnitude but opposite sign, however, and in this case the terms in $(h\nu)^2$ may also be significant; this is actually the case for CO, see section 4. Also, for a reasonably anharmonic vibration such as an X–H stretch, the anharmonicity corrections could double the electric field response. Note that while the above perturbation theory expressions should be quite accurate for most oscillators, for X–H stretch modes quantitatively better results would be obtained by employing the known analytical solution for the vibrations of a Morse oscillator.

The transition moment for the $0 \rightarrow 1$ vibrational transition is given by

$$M(F) = \langle\Psi_0(F)|\mu(F)|\Psi_1(F)\rangle \quad (19)$$

where $|\Psi_i(F)\rangle$ are the field-dependent vibrational eigenfunctions. These eigenfunctions may be expanded in terms of harmonic oscillator wave function $|\psi_j(F)\rangle$ for an oscillator of frequency $\nu_H(F)$ centered at $r = r_e(F)$. Most conveniently, the dipole moment function can be re-expanded about $r_e(F)$ as

$$\mu(F) = m_0(F) + m_1(F)[r - r_e(F)] + m_2(F)[r - r_e(F)]^2 + m_3(F)[r - r_e(F)]^3 \quad (20)$$

where

$$m_0(F) = m_0 + F\left(\alpha_0 + \frac{m_1^2}{2a_1}\right) + F^2\left(\frac{\beta_0}{2} + \frac{3m_1\alpha_1}{4a_1} + \frac{3m_1^2 m_2}{4a_1^2} - \frac{3m_1^3 a_2}{8a_1^3}\right)$$

$$m_1(F) = m_1 + F\left(\alpha_1 + \frac{m_1 m_2}{a_1}\right) + F^2\left(\frac{\beta_1}{2} + \frac{m_2\alpha_1 + 2m_1\alpha_2}{2a_1} + \frac{4m_1 m_2^2 + 3m_1^2 m_3}{4a_1^2} - \frac{3m_1^2 m_2 a_2}{4a_1^3}\right) \quad (21)$$

$$m_2(F) = m_2 + F\left(\alpha_2 + \frac{3m_1 m_3}{2a_1}\right) + F^2\left(\frac{\beta_2}{2} + \frac{3m_3\alpha_1 + 6m_1\alpha_3}{4a_1} + \frac{3m_1 m_2 m_3}{2a_1^2} - \frac{9m_1^2 m_3 a_2}{8a_1^3}\right)$$

$$m_3(F) = m_3 + F\alpha_3 + F^2\frac{\beta_3}{2}$$

allowing the ready evaluation of the dipole matrix elements

$$\mu_{ij} = \langle \psi_i(F)|\mu(F)|\psi_j(F)\rangle \qquad (22)$$

To zeroth order in perturbation theory, electrical and mechanical anharmonicities $a_2(F)$, $m_2(F)$, and $m_3(F)$ are neglected and the transition moment becomes simply

$$M_H(F) = \mu_{01} = \left(\frac{h\nu(F)}{4a_1(F)}\right)^{1/2} m_1(F) \qquad (23)$$

This can be expressed as

$$M_H(F) = M_H + A_H F + B_H F^2 \qquad (24)$$

where

$$\frac{M_H}{\gamma} = m_1$$

$$\frac{A_H}{\gamma} = \alpha_1 + \frac{5m_1 m_2}{4a_1} - \frac{3m_1^2 a_2}{8a_1^2} \qquad (25)$$

$$\frac{B_H}{\gamma} = \frac{\beta_1}{2} + \frac{m_1}{128a_1^4}(9m_1 a_2 - 14m_2 a_1)^2 + $$

$$\frac{m_1}{16a_1^2}(18\alpha_2 a_1 - 9\alpha_1 a_2 + 18m_1 m_3 - 2m_2^2) + \frac{3m_2\alpha_1}{4a_1}$$

and the constant prefactor γ is defined as

$$\gamma = \left(\frac{h\nu_H}{4a_1}\right)^{1/2} \qquad (26)$$

Our analysis verifies the factor of 5/4 in front of the $m_1 m_2/a_1$ contribution to A_H/γ, a matter of previous contention resolved by Martí and Bishop,[31] and provides also a hitherto unknown contribution.

In an alternative analysis which treats the anharmonicities more consistently, the vibrational transition moment can be obtained using first-order perturbation theory, giving

$$M_P(F) = \mu_{01} + \frac{1}{h\nu_H(F)}\left(V_{01}\mu_{00} - V_{01}\mu_{11} - \frac{V_{03}\mu_{13}}{3} - \right.$$

$$\left. V_{12}\mu_{02}\right) + \frac{1}{[h\nu_H(F)]^2}\left(V_{01}V_{12}\mu_{12} + \frac{V_{03}V_{12}\mu_{23}}{3} + \frac{V_{01}V_{14}\mu_{14}}{3} + \right.$$

$$\left. \frac{V_{03}V_{14}\mu_{34}}{9} - V_{01}^2\mu_{01} - \frac{V_{01}V_{03}\mu_{03}}{3}\right) \qquad (27)$$

where

$$V_{ij} = a_2(F)\langle\psi_i(F)|[r - r_e(F)]^3|\psi_j(F)\rangle \qquad (28)$$

are the anharmonic coupling integrals. The transition moment thus becomes

$$M_P(F) = \left(\frac{h\nu_H(F)}{4a_1(F)}\right)^{1/2}\left[m_1(F) + h\nu_H(F)\left(\frac{125m_1(F)a_2^2(F)}{192a_1^3(F)} + \right.\right.$$

$$\left.\left. \frac{3m_3(F)}{4a_1(F)} - \frac{5m_2(F)a_2(F)}{4a_1^2(F)}\right) + [h\nu_H(F)]^2\frac{347m_3(F)a_2^2(F)}{256a_1^4(F)}\right] \qquad (29)$$

which can be expressed as

$$M_P(F) = M_P + A_P F + B_P F^2 \qquad (30)$$

where

$$\frac{M_P}{\gamma} = \frac{M_H}{\gamma} + h\nu_H\left(\frac{125m_1 a_2^2}{192a_1^3} - \frac{5m_2 a_2}{4a_1^2} + \frac{3m_3}{4a_1}\right) + $$

$$(h\nu_H)^2\frac{347m_3 a_2^2}{256a_1^4} \qquad (31)$$

$$\frac{A_P}{\gamma} = \frac{A_H}{\gamma} + \frac{h\nu_H}{4a_1}\left(-\frac{1375m_1^2 a_2^3}{128a_1^4} + \frac{1465m_1 m_2 a_2^2}{64a_1^3} - \right.$$

$$\frac{193m_1 m_3 a_2}{12a_1^2} - \frac{35m_2^2 a_2}{4a_1^2} + \frac{125\alpha_1 a_2^2}{48a_1^2} + \frac{29m_2 m_3}{4a_1} - $$

$$\left. \frac{5\alpha_2 a_2}{a_1} + 3\alpha_3\right) + (h\nu_H)^2\frac{347a_2}{128a_1^4}\left(-\frac{39m_1 m_3 a_2^2}{16a_1^2} + \frac{13m_2 m_3 a_2}{8a_1} - \right.$$

$$\left. m_3^2 + \frac{\alpha_3 a_2}{2}\right) \qquad (32)$$

and

$$\frac{B_P}{\gamma} = \frac{B_H}{\gamma} + \frac{h\nu_H}{8a_1}\left(\frac{78375m_1^3 a_2^4}{1024a_1^6} - \frac{51525m_1^2 m_2 a_2^3}{256a_1^5} + \right.$$

$$\frac{4253m_1^2 m_3 a_2^2}{32a_1^4} + \frac{37075m_1 m_2^2 a_2^2}{256a_1^4} - \frac{1211m_1 m_2 m_3 a_2}{8a_1^3} + $$

$$\frac{647m_1 m_3^2}{24a_1^2} - \frac{8250m_1\alpha_1 a_2^3}{256a_1^4} + \frac{7415m_1\alpha_2 a_2^2}{192a_1^3} - \frac{647m_1\alpha_3 a_2}{24a_1^2} - $$

$$\frac{385m_2^3 a_2}{16a_1^3} + \frac{343m_2^2 m_3}{16a_1^2} + \frac{2885m_2\alpha_1 a_2^2}{96a_1^3} - \frac{105m_2\alpha_2 a_2}{4a_1^2} + $$

$$\frac{19m_2\alpha_3}{2a_1} - \frac{511m_3\alpha_1 a_2}{24a_1^2} + \frac{49m_3\alpha_2}{4a_1} + \frac{125\beta_1 a_2^2}{48a_1^2} - \frac{5\beta_2 a_2}{a_1} + $$

$$3\beta_3\right) + (h\nu_H)^2\frac{347}{256a_1^4}\left(\frac{2457m_1^2 m_3 a_2^4}{128a_1^4} - \frac{819m_1 m_2 m_3 a_2^3}{32a_1^3} - \right.$$

$$\frac{39m_1\alpha_3 a_2^3}{8a_1^2} + \frac{117m_1 m_3^2 a_2^2}{8a_1^2} + \frac{221m_2^2 m_3 a_2^2}{32a_1^2} - \frac{13m_2 m_3^2 a_2}{2a_1} + $$

$$\frac{13m_2\alpha_3 a_2^2}{4a_1} + m_3^3 - \frac{39m_3\alpha_1 a_2^3}{16a_1^2} + \frac{13m_3\alpha_2 a_2^2}{8a_1} - $$

$$\left. 3m_3\alpha_3 a_2 + \frac{\beta_3 a_2^2}{2}\right) \qquad (33)$$

The anharmonicity corrections to A_P and B_P are thus very complex, and it is difficult to draw general conclusions concerning the relative magnitudes of the terms involved. In an optically nonlinearly active device, the terms involving the hyperpolarizability β would be large and would most likely dominate the expressions; even for CO and CN stretches, however, we find that typically β_1 is the most significant contributor to B_H (and B_P).

It is difficult to provide a rigorous interpretation of the significance of $\Delta\mu$ and $\Delta\alpha$. In electronic electroabsorption spectroscopy, these quantities are identified simply as the differences in the dipole moment and polarizability between the electronic ground and excited states. A similar interpretation here would see these quantities as being the difference between the expectation values of the dipole and polarizability operators between the initial and final vibrational levels. This is clearly an inappropriate description for $\Delta\alpha$, as eq 15, etc., contain contributions from m_1, etc.; the expectation value difference may

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only contain terms in various α's and a's. It is also inappropriate for $\Delta\mu$, the discrepancy being

$$\langle\Psi_1|\mu|\Psi_1\rangle - \langle\Psi_0|\mu|\Psi_0\rangle - \Delta\mu_P =$$
$$\frac{(h\nu_H)^2 a_2^2}{4a_1^5}\left(\frac{45m_1 a_2}{4} - \frac{5m_2 a_1}{3}\right) \quad (34)$$

This term is second order in $h\nu$ and is thus expected to be small, but nevertheless it makes the interpretation of $\Delta\mu$ difficult. The differences arise as the very application of the probing electric field initiates a geometrical relaxation which causes the molecular dipole moments, polarizabilities, etc., to change; hence, the observed response does not simply reflect the intrinsic molecular properties. This is not altogether uncommon: an example is the X-ray photoelectron spectroscopy of the Creutz—Taube ion.[33]

3. Computational Strategies

The most appropriate method for evaluating, either *ab initio* or by some other method, the electric field response properties varies depending on the capabilities of the software and the properties of the calculation method. One method is to evaluate first the 11 parameters a_1, a_2, m_1, m_2, m_3, α_1, α_2, α_3, β_1, β_2, and β_3 and then evaluate the desired properties using the analytical equations developed above (eqs 15, 18, 25, and 31—33). Some electronic structure packages such as MOPAC allow μ, α, and β to be evaluated directly, either by internally evaluating energy field derivatives or by applying the Hellman—Feynman theorem and evaluating the quantities directly; the applicability of this theorem to problems of this sort, including CO, has been considered elsewhere.[34] The desired properties are then obtained simply by interpolating μ, α, and β evaluated at (at least) four different geometries using eq 8. Note that the range of potential energy spanned by the geometries chosen should be *at least* $h\nu$. Alternatively, it may be necessary to perform calculations at explicitly specified geometries and field strengths. If the Hellman—Feynman theorem holds, then it is necessary to evaluate $V(F)$ and $\mu(F)$ at (at least) four different geometries and three different field strengths. This produces 24 individual pieces of data, but the Hellman—Feynman theorem restricts the number of independent pieces of information to 16 and allows all of the parameters shown in eq 8 to be determined uniquely. If the Hellman—Feynman theorem does not hold, then $V(F)$ needs to be evaluated at (at least) four different geometries and four different field strengths.

It is also possible to evaluate the electric field response properties directly numerically from $V(F)$ (given by eq 11) and optionally $\mu(F)$ (given by eq 20). If Hellman—Feynman holds, then for each of the (at least) three field strengths used V and μ would need to be evaluated at (at least) four geometries, and hence $r_e(F)$, $a_1(F)$, $a_2(F)$, $m_1(F)$, $m_2(F)$, and $m_3(F)$ would be determined. From them, $\nu(F)$ and $M(F)$ can be determined, and differentiation as a function of the field strength gives directly the electric field response properties; for this purpose, *any* available method for determining vibrational frequencies and transition moments may be used, not only the harmonic (eq 23) and perturbation theory (eqs 16 and 27) methods presented above but possibly also an essentially exact variational analysis. If Hellman—Feynman does not hold, then $\mu(F)$ must be pre-evaluated using a further numerical differentiation of the energy with respect to field strength.

Using either approach, it is possible to simplify the procedure by ignoring the field dependence of the electrical and mechanical anharmonicities; in this fashion $\Delta\mu_H$ rather than $\Delta\mu_P$ is evaluated, etc. Then, only a_1, a_2, m_1, m_2, m_3, α_1, α_2, and β_1 or alternatively $r_e(F)$, $a_1(F)$, and $m_1(F)$ need be evaluated.

The principal advantage of the analytic approach is that it provides physical insight into the causes of the electric field response, with the observable quantities being expressed in terms of more-fundamental molecular properties. The principal difficulty of this approach stems from the complexity of the relationships involved which adversely affects both programming and interpretational aspects. Another important difference between the analytical and numerical approaches concerns the manner in which ill-defined properties are treated. While, superficially, the numerical approach appears attractive in that properties of typically dubious reliability such as at least m_3, etc., do not appear, in reality the results obtained using it are identical (in the limit of low field strength) to those that would be obtained by analyzing the same data set and involving m_3, etc., explicitly. Indeed, it is the analytical method which offers advantages in this regard in that any property either which is not adequately described by the electronic structure method in use or whose contribution to the raw data set is numerically insignificant can be excluded explicitly from the calculation. A possible computational strategy which combines the flexibility of the analytical approach with the ease of the numerical one is to first deduce all expansion parameters and modify, if necessary, and then apply eq 8 to generate a new data set, which is then processed numerically; uncustomarily small field strengths as low as 10^{-5} au should be used in this process to minimize errors.

4. Application to CO

Theoretical prediction of the vibrational electric field effect requires calculations which are both extensive and accurate, and historically CO has been the test molecule of choice. Some previous analyses have been summarized in the recent papers of Bishop.[14,31] We analyze in detail the most extensive and accurate *ab initio* results for the CO potential that are currently available, the CASSCF results of Bauschlicher,[12] determining the reliability of electric field response properties evaluated from them. Also, to be able to make predictions for large polyatomic molecules, we consider results generated using the AM1 electronic Hamiltonian. Derived molecular parameter sets are shown in Table 1, while calculated electric field response properties are shown in Table 2; note that the sign convention used sets the dipole moment of C^-O^+ as positive.

Bauschlicher[12] reports the CASSCF energies at each of four different field strengths evaluated for seven different CO bond lengths. In one approach, we take all of this data and determine the molecular constants appearing in eq 8 by interpolating the energy as a function of r using a sixth-order polynomial and differentiating to obtain the coefficients; these results are labeled E@7. Alternatively, we choose a minimal subset of the data and analyze the energy at only four different geometries around the minimum and label this E@4. If deduced properties and parameters are to be meaningful, then they should be invariant to the addition of extra data points and results for E@4 and E@7 must be similar; from Table 1, this is clearly seen to be the case, but if different subsets of four points from E@7 are selected, then very large changes to the high-order parameters m_3, α_3, β_2, and β_3 can occur. We see that in general if only a minimal number of geometries are sampled, then their variation must be *small enough* so that the numerical derivatives are accurate yet *large enough* to produce significant changes in the energy of the molecule. In addition to the energy data, Bauschlicher[12] also reports dipole moments evaluated at two different field strengths and five different geometries, but the results are given to only four significant figures. It is possible to evaluate m_0, m_1, m_2, m_3, α_0, α_1, α_2, and α_3 from this data, and the results are shown in Table 1 labeled μ@5; the reduced

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TABLE 1: Molecular Properties (in au Except Where Noted) of CO As Observed, from AM1 Calculation, and As Extracted from Bauschlicher's *ab Initio* CASSCF Results:[12] E@4, Analyzing the Energy at Four Geometries (r = 2.0, 2.1, 2.15, and 2.2 au) and Four Field Strengths (F = 0, 0.005, 0.010, and 0.015 au); E@7, Analyzing the Energy at Seven Geometries (r = 1.8, 2.0, 2.1, 2.15, 2.2, 2.5, and 3.0 au) and Four Field Strengths (F = 0, 0.005, 0.010, and 0.015 au); μ@5, Analyzing the Dipole Moment at Five Geometries (r = 2.0, 2.1, 2.15, 2.2, and 2.3 au) and Two Field Strengths (F = 0 and 0.005 au)

		CASSCF			
property	observed	E@4	E@7	μ@5	AM1
$V_0 + 112$		−0.908 463	−0.908 460		
r_e	2.132[a]	2.1388	2.1389		2.213
ν_H/cm^{-1}	2170[a,b]	2187	2179		2268
ν_P/cm^{-1}		2128	2129		2248
ν_V/cm^{-1}	2143[a]	2125	2127		2248
a_1	0.6106[a,b]	0.6205	0.6158		0.6672
a_2	±0.5528[a,b]	−0.8287	−0.7560		−0.5128
m_0	0.048[a]	0.1192	0.1191	0.114	0.024
m_1	−0.644[c]	−0.6466	−0.6467	−0.632	1.183
m_2	0.021[c]	0.138	0.142	0.025	0.247
m_3		1.44	1.57	0	−0.281
α_0		14.7	14.7	14.8	15.0
α_1		13.4	13.4	10.7	14.0
α_2		−21.7	−22.6	8	2.3
α_3		−307	−330	0	−1.2
β_0		27.0	27.0	27[d]	−20
β_1		−294	−297	0	−37
β_2		2210	2270	0	−41
β_3		29 000	33 000	0	−930

[a] From ref 36. [b] Obtained from $\omega_e\chi_e$ ignoring higher terms. [c] From ref 37. [d] From energy analysis; ν_V, exact result from variational analysis.

precision in the data prevents values for m_3 and α_3 from being determined, however. As the Hellman–Feynman theorem applies to CASSCF wave functions, the results E@4 and E@7 obtained from differentiating the energy should agree with those of μ@5 obtained from the dipole moment. From Table 1, we see that good agreement is obtained for m_0 and m_1, which are also shown therein to be quite close to the corresponding experimental values, and for α_0 and perhaps α_1 also. Large differences are seen for m_2 and α_2, however, with only m_2 from μ@5 being consistent with the experimental results. We see that despite the high quality and extensiveness of Bauschlicher's data, deduced values of at least m_2, m_3, α_2, α_3, β_2, and β_3 are unreliable.

In Table 2 are shown electric field response properties evaluated from the E@4 and E@7 data sets, as well as results obtained using the E@7 results for r_e, a_1, a_2, and β_0 and the μ@5 results for all other properties; this is labelled E@7/μ@5

and corresponds to the best estimates possible from the available data. Results are shown obtained from eqs 15 and 25, which assume that ν(F) and μ(F) are harmonic, from the perturbation treatment of the anharmonicities, eqs 18 and 31–33, and from an essentially exact analysis obtained variationally from $V(F)$ and $M(F)$ using all available data (e.g., all expansion coefficients of up to r^6 in function E@7, not all of which are given in Table 1). Almost all properties do not change significantly from E@4 to E@7, indicating that they are stable with respect to the inclusion of additional geometries; the exception to this is $\Delta\alpha$, which arises as a near cancelation of two large terms in eq 15 and is hence quite sensitive. Note, however, that the perturbation theory corrections are more sensitive to the high-order parameters than are the harmonic theory expressions, and so greater variation is seen between E@4 and E@7 results at the perturbation and exact levels of treatment. Much larger variations are seen when the combined E@7/μ@5 results are used, however, with the $\Delta\alpha$ and B being particularly sensitive. Also shown in Table 2 are results obtained for E@4 and E@7 either using the analytical expressions or by numerically differentiating ν(F) and $M(F)$; they differ due to the finite-field strength used in the numerical procedure, but these differences are not significant at the field strengths used. The corrections due to the use of perturbation theory are seen to be quite small for $\Delta\mu$, being only on the order of 10%; they are somewhat larger for A but are found to be extremely important for $\Delta\alpha$ and B, being for B actually *larger* than the harmonic theory estimates. In all cases, the perturbation theory estimates are seen to be very good approximations to the exact solution, and this method appears to be quite useful.

The electroabsorption signal predicted by eq 6 using D_e, F_e, and H_e obtained from E@7/μ@5 using variational analysis was shown previously in Figure 1. Here, despite the small value of $\Delta\mu$ = −0.0101 au, the electroabsorption response remains dominated by the second-derivative term. The first-derivative term is much smaller than this and is dominated by $2A\Delta\mu/M$ rather than the polarizability change $\Delta\alpha$, while contributions from the constant term are almost indetectable in Figure 1.

The AM1 results shown in Tables 1 and 2 are in general quite remote from the observed and CASSCF results. At first thought, this may not be a general result, as CO is a special case with all but the highest quality methods failing to predict m_0 accurately. We see that it also predicts poor results for m_1 and m_2, however, although it does predict reasonable values of α_0 and α_1. While AM1 will be useful in interpreting qualitatively the difference in electric field response between say nonlinear optically active and inactive molecules, its usefulness for quantitative analysis as suggested by these CO results is

TABLE 2: Electric Field Response Properties Evaluated Using Various Methods: Numerical, Obtained Directly from $V(F)$ and $M(F)$ Evaluated at Finite-Field Strengths F; Analytical, True Derivatives Obtained from the Parameters Given in Table 1; Harmonic, Obtained from ν_H and M_H Using Eqs 15 and 25; Perturbation, Obtained Using First-Order Perturbation Theory, i.e., from ν_P and M_P Analysis Using Eqs 18 and 31–33; Exact, Obtained Using a Variational Analysis of the Energy and Dipole Functions (This Includes *All* Terms of Up to r^6; Note that for Conciseness, Coefficients of Terms $> r^3$ Are Not Shown in Table 1)

| electric field response | harmonic analytical | | perturbation theory calculation | | | | | | exact analytical | |
| | | | numerical | | analytical | | | | | |
	E@7	E@7/μ@5	E@4	E@7	E@4	E@7	E@7/μ@5	AM1	E@7	E@5/μ@7
M/γ	−0.6466	−0.632	−0.6366	−0.6366	−0.6366	−0.6366	−0.6414	1.191	−0.6281	−0.6368
$\Delta\mu$	−0.0085	−0.0092	−0.0094	−0.0076	−0.0094	−0.0083	−0.0100	0.0128	−0.0083	−0.0101
$\Delta\alpha/2$	−0.0008	0.1244	−0.0588	−0.0947	−0.0826	−0.1016	0.1376	0.0914	−0.1101	0.1391
A/M	−20.9	−17.4	−14.5	−14.0	−14.5	−14.0	−17.7	12.8	−13.6	−17.7
$2A\delta\mu/M$	0.353	0.319	0.274	0.213	0.271	0.232	0.355	0.328	0.226	0.358
F_e	0.353	0.443	0.215	0.118	−0.189	0.130	0.493	0.420	0.116	0.497
$2B/M$	394	54	−310	−340	−340	−400	60	−4	−430	59
A^2/M^2	437	301	210	200	210	200	310	160	190	310
D_e	831	355	−100	−140	−130	−200	370	164	−240	370

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restricted. More comprehensive investigations of this approach have been performed by Martí et al.[25]

5. Extension of Formalism

This formalism may easily be extended to other related situations including the treatment of overtone and combination bands and may also be applied to the vibrations of polyatomic molecules. Polyatomic molecules are treated via the introduction of normal coordinates. At the simplest level, one normal coordinate can be considered independent of all of the others, an approach which stems formally from the neglect of all electrical and mechanical anharmonicities which connect the mode of interest with the other modes. It is then a simple matter to determine the effective mass of the normal coordinate and an effective one-dimensional displacement r which includes appropriately weighted contributions from all of the atoms in the molecule. The above analysis for a diatomic molecule can then be immediately applied; we[35] have taken this approach and treated the CN stretch in HCN and CH_3CN.

The treatment of cases with anharmonic intermode coupling, as well the treatment of overtone or combination modes, proceeds first by determining, either analytically or numerically, expressions for the mode's vibration frequency and transition moment as a function of the applied field strength, i.e., by equations analogous to eqs 16 and 27. If the numerical approach is adopted, then *any* method capable of determining these quantities (e.g., harmonic theory, perturbation theory, Morse oscillator theory, variational theory, or even semiclassical dynamics) may be used; use of analytical functions would allow for the direct expression of the electroabsorption responses in terms of the fundamental molecular properties, however. As an example, we consider a $0 \rightarrow 2$ vibrational absorption band. Assuming that $V(F)$ is harmonic and that $M(F)$ originates only from $m_2(F)$ results in $\Delta\mu_{02}$ and $\Delta\alpha_{02}$ being precisely twice the values of $\Delta\mu_H$ and $\Delta\alpha_H$, which as before are the responses for the $0 \rightarrow 1$ transition, while

$$\gamma_{02} = \frac{2^{-1/2}h\nu_H}{a_1}, \quad \frac{M_{02,H}}{\gamma_{02}} = m_2$$

$$\frac{A_{02,H}}{\gamma_{02}} = \alpha_2 + \frac{6m_1m_3 + m_2^2}{4a_1} - \frac{3m_1m_2a_2}{8a_1^2}$$

$$\frac{B_{02,H}}{\gamma_{02}} = \frac{\beta_2}{2} + \frac{3(m_2\alpha_2 + 4m_1\alpha_3 + 2m_3\alpha_1)}{8a_1} +$$
$$\frac{(72m_1m_2m_3 - 12m_1\alpha_2a_2 + 5m_2^3 - 6m_2\alpha_1a_2)}{32a_1^2} -$$
$$\frac{27m_1a_2(2m_1m_3 + m_2^2)}{32a_1^3} + \frac{81m_1^2m_2a_2^2}{128a_1^4} \quad (35)$$

Perturbation theory corrections for the anharmonicities $a_2(F)$, etc., can be introduced, as before. For the transition frequency, this produces

$$\nu_{02,P}(F) = 2\nu_H(F)\left(1 - \frac{45a_2^2(F)}{32a_1^3(F)}h\nu_H(F)\right) \quad (36)$$

It is then possible to deduce equations for $\Delta\nu_{02,P}$ and $\Delta\alpha_{02,P}$ by analogy to eq 18, with changes restricted to the coefficients of the terms second order in $h\nu_H$; any differences observed between $\Delta\mu_{02,P}$ and $2\Delta\mu_P$, etc., could thus be attributed directly to the $a_2(F)$ corrections.

If the electroabsorption spectra of both a vibrational fundamental and its first overtone could be determined, a total of eight unique pieces of information would be available, these being ν, D_e, F_e, and H_e for each band. These are sensitive to 11 of the 16 parameters appearing in eq 8, and so it is still not possible, *in principle*, to determine unique values for the molecular properties. Progress could be made by assuming $\alpha_3 = \beta_2 = \beta_3 = 0$, producing eight equations in eight unknowns, a solvable problem. Whether or not such an analysis could be successfully completed *in practice* would depend on the quality of the experimental data available: the data must be of such quality as to resolve the high-order effects introduced by the anharmonicities $a_2(F)$, etc.

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