# 7

# Vibrational Stark Effects of Nitriles II. Physical Origins of Stark Effects from Experiment and Perturbation Models

Submitted to:

*J. Phys. Chem. A* . **2001**

> *The writers therefore concede that there may be* some *people whose states of mind are best described by coherent or incoherrent quantum mechanical superpositions.*
>
> — J.S. Bell
>
> *Speakable and unspeakable in quantum mechanics.*

## Abstract

Vibrational Stark effects, which are the effects of electric fields on vibrational spectra, were measured previously for the C-N stretch mode of several small nitriles, yielding difference dipole moments, difference polarizabilities, and transition polarizabilities for each species [Andrews, S.S.; Boxer, S.G. *J. Phys. Chem. A* **2000**, *104*, 11853]. This paper explains the physical origins of the observed Stark effects using two theoretical models and, in the process, computes several molecular parameters for each nitrile. A model with a single vibrational mode, developed with first and second order perturbation theory, is found to explain most of the experimental Stark effects. Since it cannot account for coupling between modes, which is ubiquitous and important for resonant vibrations and for combination mode absorption, another model is developed which considers multiple vibrational modes and three spatial degrees of freedom. It is found that difference dipole moments arise from a combination of mechanical anharmonicity and electronic perturbations of chemical bonds, where the two factors have about equal magnitudes for nitriles. Transition polarizabilities are dominated by the effects of electronic polarizability of the sample molecule, which alters the partial charges on atoms in an electric field. For overtone and combination transitions, Stark shifts are predicted to be the sums of the shifts of the component transitions. Stark effects of resonant transitions are predicted to be linear combinations of the effects for the basis states, plus a coupling term, explaining observed Stark effects of Fermi resonant bands.

## Introduction

Molecular vibrations are sensitive to the local electrostatic field, leading to field-induced changes in the infrared absorption spectrum, called the vibrational Stark effect. It has recently become relatively simple to measure these effects for a wide variety of condensed phase samples, where results include those for small nitriles dissolved in frozen 2-methyl-tetrahydrofuran[1] and carbon monoxide[2] and nitric oxide[3] bound to the heme iron in myoglobin. Knowledge of the sensitivity of a vibrational frequency to an electric field, the Stark tuning rate, calibrates the transition for use as an empirical probe of local electric fields[2]. Vibrational Stark effects can also be used to lend insight into the physics of molecular vibrations, which is the focus of this paper.

Several theoretical approaches are available for studying vibrational Stark effects. For very small molecules, *ab initio* methods have been used to calculate vibrational frequencies and intensities in varying electric fields[4-8]. While the best results are likely to be very accurate for vapor phase samples[9], they are difficult to extend to either larger molecules or to condensed phase samples; also they have not been in good agreement with experiment[1,10]. The semi-empirical AM1 method has been shown to yield results in good agreement with *ab initio* theory[11], which allows calculations for more complex systems but does not improve the accuracy. Starting from a less fundamental level, the classic "balls and springs" model can also be used, in which field effects are given in terms of chemical bond force constants and bond anharmonicities. This standard method[12-18] is used below and yields results that are easy to interpret and that are readily generalizable to large molecules and condensed phase samples. It also serves as a useful intermediate level of theory, connecting parameters that can be measured experimentally with those that can be calculated from first principles.

In a previous paper[1], a complete set of six Stark parameters was reported for acetonitrile and 4-chloro-benzonitrile, and three of the parameters were reported for a variety of other small nitriles. The parameters are the dominant terms of the difference dipole moment, $\Delta\boldsymbol{\mu}$, the difference polarizability, $\Delta\boldsymbol{\alpha}$, and the transition polarizability, **A**. These parameters, along with the zero field transition dipole moment, **M**, and the transition hyperpolarizability, **B**, are defined by expansions of the field-induced vibrational frequency shift and the vibrational transition dipole moment in terms of the electric field, **F**:

$$\Delta\tilde{\nu}(\mathbf{F}) = -\frac{1}{hc}\left[\Delta\boldsymbol{\mu}\cdot\mathbf{F} + \frac{1}{2}\mathbf{F}\cdot\Delta\boldsymbol{\alpha}\cdot\mathbf{F} + \cdots\right] \tag{1}$$

$$\mathbf{M}(\mathbf{F}) = \mathbf{M} + \mathbf{A}\cdot\mathbf{F} + \mathbf{F}\cdot\mathbf{B}\cdot\mathbf{F} + \cdots \tag{2}$$

**M** is used to define the molecular *z* axis. We showed that Δ□ values were largely explained by bond anharmonicity but several questions were left unanswered, such as (*i*) does this relationship stand up to a more thorough treatment, and what accounts for the remainder of Δ□, (*ii*) what are the physical origins of Δ□ and **A**, (*iii*) can **B** be estimated, and is it really appropriate to ignore it, (*iv*) how does coupling between modes affect Stark effects, (*v*) what would cause the vector and matrix Stark parameters to have components that are not parallel to the transition dipole moment, and (*vi*) what should be expected for Fermi resonant transitions? These questions are addressed below. The results are useful both for a more thorough understanding of the current experimental data and for the prediction of Stark effects of other vibrational transitions.

## Theory

A normal mode analysis of the vibrations of a molecule, including only lowest order terms, yields a set of vibrational frequencies and normal modes[19,20]. In this zeroth order approximation the modes may be considered as uncoupled quantum harmonic oscillators, each with uniformly spaced energy levels and transition dipoles that only allow transitions between adjacent states. However, interatomic forces are not perfectly harmonic, having both anharmonicity in the normal modes and anharmonic coupling between the modes. Among other things, anharmonicities lead to intramolecular energy redistribution[21], overtone and combination mode absorption[19], vibrational solvatochromism[22], and Fermi resonance[23]. They also contribute to vibrational Stark effects, as shown below and elsewhere[13,14,17,18].

Molecular vibrations are affected by a weak electrostatic field in two ways[15]: mechanical effects arise from electrical forces on atoms with partial electric charges, and electronic effects arise from the interaction of the field with the molecular electron cloud, which perturbs chemical bonds and alters the charge distribution in the molecule. These effects are made quantitative with the perturbation models given below.

***Single mode theory.*** For vibrations in which the normal mode is highly localized to just a pair of atoms, it is possible to ignore coupling to other vibrational modes, at least as a first approximation. In this model, the atoms are separated a distance *x* away from their equilibrium distance, the reduced mass is *m*, and the effective electric charge is $q$[24]. The harmonic vibrational frequency, □, is equal to $(\square/m)^{1/2}$, where □ is the quadratic force constant. To include both mechanical and electronic effects, the potential energy, $V$, is expanded in terms of the atomic separation and the component of the electric field that is parallel to the bond, $F$. The expansion can be expressed compactly with a matrix,

$$V = \begin{bmatrix} 1 & F & F^2 \end{bmatrix} \begin{bmatrix} 0 & \frac{\square}{2} & v_3 & v_4 \\ -q & v_2' & v_3' & 0 \\ v_1'' & v_2'' & 0 & 0 \end{bmatrix} \begin{bmatrix} x \\ x^2 \\ x^3 \\ x^4 \end{bmatrix} \tag{3}$$

The terms equal to □/2 and $-q$ are non-zero for a simple harmonic oscillator; for the perturbation parameters, the number of primes gives the power of the field dependence and the subscript gives the power of the $x$ dependence. The terms in the lower right corner, as well as higher order terms that are not shown, are set to 0 since they are expected to be negligible. In this standard expansion, the rows of the matrix give the potential function, the dipole function, and the polarizability function, respectively[16].

An alternate view of the double expansion is that the columns of the matrix give the field dependencies of the linear, quadratic, and anharmonic force constants. Using perturbation theory[25], we solved for the eigenstate energies and for the transition dipole moments between the states of an anharmonic oscillator. Results were carried out to first order in the quartic anharmonicity and to second order in the cubic anharmonicity. The reason for going to second order for some terms is that the second order cubic anharmonicity term is typically larger than the first order quartic anharmonicity term. This relationship can be seen in many ways: the first overtone transition energy is invariably less than twice the fundamental transition energy, despite $v_4$ being positive for most vibrations; by Taylor expansion of a Morse potential[26] it is found that $v_4 \approx v_3^2/\square$; and by substitution of experimental values in the equations below. Force constants and the effective charge were then expanded in terms of the field, using the molecular parameters defined in eq. 3. Using Mathematica software[27], the results were expressed as a series in $F$, yielding the Stark parameters defined by eqs. 1 and 2. As this model considers only a single normal mode, it predicts that all Stark effect parameters are parallel to the normal coordinate. Carried out to second order in $v_3$, $v_2'$, and $v_1''$ and first order in $v_4$, $v_3'$, and $v_2''$, the results for transitions between the ground and first excited states are:

$$\square E = \hbar\square\left(1 + \frac{3\hbar\square v_4}{\square^2} \square \frac{15\hbar\square v_3^2}{2\square^3}\right) \tag{4}$$

$$\square\square = \hbar\square\left(\square\frac{3qv_3}{\square^2} \square \frac{v_2\square}{\square}\right) \tag{5}$$

$$\square\square_{\parallel} = \hbar\square\left(\square\frac{12q^2v_4}{\square^3} \square \frac{6qv_3\square}{\square^2} \square \frac{2v_2\square\square}{\square} + \frac{18q^2v_3^2}{\square^4} + \frac{18qv_3v_2\square}{\square^3} + \frac{v_2\square^2}{\square^2} + \frac{6v_3v_1\square\square}{\square^2}\right) \tag{6}$$

$$M = q\sqrt{\frac{\hbar\square}{2\square}}\left(1 \square \frac{3\hbar\square v_4}{2\square^2} + \frac{103\hbar\square v_3^2}{12\square^3}\right) \tag{7}$$

$$A_{\parallel} = q\sqrt{\frac{\hbar\square}{2\square}}\left(\square\frac{3qv_3}{2\square^2} \square \frac{v_2\square}{2\square} \square \frac{v_1\square\square}{q}\right) \tag{8}$$

$$B_{\parallel} = q\sqrt{\frac{\hbar\square}{2\square}}\left(\square\frac{3q^2v_4}{\square^3} \square \frac{3qv_3\square}{2\square^2} \square \frac{v_2\square\square}{2\square} + \frac{189q^2v_3^2}{8\square^4} + \frac{27qv_3v_2\square}{4\square^3} + \frac{5v_2\square^2}{8\square^2} + \frac{3v_3v_1\square\square}{\square^2} + \frac{v_2\square v_1\square\square}{2q\square}\right) \tag{9}$$

It has been pointed out that while $\Delta\square$ is typically called the difference dipole moment, it is not actually the same as the difference in dipole moments between the ground and excited states[1,18]. This can be seen in eq. 5; the first term gives the effect of anharmonicity and leads to an actual difference in dipole moments, while the second term gives the field dependence of the harmonic force constant and does not affect the dipole moment of either the ground or the excited state. Using the language introduced above, the first term represents the mechanical contribution to the Stark effect while the second term represents the electronic contribution. Similarly, most terms in $\Delta\square_{\parallel}$ do not represent a physical difference in the polarizability of the two states. It would be more accurate to call $\Delta\square$ and $\Delta\square_{\parallel}$ the linear and quadratic Stark shift rates, but the traditional terminology is retained throughout this paper.

The terms in $\Delta\square$ and $A_{\parallel}$ are expected to be relatively large, since the perturbation parameters are the low-order terms of the Taylor expansion. In contrast, $\Delta\square_{\parallel}$, $B_{\parallel}$, and the perturbation components of $\Delta E$ and $M$ are expected to be much smaller, since all of their terms include either higher order terms of the Taylor expansion or products of low-order terms. While they are not shown above or considered elsewhere, it was found that the $F^3$ terms of eqs. 1 and 2, the difference hyperpolarizability and transition hyperpolarizability, respectively, are zero to consistent order in the perturbation parameters, justifying the fact that they are ignored.

Finally, it can be seen that $A_{\parallel}$ is closely related to $\Delta\square$,

$$A_{\parallel} = \frac{M\square\square}{2\square E} \square \frac{M v_{1}\square}{q} \tag{10}$$

The first term arises from perturbations of quantum eigenstates by the electric field, while the second term represents the field dependence of the effective charge due to electronic polarizability. Eq. 10 allows $v_1''$ to be calculated from experimental data with minimal assumptions for other parameters.

***Multi-mode theory.*** The single mode theory given above is expected to capture the most important aspects of vibrational Stark effects, but is incomplete since it ignores the coupling of different vibrational modes by anharmonicity. It also does not allow the interpretation of angle-dependent data, such as whether $\Delta\boldsymbol{\square}$ can be non-parallel to $\mathbf{M}$ and which elements of $\mathbf{A}$ are expected to be non-zero. Thus, the theory was re-written for an arbitrary set of $N$ vibrational modes. The derivation of the multi-mode equations is completely analogous to the single mode theory but is more complex, since most scalars are replaced with vectors, matrices, or higher-order tensors. Also, the coordinate system requires more attention to account for the multiple modes, for mixing of modes, and for the three spatial degrees of freedom. Due to the increased complexity, perturbation theory is carried out to lower order, with the result that cubic anharmonicity is considered to first order and quartic anharmonicity is ignored.

As a starting point, it is assumed that normal coordinates have been found for the system of interest in the absence of an electric field and that there is no degeneracy.

Following the notation of Wilson *et al.*[19], the mass-weighted normal coordinates are given by $Q_i$, while the linear force constants are $f_i$, the quadratic force constants are $f_{ij}$, and cubic force constants are $f_{ijk}$. These are fully symmetric tensors, meaning, for example, that $f_{ij}=f_{ji}$ and $f_{ijk}=f_{jki}=f_{kji}$. In the absence of an electric field, the force constants are in a normal coordinate system so $f_i$ and the off-diagonal terms of $f_{ij}$ are all zero, and the normal mode frequencies are $(f_{ii})^{1/2}$. The potential and kinetic energies are[28]

$$V = V_0 + f_i Q_i + \frac{1}{2} f_{ij} Q_i Q_j + \frac{1}{6} f_{ijk} Q_i Q_j Q_k \tag{11}$$

$$T = \frac{1}{2} \dot{Q}_i \dot{Q}_i \tag{12}$$

The permanent dipole moment of the molecule in the absence of a field is given by the three dimensional vector □. The change of the molecular dipole moment upon motion in the *i*'th normal mode, called a dipole gradient, turns out to be more useful here and is analogous to the effective charge considered in the single mode situation,

$$\Box_i \equiv \frac{\partial \Box}{\partial Q_i} \tag{13}$$

Upon applying an external electric field, all the force constants, including off-diagonal elements, change slightly due to electronic perturbations of the chemical bonds. Also, the linear force constants become non-zero because of the interaction of the electric field with the dipole gradients. Finally, the dipole gradients themselves are functions of the electric field, because electronic polarizability changes the partial charges on the atoms. These shift the equilibrium point of the system, which physically represents an adjustment of the equilibrium bond lengths to achieve the lowest energy configuration. The shifts are approximately

$$Q_i^\circ \equiv \Box \frac{f_i}{f_{ii}} \tag{14}$$

The potential energy, with the coordinates shifted by $Q_i^\circ$, is rewritten as

$$V = \left[V_0 + \frac{1}{2} f_i Q_i^\circ + \frac{1}{6} f_{ijk} Q_i^\circ Q_j^\circ Q_k^\circ\right] + \left[\frac{1}{2} f_{ijk} Q_j^\circ Q_k^\circ\right]\left(Q_i - Q_i^\circ\right) \\ + \frac{1}{2}\left(f_{ij} + f_{ijk} Q_k^\circ\right)\left(Q_i - Q_i^\circ\right)\left(Q_j - Q_j^\circ\right) + \frac{1}{6} f_{ijk}\left(Q_i - Q_i^\circ\right)\left(Q_j - Q_j^\circ\right)\left(Q_k - Q_k^\circ\right) \tag{15}$$

The quadratic term is no longer diagonal because of the coordinate shift and electronic perturbations. To first order, the off-diagonal elements do not contribute to the vibrational eigenvalues, $\lambda_i$, but do contribute to the eigenvectors, $a_{ij}$, unitless terms which rotate the normal modes to account for the electric field:

$$\lambda_i = f_{ii} + f_{iik} Q_k^\circ \tag{16}$$

$$a_{ij} = \begin{cases} 1 & i = j \\ -\dfrac{f_{ij} + f_{ijk} Q_k^\circ}{\lambda_i - \lambda_j} & i \neq j \end{cases} \tag{17}$$

A new set of notation is introduced for the shifted and rotated coordinate system. The variables $q_i$ are the mass-weighted normal coordinates in a field, $V_\mathrm{F}$ is the energy at the new origin, and the new force constants are $k_i$, $k_{ij}$, and $k_{ijk}$:

$$q_j \equiv \left(Q_i - Q_i^\circ\right) a_{ij} \tag{18}$$

$$V_\mathrm{F} \equiv V_0 + \frac{1}{2} f_i Q_i^\circ + \frac{1}{6} f_{ijk} Q_i^\circ Q_j^\circ Q_k^\circ \tag{19}$$

$$k_l \equiv \frac{1}{2} f_{ijk} Q_j^\circ Q_k^\circ a_{il} \tag{20}$$

$$k_{lm} \equiv \left(f_{ij} + f_{ijk} Q_k^\circ\right) a_{il} a_{jm} \tag{21}$$

$$k_{lmn} \equiv f_{ijk} a_{il} a_{jm} a_{kn} \tag{22}$$

The new definitions simplify the potential expression to resemble eq. 11,

$$V = V_\mathrm{F} + k_i q_i + \frac{1}{2} k_{ij} q_i q_j + \frac{1}{6} k_{ijk} q_i q_j q_k \tag{23}$$

Now, the linear force constants are proportional to $f_{ijk}$, allowing them to be treated as perturbation parameters, and the off-diagonal elements of the quadratic term are zero to first order.

Using perturbation theory to solve for the quantum energies of the system, it is found that neither the linear nor the cubic terms couple energy levels to first order. Using $n_i$ as the quantum number of the $i$'th mode, the quantum energy levels are just the sum of the energies for each separate normal mode,

$$E(\mathbf{F}) = V_{\mathrm{F}} + \hbar k_{ii}^{1/2}\left(n_i + \frac{1}{2}\right) \tag{24}$$

Transition dipoles are defined as the bracket $\mu_i(\mathbf{F})\langle\psi_{\mathrm{initial}}|Q_i|\psi_{\mathrm{final}}\rangle$ where $\mu_i(\mathbf{F})$ is a field dependent dipole gradient. For excitation by a single quantum level in the $i$'th normal mode, it is found again that the linear and cubic terms do not enter into the result to first order. However, the coordinate rotation serves to mix the dipole gradients,

$$\mathbf{M}_{n_i\to n_i+1}(\mathbf{F}) = a_{ij}\mu_j(\mathbf{F})\sqrt{\frac{\hbar(n_i+1)}{2k_{ii}^{1/2}}} \tag{25}$$

Excitation by two quantum levels, yielding either overtone absorption or combination mode absorption, is forbidden in the absence of anharmonicity, but is possible in the anharmonic system considered here. These transition dipoles are, respectively,

$$\mathbf{M}_{n_i\to n_i+2}(\mathbf{F}) = \frac{3\hbar a_{jk}\mu_k(\mathbf{F})k_{iij}}{4k_{ii}^{1/2}k_{jj}^{1/2}}\left(\frac{1}{2k_{ii}^{1/2}-k_{jj}^{1/2}} - \frac{1}{2k_{ii}^{1/2}+k_{jj}^{1/2}}\right)\sqrt{(n_i+1)(n_i+2)} \tag{26}$$

$$\mathbf{M}_{\substack{n_i\to n_i+1\\ n_j\to n_j+1}}(\mathbf{F}) = \frac{3\hbar a_{kl}\mu_l(\mathbf{F})k_{ijk}}{2k_{ii}^{1/4}k_{jj}^{1/4}k_{kk}^{1/2}}\left(\frac{1}{k_{ii}^{1/2}+k_{jj}^{1/2}-k_{kk}^{1/2}} - \frac{1}{k_{ii}^{1/2}+k_{jj}^{1/2}+k_{kk}^{1/2}}\right)\sqrt{(n_i+1)(n_j+1)} \tag{27}$$

Terms worth noting in eqs. 27 and 28 are the ones with frequency differences in the denominators; these give rise to strong intensity sharing between nearby transitions, which is one aspect of Fermi resonance. Since non-degenerate perturbation theory was used, the equations are progressively less accurate as the frequencies approach each other.

As in the single mode theory, the $f_i$, $f_{ij}$, and $f_{ijk}$ force constants are expanded in terms of the electric field,

$$V = \begin{bmatrix} 1 & \mathbf{F} & \mathbf{F}^2 \end{bmatrix} \begin{bmatrix} 0 & v_{ij} & v_{ijk} \\ -\mu_i & \mathbf{v}'_{ij} & 0 \\ -\mathbf{v}''_i & 0 & 0 \end{bmatrix} \begin{bmatrix} Q_i \\ Q_iQ_j \\ Q_iQ_jQ_k \end{bmatrix} \tag{28}$$

Since normal coordinates were assumed at the beginning, $v_{ij}$ is diagonal. The quadratic force constants, using mass-weighted coordinates, are $\kappa_i=2v_{ii}$ and the harmonic frequencies are $\omega_i=(\kappa_i)^{1/2}$. Substituting for $k_{ii}$ in eq. 24 yields the field dependent energy levels,

$$E = V_{\mathrm{F}} + \hbar\omega_i\left(1 + \frac{3v_{iij}\mu_j}{\kappa_i\kappa_j}\mathbf{F} + \frac{\mathbf{v}'_{ii}}{\kappa_i}\mathbf{F}\right)\left(n_i + \frac{1}{2}\right) \tag{29}$$

This can be simplified to give the Stark shift for the excitation of the $i$'th mode by one quantum level,

$$\Delta\mu_{n_i\to n_i+1} = -\hbar\omega_i\left(\frac{3v_{iij}\mu_j}{\kappa_i\kappa_j} + \frac{\mathbf{v}'_{ii}}{\kappa_i}\right) \tag{30}$$

To first order, there is no difference polarizability. Not surprisingly, the difference dipole, eq. 30, is similar to its single mode analog in eq. 5. As before, the first term represents the mechanical contribution, from the force of the field on charged atoms. Since the shift of equilibrium positions is typically not along a single normal coordinate, this term involves a sum over the normal modes. The second term, representing electronic interactions, is a vector since different field directions may have different effects on a quadratic force constant. Eq. 29 is a more general result and shows that Stark shifts for overtone transitions and combination transitions are the sums of the shifts for single transitions. For example, a first overtone absorption is expected to have twice the Stark shift of the corresponding fundamental absorption. This property was also found in the single mode analysis for both $\Delta\mu$ and $\Delta\alpha_{\|}$, to the higher-order theory used in the previous section.

Substitutions in eq. 25 yield the transition dipole and transition polarizability for excitation by one quantum level,

$$\mathbf{M}_{n_i \square\, n_i+1} = \square_i \sqrt{\frac{\hbar\square_i(n_i+1)}{2\square_i}} \tag{31}$$

$$\mathbf{A}_{n_i \square\, n_i+1} = \sqrt{\frac{\hbar\square_i(n_i+1)}{2\square_i}} \square \square \frac{\square_i \mathbf{v}_{ii}\square^{\mathrm{T}}}{2\square_i} \square \frac{3\square_i v_{iij}\square_j^{\mathrm{T}}}{2\square_i\square_j} \square \mathbf{v}_i\square + \square_{k\neq i} \square_k \frac{2\square_j \mathbf{v}_{ik}\square^{\mathrm{T}} + 6v_{ijk}\square_j^{\mathrm{T}}}{\square_j(\square_i \square \square_k)} \square \tag{32}$$

The $^{\mathrm{T}}$ symbols in eq. 32 denote vector transposes, with the result that all vector products are outer products and **A** is a matrix, as it should be. In the absence of a field (eq. 31), the transition dipole is parallel to the dipole gradient. The terms in the transition polarizability were seen in the single mode analog, eq. 8, with the exception of the final sum, which arises from the coordinate rotation and the corresponding mixing of dipole gradients. While it was seen that the Stark shifts for overtone and combination transitions are the sums of the shifts for single transitions, this relationship does not hold for the transition dipole relationships. In the absence of a field, these transition dipoles are

$$\mathbf{M}_{n_i \square\, n_i+2}(\mathbf{F}) = \frac{3\hbar\square_j k_{iij}}{4\square_i\square_j} \square \frac{1}{2\square_i \square \square_j} \square \frac{1}{2\square_i + \square_j} \square \sqrt{(n_i+1)(n_i+2)} \tag{33}$$

$$\mathbf{M}_{\substack{n_i \square\, n_i+1 \\ n_j \square\, n_j+1}}(\mathbf{F}) = \frac{3\hbar\square_k k_{ijk}}{2\square_i^{1/2}\square_j^{1/2}\square_k} \square \frac{1}{\square_i + \square_j \square \square_k} \square \frac{1}{\square_i + \square_j + \square_k} \square \sqrt{(n_i+1)(n_j+1)} \tag{34}$$

Transition polarizabilities for overtone and combination transitions are zero to first order.

***Resonant transitions.*** So far, it has been assumed that the energy levels are non-degenerate. However, even small molecules typically have enough vibrational modes or enough symmetry that degeneracy is common. For degenerate or nearly degenerate systems not in an electric field, the $f_{ij}$ matrix has two or more diagonal elements that are the same or nearly the same, and off-diagonal elements that are zero, as before. Also as before, a field perturbs both the diagonal and the off-diagonal elements.

For vibrational modes that are completely degenerate in the absence of a field, the normal modes may be expressed in any of several representations, making it possible to choose one in which the off-diagonal elements of $f_{ij}$ remain zero in an electric field. As a result, the elements of the rotation matrix given in eq. 17 that would otherwise become singular, due to multiple $\omega_i$ terms with the same value, are instead equal to zero. With this representation, it is found that the rest of the analysis in the previous section remains correct to first order. In particular, eqs. 30 and 32 give the Stark effects for degenerate modes, as well as for non-degenerate modes.

More generally, there is often coupling between the vibrational modes of a molecule, as in the degenerate system discussed above or in Fermi resonance. In these cases, the normal modes are linear combinations of basis state modes. It is sometimes desirable to calculate the Stark effects of the resonant modes from a knowledge of the Stark effects of the basis states, or *vice versa*, which can be demonstrated with a two level model system. The vibrationally excited basis states are taken to be $|A\rangle$ and $|B\rangle$; the superposition states are written in terms of a real mixing coefficient $c$,

$$|A'\rangle \equiv \sqrt{1-c^2}\,|A\rangle + c|B\rangle \qquad |B'\rangle \equiv -c|A\rangle + \sqrt{1-c^2}\,|B\rangle \tag{35}$$

The transition dipoles and transition polarizabilities of excitations to the superposition states are found with the transition dipole operator, resulting in the same linear combinations as for the quantum states. Using $M_\alpha$ and $\mathbf{A}_\alpha$ as the transition dipole and transition polarizability for excitation to excited state $|\alpha\rangle$,

$$M_{A'} = \sqrt{1-c^2}\,M_A + cM_B \qquad M_{B'} = -cM_A + \sqrt{1-c^2}\,M_B \tag{36}$$

$$\mathbf{A}_{A'} = \sqrt{1-c^2}\,\mathbf{A}_A + c\mathbf{A}_B \qquad \mathbf{A}_{B'} = -c\mathbf{A}_A + \sqrt{1-c^2}\,\mathbf{A}_B \tag{37}$$

The difference dipole moments are found by transforming the $f_{ij}$ and $f_{ijk}$ force constants from the $|A\rangle, |B\rangle$ basis to the $|A'\rangle, |B'\rangle$ basis, yielding the results

$$\Delta\boldsymbol{\mu}_{A'} = \left(1-c^2\right)\Delta\boldsymbol{\mu}_A + c^2\Delta\boldsymbol{\mu}_B - 2c\sqrt{1-c^2}\,\frac{\hbar}{\omega_{A'}}\left[\frac{-3v_{ABj}\boldsymbol{\mu}'_j}{\omega_j} + \mathbf{v}'_{AB}\right] \tag{38}$$

$$\Delta\mu_{B'} = \left(1-c^2\right)\Delta\mu_B + c^2\Delta\mu_A + 2c\sqrt{1-c^2}\,\frac{\hbar}{\omega_{B'}}\left(-\frac{3v_{ABj}\mu_j}{\omega_j} + \mathbf{v}'_{AB}\right) \qquad (39)$$

For example, if a molecule has an intense band with a large Stark effect near a weak band with no Stark effect, small amounts of resonance will transfer about the same fraction of absorption band area and $\Delta\mu$ from the strong band to the weak band, explaining a phenomenon seen for the Stark effect of $^{15}$NO bound to myoglobin[3].

## Results and Discussion

***Single mode analysis of acetonitrile and 4-chlorobenzonitrile.*** Our previously published Stark effect data for acetonitrile and 4-chloro-benzonitrile[1] were analyzed using the single mode theory, for which the results are presented in Table 1. The sign convention is that the positive $z$ axis points from the nitrile carbon to the nitrogen. Using electronegativity arguments or results from *ab initio* calculations[29], the carbon has a partial positive charge while the nitrogen has a partial negative charge. Several signs of the parameters in the single mode theory were assigned from this physical picture, yielding negative values for the transition dipole, the difference dipole, and the effective charge. While most of the necessary parameters for the theory were directly measured by experiment, several had to be taken from the literature or from calculation. Our previous paper[1] reported Stark effect results in terms of a local field correction factor, $f$; as in that paper we assume here that $f$ has a value of 1.1. The acetonitrile absorption frequency is known to be shifted below the frequency of just the nitrile stretch mode because of a Fermi resonant interaction, so the analysis uses a frequency which has been corrected for Fermi resonance[30]. The reduced masses of the nitrile stretch modes were calculated from a normal coordinate analysis of the molecules[29] using a 6-31G* *ab initio* calculation for acetonitrile and an AM1 semi-empirical calculation for 4-chloro-benzonitrile. The uncertainties of the corrected absorption frequency and the masses could not be estimated reliably but are expected to be much smaller than other errors, so they were ignored. Since the Stark effect cannot separate anharmonicity contributions (the $v_3$ term) from the field effect on the force constant ($v_2'$), we used published anharmonicity values from

**Table 1. Single Mode Results for Acetonitrile and 4-chloro-benzonitrile**

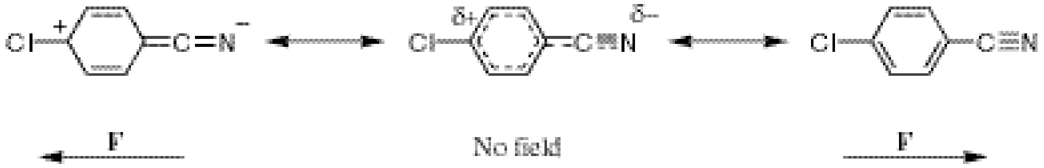
| Variable | Unit | Acetonitrile | | 4-Cl-benzonitrile | | Source |
|---|---|---|---|---|---|---|
| Parameters used by theory[a] | | | | | | |
| □ | $\text{cm}^{-1}$ | 2270.6 | | 2230.6 | | ref. 30; ref. 1 |
| $M$ | $10^{-3}$ aC Å | –1.94 | ±0.02 | –2.97 | ±0.03 | ref. 1 |
| $\Delta$□ | $10^{-3}$ aC Å | –0.965 | ±0.005 | –1.277 | ±0.012 | ref. 1 |
| $\Delta\square_{\parallel}$ | $10^{-3}$ aC $\text{Å}^2$ $\text{V}^{-1}$ | –8.1 | ±1.8 | –2.7 | ±2.9 | ref. 1 |
| $A_{\parallel}$ | $10^{-3}$ aC $\text{Å}^2$ $\text{V}^{-1}$ | 9.67 | ±0.76 | 13.34 | ±0.89 | ref. 1 |
| $m$ | $10^{-28}$ kg | 108.7 | | 109.0 | | note *b* |
| $v_3$ | aJ $\text{Å}^{-3}$ | –20.99 | ±0.23 | –20.99 | ±0.23 | ref. 29 |
| $v_4$ | aJ $\text{Å}^{-4}$ | 24.2 | ±1.2 | 24.2 | ±1.2 | ref. 29 |
| Calculated results[c] | | | | | | |
| □ | $\text{fs}^{-1}$ | 0.4323 | ±0.0003 | 0.4252 | ±0.0003 | eq. 4 |
| □ | aJ $\text{Å}^{-2}$ | 20.32 | ±0.02 | 19.70 | ±0.03 | $m\square^2$ |
| $q$ | aC | –0.0570 | ±0.0005 | –0.0863 | ±0.0009 | eq. 7 |
| $v_2'$ | aC $\text{Å}^{-1}$ | 0.254 | ±0.003 | 0.837 | ±0.006 | eq. 5 |
| $v_1''$ | aC Å $\text{V}^{-1}$ | –0.28 | ±0.02 | –0.39 | ±0.03 | eq. 10 |
| $\Delta$□ term 1[d] | $10^{-3}$ aC Å | –0.396 | ±0.005 | –0.627 | ±0.008 | eq. 5 |
| $A_{\parallel}$ term 3[e] | $10^{-3}$ aC $\text{Å}^2$ $\text{V}^{-1}$ | 9.65 | ±0.76 | 13.30 | ±0.89 | eq. 8 |
| $\Delta\square_{\parallel}$ term 7[f] | $10^{-3}$ aC $\text{Å}^2$ $\text{V}^{-1}$ | 3.9 | ±0.3 | 5.6 | ±0.4 | eq. 6 |
| $\Delta\square_{\parallel}$ terms 2,3[f] | $10^{-3}$ aC $\text{Å}^2$ $\text{V}^{-1}$ | –12.1 | ±1.8 | –8.6 | ±2.9 | eq. 6 |
| $B_{\parallel}/M$ | $\text{Å}^2$ $\text{V}^{-2}$ | 0.01 | ±0.01 | 0.11 | ±0.01 | eq. 9 |

*a*) Uncertainties for $M$, $\Delta$□, $\Delta\square_{\parallel}$, and $A_{\parallel}$ were calculated from the original data; uncertainties for $v_3$ and $v_4$ are those published in ref. 31. *b*) Masses are from normal mode calculations, as described in the text. *c*) Uncertainties were found as described in the text. *d*) Anharmonicity contribution to $\Delta$□ from eq. 5. *e*) Electronic polarizability contribution to $A_{\parallel}$ from eq. 8. *f*) Seventh term and sum of second and third terms of $\Delta\square_{\parallel}$ from eq. 6.

spectroscopic data of HCN [31]. These values are for HCN rather than the molecules analyzed here and they represent just the anharmonicity of the nitrile bond rather than the anharmonicity of the normal mode. However, they are expected to be good approximations of the correct values since nitrile bond force constants have been shown to be transferable among a large collection of benzonitriles[32,33] and the normal mode of interest is highly localized to the nitrile bond[34]. For acetonitrile, a more accurate analysis is discussed below and is in good agreement with these single mode results, whereas for 4-chloro-benzonitrile more accurate anharmonicities are not available. The uncertainties in the anharmonicities used in Table 1 are those published with the original values[31], but are lower limits for this application because of the these limitations.

The calculated uncertainties in Table 1 were found by carrying out computations several thousand times, using input parameters that were normally distributed about the best available values and with standard deviations that matched their uncertainties. The standard deviations of the results computed in this way are reported as their uncertainties. Table 1, and the other tables, use an especially convenient set of SI derived units. Using angstroms ($10^{-10}$ m), $10^{-28}$ kilograms, femtoseconds ($10^{-15}$ s), attocoulombs ($10^{-18}$ C), attojoules, and volts eliminates the need for unit conversion and leads to values for most fundamental constants and most molecular quantities between $10^{-3}$ and $10^{3}$. Conversion factors to common non-SI units include 1 Debye = 0.03336 aC Å, 1 Å$^3$ of polarizability volume = 0.01113 aC Å$^2$/V, 1 cm$^{-1}$ of energy = $1.9865\times10^{-5}$ aJ, 1 MV/cm = 0.01 V/Å, and 1 mdyne = 1 aJ/Å.

It is seen that anharmonicity accounts for about 40% of $\Delta\mu$ for acetonitrile and about 50% of $\Delta\mu$ for 4-chloro-benzonitrile. These are significant decreases from our earlier estimate of 70% for all nitriles[1], because the previous estimate only considered the slope of the correlation between $\Delta\mu$ and the effective charge and it also incorrectly adjusted for the local field correction (we divided by $f$ where we should have multiplied by $f$). The remainder of the $\Delta\mu$ term results from $v_2'$, which represents the effect of the electric field on the harmonic force constant. Its value implies a 0.01% and a 0.04% increase in the harmonic force constant upon application of a 1 MV/cm field parallel to the nitrile bond of acetonitrile and 4-chloro-benzonitrile, respectively. The larger value for 4-chloro-benzonitrile is expected; the nitrile bond is conjugated to an aromatic ring which has charge-separated resonance structures that are stabilized or destabilized by an electric field, depending on the field direction. The field influences the harmonic force constant since the resonant structures have different nitrile bond strengths:



While anharmonicity accounts for a significant fraction of $\Delta\square$, it accounts for much less than 1% of $A_{\parallel}$. Instead, $A_{\parallel}$ arises almost exclusively from $v_1''$, which represents the field dependence of the effective charge, due to electronic polarizability. In the same 1 MV/cm field, $v_1''$ yields about a 5% increase in the effective charge for both species (the effective charge becomes less negative). The resonance structures shown above for 4-chloro-benzonitrile are in qualitative agreement with this $v_1''$ behavior.

The physical origin for $\Delta\square_{\parallel}$ is less intuitive, but can considered in terms of the relative sizes of the seven terms in eq. 6. Using results from $\Delta\square$ and $A_{\parallel}$, the first, fourth, fifth, and sixth terms of $\Delta\square_{\parallel}$ contribute insignificantly to the measured result. Since the first and fourth terms are the only terms that include just mechanical effects, this origin of $\Delta\square_{\parallel}$ is ruled out, and electronic effects are seen to be important. The seventh term yields a significant positive contribution to $\Delta\square_{\parallel}$ which must be offset by the second and third terms since $\Delta\square_{\parallel}$ was determined to be negative. While the values of these final two terms cannot be separated with the available information, there is sufficient information to see that they significantly contradict results from *ab initio* theory. The sign of $v_2''$ has been consistently calculated to be negative for a wide variety of systems[4,8-10], implying that $v_3'$, the effect of the field on the cubic anharmonicity, must be negative and large enough that the second term offsets all other contributions to $\Delta\square_{\parallel}$. In contrast, calculations find that $v_3'$ is positive and small enough that the second term is negligible[10].

In the original analysis[1], the transition hyperpolarizability was assumed to be zero since it could not be measured independently. Using results that are largely independent of this assumption, $B$ was calculated with eq. 9 and found to change the transition dipole by 1 part in $10^6$ for acetonitrile and 1 part in $10^5$ for 4-chloro-benzonitrile, for molecules oriented parallel to a 1 MV/cm field. These values could be substituted back into the data analysis to further refine all the values, but the improvement would be well within the experimental uncertainty.

**Table 2: Potential Energy Matrix Components (Eq. 3) for Mononitriles**[a]

| compound | □ | $q$ | $v_2'$ | $v_1''$ | $\Delta$□$_{\|\|}$ terms 2,3[b] |
|---|---|---|---|---|---|
| | aJ Å$^{-2}$ | aC | aC Å$^{-1}$ | aC Å V$^{-1}$ | $10^{-3}$ aC Å$^2$ V$^{-1}$ |
| acetonitrile | 20.32[c] | –0.0570 | 0.245 | –0.19 | –13.6 |
| propionitrile | 19.85 | –0.0548 | 0.274 | –0.18 | –12.3 |
| butyronitrile | 19.90 | –0.0561 | 0.281 | –0.19 | –9.3 |
| valeronitrile | 19.78 | –0.0629 | 0.230 | –0.08 | 0.6 |
| hexanenitrile | 19.84 | –0.0554 | 0.276 | –0.09 | –8.3 |
| acetonitrile-d3 | 19.87 | –0.0611 | 0.249 | –0.21 | –18.5 |
| benzonitrile | 19.43 | –0.0892 | 0.284 | –0.35 | –14.0 |
| 2-Cl-benzonitrile | 19.73 | –0.0684 | 0.276 | –0.31 | –9.3 |
| 3-Cl-benzonitrile | 19.74 | –0.0699 | 0.290 | –0.29 | –7.4 |
| 4-Cl-benzonitrile | 19.70 | –0.0863 | 0.285 | –0.35 | –8.7 |
| 4-methoxybenzonitrile | 19.58 | –0.1201 | 0.412 | –0.17 | –2.9 |

*a*) Computed using Stark effect data from ref. 1, anharmonicity data from ref. 31, masses from AM1 calculation, and using the single mode theory (eqs. 4-9). *b*) Sum of second and third terms of $\Delta$□$_{\|\|}$ expression in eq. 6. *c*) Fermi resonance corrected frequency from ref. 30.

***Analysis of mononitriles.*** A single mode analysis of other mononitriles, results of which are shown in Table 2, yields the same overall picture as that found for acetonitrile and 4-chlorobenzonitrile. Figure 1 shows the correlation of $\Delta$□ with $q$ for all the nitriles, as well as the anharmonicity contribution of $\Delta$□. The best fit line has a slope of 0.012 Å and an intercept of $-2.9$□$10^{-4}$ aC Å, while the line representing the anharmonicity contribution has a slope of 0.0072 Å. As before, anharmonicity accounts for about half of the difference dipole.

***Multi-mode analysis of acetonitrile.*** A more thorough analysis of acetonitrile is presented in Table 3, using mass-weighted normal coordinates and published anharmonicities for the four normal modes with $A_1$ symmetry[35]. For the nitrile stretch mode (mode 2), the dipole gradient was calculated from our experimental results since this is more accurate for the environment in which the Stark data were taken, whereas the published dipole gradients[35] were used for the other modes. The experimental nitrile dipole gradient was 17% larger than the corresponding published value, indicating that

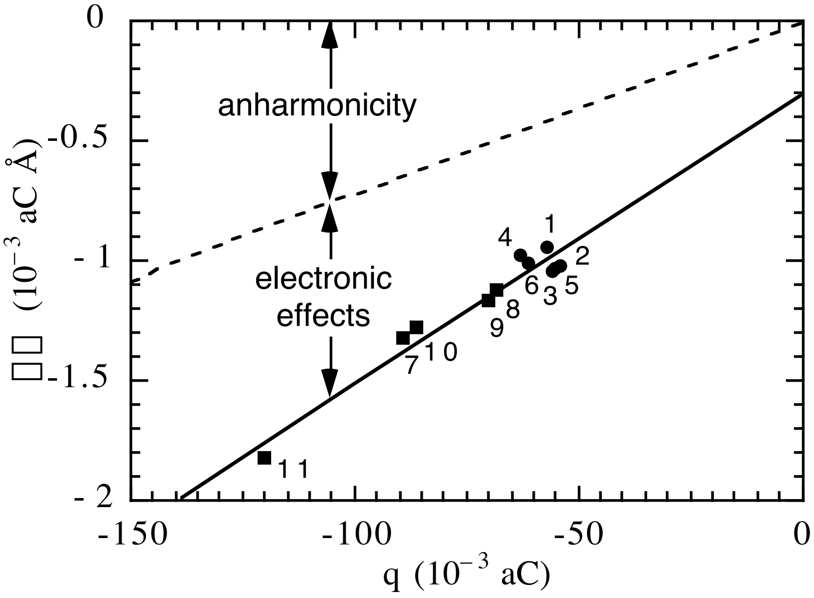


**Figure 1**. Correlation of difference dipoles with effective charges for mononitriles. Difference dipole data are from ref. 1 and assume a local field correction value of 1.1; effective charge data are calculated from the transition dipole data in ref. 1, using the single mode theory. Circles represent aliphatic compounds, numbered as: 1. acetonitrile, 2. propionitrile, 3. butyronitrile, 4. valeronitrile, 5. hexanenitrile, and 6. deuterated acetonitrile. Squares represent aromatic compounds, numbered as: 7. benzonitrile, 8. 2-Cl-benzonitrile, 9. 3-Cl-benzonitrile, 10. 4-Cl-benzonitrile, and 11. 4-methoxy-benzonitrile. The solid line is the best fit to the data, with a slope of 0.0122 Å and an intercept of –0.00029 aC Å. The dashed line, which has a slope of 0.0072 Å, represents the expected difference dipole if only anharmonicity contributed.

the other dipole gradients are likely to be reasonably accurate as well. In agreement with the single mode analysis above, it is found that 40% of $\Delta$□ arises from anharmonicity in the nitrile mode. Coupling to the other modes adds another 10% to the total anharmonicity contribution: 7% is from coupling to the symmetric C-H bend mode, 3% is from the C-C stretch mode, and 0.3% is from the symmetric C-H stretch mode.

**Table 3A: Multi-mode Analysis of Acetonitrile[a]**

| Parameter | Unit | Mode 1 | Mode 2 | Mode 3 | Mode 4 |
|---|---|---|---|---|---|
| | | CH stretch | CN stretch | CH bend | CC stretch |
| □[b] | $\mathrm{cm}^{-1}$ | 2292.7 | 2270.6 | 1390 | 915.4 |
| $\square_i$ | $\mathrm{fs}^{-1}$ | 0.5505 | 0.4277 | 0.2618 | 0.1724 |
| $\square_i$ | $10^{11}\ \mathrm{aC\ kg}^{-1/2}$ | –7.14[b] | –5.53[c] | –8.78[b] | –0.32[b] |
| $v_{ii2}$ | $10^{-3}\ \mathrm{aJ}^{-1/2}\ \mathrm{fs}^{-3}$ | –0.179 | –17.38 | –0.706 | –3.66 |
| Δ□ term 1[d] | $10^{-6}$ aC Å | –3.13 | –388.5 | –66.9 | –29.1 |

**Table 3B: Vector and Matrix Components of Acetonitrile Stark Effects**

| | | | | |
|---|---|---|---|---|
| Δ□ term 1[e] | $10^{-6}$ aC Å | $x$: 0 | $y$:0 | $z$:–487.6 |
| $\mathbf{v}_{22}'$ | Å $\mathrm{V}^{-1}\ \mathrm{fs}^{-2}$ | $x$: 0 | $y$: 0 | $z$: 0.00192 |
| $\mathbf{v}_1''$[f] | $10^{11}$ aC Å $\mathrm{V}^{-1}\ \mathrm{kg}^{-1/2}$ | $xx$: –10.7 | $yy$: –10.7 | $zz$: –27.5 |

*a*) Computed using Stark effect data from ref. 1. *b*) Ref. 35. *c*) Computed from data in ref. 1, as described in text. *d*) Anharmonicity contribution to Δ□ from coupling to each normal mode, using eq. 30. *e*) Total anharmonicity contribution to Δ□. *f*) Off-diagonal elements are zero, by symmetry.

The transition polarizability is not modified significantly from the single mode result. From eq. 32, three component cubic anharmonicities, $v_{ijk}$ where $i\neq j\neq k$, would be expected to add a small contribution to **A** from resonance with other fundamental frequencies (the observed Fermi resonance with a combination mode does not enter the result to first order). However, these anharmonicities are expected to be even smaller than the two component anharmonicities (which are typically much smaller than one component anharmonicities[35]) and are also unavailable in the literature. Ignoring this probably negligible correction yields the same result found before, that 99.8% of the transition polarizability arises from $\mathbf{v}_2''$. It was found previously that the transition polarizability has a significant perpendicular component[1], which was attributed to a non-conserved lineshape due to interaction with the Fermi resonant band 50 $\mathrm{cm}^{-1}$ to higher energy. While this is possible, it was surmised on the incorrect belief that **A** could not have perpendicular components for a rotationally symmetric system. Instead, it is probable that **A** does have perpendicular components, which arise from perpendicular components of $\mathbf{v}_i''$, a term which represents a change of molecular electronic polarizability with motion in the *i*'th normal mode. Like all molecules, acetonitrile is polarizable on all axes, so it is not surprising that the polarizablility perpendicular to the symmetry axis changes slightly with motion in the nitrile stretch mode. With this identification, nearly all the observed Stark effect results for acetonitrile are explained.

## Conclusions

Previous experimental results[1,3] inspired many questions on the physical origins of vibrational Stark effects, which are addressed in this paper. It is found that the dominant Stark effect, $\Delta$□, which represents the linear Stark tuning rate, arises from a combination of mechanical and electronic effects. Mechanical effects, due to anharmonicity of the vibrational coordinates, account for about 50% of the value of $\Delta$□ for the nitrile stretch mode of acetonitrile, of which 40% arises from anharmonicity in the nitrile mode and 10% arises from anharmonic coupling to other modes. The other half of $\Delta$□ arises from electronic perturbations of the chemical bonds, in which the quadratic force constant of the normal mode is affected by an electric field.

The transition polarizability, **A**, arises almost exclusively from the molecular electronic polarizability, in which partial charges on atoms are moved around by a field. For acetonitrile, only 0.2% of **A** arises from the other contribution, the perturbation of basis states by an electric field. It is predicted that **A** is sensitive to resonant transitions, an effect that has not been seen experimentally due to its relatively small size for the systems considered to date.

The quadratic Stark shift, $\Delta$□, is found to be a sum of terms that represent anharmonicity, electronic perturbations of force constants, and products of these factors. Since all the terms in $\Delta$□ are either high-order terms in a Taylor expansion (eq. 3) or are products of low-order terms, $\Delta$□ is expected to be small, which is in agreement with experiment, where $\Delta$□ was found to have a minimal effect on Stark spectra. $\Delta$□ depends to a significant extent on the product of the cubic anharmonicity and the electronic polarizability, $v_3 v_1''$. It also depends on two other terms involving electronic perturbations, whose effects cannot be separated but which are shown to contrast *ab initio* results.

The smallest Stark parameter considered is the transition hyperpolarizability, which was shown to contribute up to only 1 part in $10^5$ to the transition dipole in a 1 MV/cm field. Unless experimental methods improve dramatically, it is appropriate to neglect the transition hyperpolarizability.

Difference dipoles are found to be additive for multiple transitions. For degenerate transitions, Stark effects are identical to those for non-degenerate transitions if a normal mode representation is chosen in which an electric field does not couple the modes. More generally, Stark effects for resonant transitions are predicted to be linear combinations of the effects for the uncoupled states, plus a coupling term for difference dipoles. This explains behavior seen for resonant transitions, including Stark effects of NO bound to myoglobin[36].

The analytical theory presented explains nearly all of the vibrational Stark phenomena seen to date with parameters that are easy to interpret and that can be generalized to other systems. Most of the parameters determined here have not been measured in other ways and differ significantly from *ab initio* calculations. This demonstrates the unique capabilities of vibrational Stark spectroscopy, but also implies that the theory is largely untested. In particular, it makes several predictions which have not been verified, and for which experimental data are needed.

## Acknowledgements

We thank Prof. Noel Hush for helpful discussions. This work was supported in part by a grant from the NSF Chemistry Division.

**References**

(1) Andrews, S. S.; Boxer, S. G. *J. Phys. Chem. A* **2000**, *104*, 11853.

(2) Park, E. S.; Andrews, S. S.; Hu, R. B.; Boxer, S. G. *J. Phys. Chem. B* **1999**, *103*, 9813.

(3) Park, E. S.; Thomas, M. R.; Boxer, S. G. *J. Am. Chem. Soc.* **2000**, *122*, 12297.

(4) Hush, N. S.; Williams, M. L. *J. Molec. Spec.* **1974**, *50*, 349.

(5) Gready, J. E.; Bacskay, G. B.; Hush, N. S. *Chem. Phys.* **1978**, *31*, 467.

(6) Bauschlicher, C. W. J. *Chem. Phys. Lett.* **1985**, *118*, 307.

(7) Andrés, J. L.; Duran, M.; Lledós, A.; Bertrán, J. *Chem. Phys.* **1991**, *151*, 37.

(8) Hermansson, K.; Tepper, H. *Molec. Phys.* **1996**, *89*, 1291.

(9) Reimers, J. R.; Hush, N. S. *J. Phys. Chem. A* **1999**, *103*, 10580.

(10) Reimers, J. R.; Zeng, J.; Hush, N. S. *J. Phys. Chem.* **1996**, *100*, 1498.

(11) Martí, J.; Lledós, A.; Bertrán, J.; Duran, M. *J. Comp. Chem.* **1992**, *13*, 821.

(12) Gready, J. E.; Bacskay, G. B.; Hush, N. S. *Chem. Phys.* **1977**, *24*, 333.

(13) Lambert, D. K. *Phys. Rev. Lett.* **1983**, *51*, 2233.

(14) Lambert, D. K. *Phys. Rev. Lett.* **1983**, *50*, 2106.

(15) Bagus, P. S.; Nelin, C. J.; Muller, W.; Philpott, M. R.; Seki, H. *Phys. Rev. Lett.* **1987**, *58*, 559.

(16) Dykstra, C. E. *J. Chem. Ed.* **1988**, *65*, 198.

(17) Bishop, D. M. *J. Chem. Phys.* **1993**, *98*, 3179.

(18) Hush, N. S.; Reimers, J. R. *J. Phys. Chem.* **1995**, *99*, 15798.

(19) Wilson, E. B. J.; Decius, J. C.; Cross, P. C. *Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra.*; Dover Publications: New York, 1955.

(20) Goldstein, H. *Classical Mechanics*, Second ed.; Addison-Wesley: Reading, MA, 1980.

(21) Nesbitt, D. J.; Field, R. W. *J. Phys. Chem.* **1996**, *100*, 12735.

(22) Buckingham, A. D. *Trans. Faraday Soc.* **1960**, *56*, 753.

(23) Fermi, E. *Z. Physik* **1931**, *71*, 250.

(24) For a diatomic molecule, $m=m_1m_2/(m_1+m_2)$ and $q=m(q_1/m_1-q_2/m_2)$.

(25) Sakurai, J. J. *Modern Quantum Mechanics*, Revised ed.; Addison-Wesley: Reading, MA, 1995.

(26) Morse, P. M. *Phys. Rev.* **1929**, *34*, 57.

(27) Mathematica; 2.2.2 ed.; Wolfram Research, Inc.: Champaign, IL, 1994.

(28) This paper uses the convention that summation is implied for all repeated indicies.

(29) MacSpartan; Wavefunction, Inc.: Irvine, CA, 1997.

(30) Duncan, J. L.; McKean, D. C.; Tullini, F.; Nivellini, G. D.; Peña, J. P. *J. Mol. Spectrosc.* **1978**, *69*, 123.

(31) Strey, G.; Mills, I. M. *Molec. Phys.* **1973**, *26*, 129.

(32) Kumar, A. P.; Rao, G. R. *Sepctrochim. Acta Part A* **1997**, *53*, 2033.

(33) Kumar, A. P.; Rao, G. R. *Spectrochim. Acta Part A* **1997**, *53*, 2041.

(34) Kumar, A. P.; Rao, G. R. *Spectrochim. Acta Part A* **1997**, *53*, 2023.

(35) Westlund, P.-O.; Lynden-Bell, R. M. *Molec. Phys.* **1987**, *60*, 1189.

(36) Park, E. S.; Boxer, S. G. *In preparation* **2001**.