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

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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*, 11 853]. 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 perturbation theory, is found to explain most of the experimental Stark effects. Because 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. Stark effects of resonant transitions are found to be equal to linear combinations of the effects for the basis states, which explains an experimental observation. For overtone and combination transitions, Stark shifts are predicted to be the sums of the shifts of the component transitions. Absolute overtone intensities can be calculated from difference dipole results, which is experimentally verified. In summary, these theories largely explain the physical origins of observed vibrational Stark effects and can predict Stark effects for a wide variety of other systems.

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] This has been used to measure electric field changes within the myoglobin protein[2,3] upon protonation and mutation. Current work involves engineering Stark effect probes into proteins to serve as extremely small and versatile electric field sensors, with potential applications in electron-transfer research, studies of protein conformational changes, and studies of protein−ligand interactions. Challenges of this work include the identification and selection of highly sensitive probes and the interpretation of results. This paper addresses the underlying physics of vibrational Stark effects, which can be used to predict effects for a wide variety of probes in various environments, as well as to lend insight into the physics of molecular vibrations.

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] Although 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 semiempirical 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[12−19] 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; three of the parameters were reported for a variety of other small nitriles as well. 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**

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

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

M is used to define the molecular *z* axis. We showed that $\Delta\boldsymbol{\mu}$

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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 $\Delta\boldsymbol{\mu}$, (*ii*) what are the physical origins of $\Delta\boldsymbol{\alpha}$ 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 overtone, combination, and resonant transitions? These questions are addressed below.

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.[20,21] 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,[22] overtone and combination mode absorption,[20] vibrational solvatochromism,[23] and Fermi resonance.[24] They also contribute to vibrational Stark effects.[13−15,18,19]

Molecular vibrations are affected by a weak electrostatic field in two ways:[16] mechanical effects arise from electrical forces on atoms with partial electric charges; 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 a normal mode is highly localized to just a pair of atoms, it is possible to ignore its 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.[25] The harmonic vibrational frequency, ω, is equal to $(\kappa/m)^{1/2}$, where κ 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

$$V = V_0 + [1 \quad F \quad F^2]\begin{bmatrix} 0 & \frac{\kappa}{2} & v_3 & v_4 \\ -q & v_2' & v_3' & 0 \\ v_1'' & v_2'' & 0 & 0 \end{bmatrix}\begin{bmatrix} x \\ x^2 \\ x^3 \\ x^4 \end{bmatrix} \tag{3}$$

The terms equal to $\kappa/2$ and $-q$ are nonzero 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 because 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.[17] An alternate view of the double expansion, which is more relevant to the derivations below, is that the columns of the matrix give the field dependencies of the linear, quadratic, and anharmonic force constants. The only approximations in a Hamiltonian constructed with eq 3 as the nuclear potential function are the Born−Oppenheimer approximation and the neglect of higher order terms.

The notation used in eq 3 was chosen for clarity here and in the equations below and to emphasize the relationship between the expansion parameters and the potential energy. Other treatments use a plethora of different notations; ours corresponds respectively with that of Hush,[9,10,19] Lambert,[11,15] and Dykstra[17] as follows[26]

$$\kappa = 2a_1 = 2a_{20} = 2c \tag{4}$$

$$v_3 = a_2 = a_{30} = 0 \tag{5}$$

$$v_4 = 0 = a_{40} = 0 \tag{6}$$

$$q = m_1 = -a_{11} = \boldsymbol{\mu}_0 \tag{7}$$

$$v_2{}' = -m_2 = a_{21} = -g_1 \tag{8}$$

$$v_3{}' = -m_3 = a_{31} = 0 \tag{9}$$

$$2v_1{}'' = -\boldsymbol{\alpha}_1 = 2a_{12} = -\boldsymbol{\alpha}_0 \tag{10}$$

$$2v_2{}'' = -\boldsymbol{\alpha}_2 = 2a_{22} = -g_2 \tag{11}$$

Terms in eqs 4 to 11 shown as being equal to zero were not included in the original expansion. Several other sets of notation have been used as well.[4,8,12,16,27]

Using perturbation theory,[28] we solved for the eigenstate energies of an anharmonic oscillator; we also calculated transition dipoles between the eigenstates using the dipole operator

$$\hat{\mathrm{M}}(x,F) = -\frac{\partial V(x,F)}{\partial F} \tag{12}$$

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,[29] it is found that $v_4 \approx v_3{}^2/\kappa$; 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,[30] the results were expressed as a series in F, yielding the Stark parameters defined by eqs 1 and 2. Although the intermediate equations are not presented here, comparable ones are presented in the next section, where the theory is considered for multiple modes. 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 as follows[31]

$$\Delta E = \hbar\omega\left(1 + \frac{3\hbar\omega v_4}{\kappa^2} - \frac{15\hbar\omega v_3{}^2}{2\kappa^3}\right) \tag{13}$$

$$\Delta\boldsymbol{\mu} = \hbar\omega\left(-\frac{3qv_3}{\kappa^2} - \frac{v_2'}{\kappa}\right) \tag{14}$$

$$\Delta\boldsymbol{\alpha}_{||} = \hbar\omega\left(-\frac{12q^2\upsilon_4}{\kappa^3} - \frac{6q\upsilon_3'}{\kappa^2} - \frac{2\upsilon_2''}{\kappa} + \frac{18q^2\upsilon_3^{\,2}}{\kappa^4} + \frac{27q\upsilon_3\upsilon_2'}{\kappa^3} + \frac{\upsilon_2'^2}{\kappa^2} + \frac{6\upsilon_3\upsilon_1''}{\kappa^2}\right) \quad (15)$$

$$M = q\sqrt{\frac{\hbar\omega}{2\kappa}}\left(1 - \frac{3\hbar\omega\upsilon_4}{2\kappa^2} + \frac{103\hbar\omega\upsilon_3^{\,2}}{12\kappa^3} + \frac{5\hbar\omega\upsilon_3\upsilon_2'}{\kappa^2 q} - \frac{3\hbar\omega\upsilon_3'}{2\kappa q}\right) \quad (16)$$

$$A_{||} = q\sqrt{\frac{\hbar\omega}{2\kappa}}\left(-\frac{3q\upsilon_3}{2\kappa^2} - \frac{5\upsilon_2'}{2\kappa} - \frac{2\upsilon_1''}{q}\right) \quad (17)$$

$$B_{||} = q\sqrt{\frac{\hbar\omega}{2\kappa}}\left(-\frac{3q^2\upsilon_4}{\kappa^3} - \frac{9q\upsilon_3'}{2\kappa^2} - \frac{9\upsilon_2''}{2\kappa} + \frac{189q^2\upsilon_3^{\,2}}{8\kappa^4} + \frac{63q\upsilon_3\upsilon_2'}{4\kappa^3} + \frac{45\upsilon_2'^2}{8\kappa^2} + \frac{9\upsilon_3\upsilon_1''}{2\kappa^2} + \frac{3\upsilon_2'\,\upsilon_1''}{\kappa q}\right) \quad (18)$$

The difference in molecular dipole moments between the ground and the excited states, using the dipole operator given in eq 12, yields the same result as is given in eq 14. Thus, $\Delta\boldsymbol{\mu}$, which is called the difference dipole moment, is also equal to the difference in physical dipole moments between the ground and excited states, to the level of approximation used here. This identification breaks down at higher levels of theory.[19] Using the language introduced above, the first term in eq 14 represents the mechanical contribution to the dipole moment difference, whereas the second term represents the electronic contribution, both of which can be understood qualitatively. The first term arises from the dipole moment difference created by moving the effective charge, q, a small distance upon vibrational excitation; the distance is the change in the average bond length and is proportional to the cubic anharmonicity, υ_3. The second term is more subtle: υ_2' expresses the degree to which the harmonic force constant can be varied by an applied electric field, due to the influence of the field on the molecular electron cloud. Alternatively, in the absence of an external field, the total energy of an excited vibrational state can be minimized by shifting the electron cloud in a way that lowers the harmonic force constant. In the process, the shifted electron cloud yields a difference in molecular dipole moments, as given by the second term of eq 14.

The terms in $\Delta\boldsymbol{\mu}$ and $A_{||}$ are expected to be relatively large because the perturbation parameters are the low-order terms of the Taylor expansion. In contrast, $\Delta\boldsymbol{\alpha}_{||}$, $B_{||}$, and the perturbation components of ΔE and M are expected to be much smaller because all of their terms include either higher order terms of the Taylor expansion or products of low-order terms. Although 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.

All of the expansion parameters in eq 3 are treated as independent terms to allow maximal versatility, although several simplifications are possible. In particular, about half of the parameters are equal to zero for symmetric systems, such as the antisymmetric stretch mode of CO_2 or the vibration of N_2. For nonsymmetric systems, as well as some symmetric ones, the assumption of a Morse potential[29] can be used to relate some of the parameters to each other, such as υ_3 and υ_4. Finally, a more detailed consideration of the vibronic coupling is likely to yield υ_2' and other parameters in terms of electronic observables.

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 $\Delta\boldsymbol{\mu}$ can be nonparallel to $\mathbf{M}$ and which elements of $\mathbf{A}$ are expected to be nonzero. Thus, the theory was rewritten for an arbitrary set of vibrational modes. The derivation of the multimode equations is completely analogous to the single mode theory but is more complex because most scalars are replaced with vectors, matrixes, 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 vibrational modes have been found for the molecule of interest in the absence of an electric field and that there is no degeneracy. Following the notation of Wilson et al.,[20] the mass-weighted normal coordinates are given by Q_i, 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 the normal-mode frequencies are $(f_{ii})^{1/2}$, the f_i terms are zero, and the off-diagonal components of f_{ij} are all zero. However, in a field, all components of all force constants may change slightly, arising from mechanical and electronic effects. Leaving the field arbitrary at present, the potential and kinetic energies are[32]

$$V = V_0 + f_iQ_i + \frac{1}{2}f_{ij}Q_iQ_j + \frac{1}{6}f_{ijk}Q_iQ_jQ_k \quad (19)$$

$$T = \frac{1}{2}\dot{Q}_i\dot{Q}_i \quad (20)$$

An electric field shifts the equilibrium point of the system, which physically represents an adjustment of the equilibrium bond lengths to achieve the lowest energy configuration. An approximate value for the shift of the equilibrium of the i'th mode is given by Q_i°, defined by

$$f_{ij}Q_j^\circ \equiv -f_i \quad (21)$$

The potential energy, with the coordinates shifted by Q_i°, is rewritten as

$$V = \left(V_0 + \frac{1}{2}f_iQ_i^\circ + \frac{1}{6}f_{ijk}Q_i^\circ Q_j^\circ Q_k^\circ\right) + \left(\frac{1}{2}f_{ijk}Q_j^\circ Q_k^\circ\right)(Q_i - Q_i^\circ) + \frac{1}{2}(f_{ij} + f_{ijk}Q_k^\circ)(Q_i - Q_i^\circ)(Q_j - Q_j^\circ) + \frac{1}{6}f_{ijk}(Q_i - Q_i^\circ)(Q_j - Q_j^\circ)(Q_k - Q_k^\circ) \quad (22)$$

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, λ_i. However, they do contribute to the eigenvectors, a_{ij}, which are unitless terms that can be used to rotate the coordinate system to account for the electric field

$$\lambda_i = f_{ii} + f_{iik}Q_k^\circ \tag{23}$$

$$a_{ij} = \begin{cases} 1 & i = j \\ \dfrac{f_{ij} + f_{ijk}Q_k^\circ}{\lambda_j - \lambda_i} & i \neq j \end{cases} \tag{24}$$

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 an arbitrary field, V_F is the energy at the new origin, and the new force constants are k_i, k_{ij}, and k_{ijk}

$$q_j \equiv (Q_i - Q_i^\circ)a_{ij} \tag{25}$$

$$V_F \equiv V_0 + \frac{1}{2}f_iQ_i^\circ + \frac{1}{6}f_{ijk}Q_i^\circ Q_j^\circ Q_k^\circ \tag{26}$$

$$k_l \equiv \frac{1}{2}f_{ijk}Q_j^\circ Q_k^\circ a_{il} \tag{27}$$

$$k_{lm} \equiv (f_{ij} + f_{ijk}Q_k^\circ)a_{il}a_{jm} \tag{28}$$

$$k_{lmn} \equiv f_{ijk}a_{il}a_{jm}a_{kn} \tag{29}$$

The new definitions simplify the potential expression to resemble eq 19

$$V = V_F + k_iq_i + \frac{1}{2}k_{ij}q_iq_j + \frac{1}{6}k_{ijk}q_iq_jq_k \tag{30}$$

The reason for shifting and rotating the coordinates is that the new linear force constants, k_i, are proportional to the cubic anharmonicity, allowing them to be treated as perturbation parameters. Also, 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 of eq 30 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 mode

$$E(\mathbf{F}) = V_F + \hbar k_{ii}^{1/2}\left(n_i + \frac{1}{2}\right) \tag{31}$$

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

$$V = V_0 + [1 \;\; \mathbf{F} \;\; \mathbf{F}^2]\begin{bmatrix} 0 & \upsilon_{ij} & \upsilon_{ijk} \\ -\boldsymbol{\mu}_i & \mathbf{v}'_{ij} & 0 \\ \mathbf{v}''_i & 0 & 0 \end{bmatrix}\begin{bmatrix} Q_i \\ Q_iQ_j \\ Q_iQ_jQ_k \end{bmatrix} \tag{32}$$

$\boldsymbol{\mu}_i$ is called a dipole gradient because it is the change of the dipole moment upon motion in the i'th mode, and is analogous to the effective charge considered in the single mode theory. Because normal coordinates were assumed at the beginning, υ_{ij} is diagonal and is more conveniently represented with κ_i, where $\kappa_i = 2\upsilon_{ii}$; the harmonic frequencies are $\omega_i = (\kappa_i)^{1/2}$. Substituting for k_{ii} in eq 31 yields the field dependent energy levels

$$E = V_F + \hbar\omega_i\left(1 + \frac{3\upsilon_{iij}\boldsymbol{\mu}_j}{\kappa_i\kappa_j}\mathbf{F} + \frac{\mathbf{v}'_{ii}}{\kappa_i}\mathbf{F}\right)\left(n_i + \frac{1}{2}\right) \tag{33}$$

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

$$\Delta\boldsymbol{\mu}_{n_i-1\rightarrow n_i} = -\hbar\omega_i\left(\frac{3\upsilon_{iij}\boldsymbol{\mu}_j}{\kappa_i\kappa_j} + \frac{\mathbf{v}'_{ii}}{\kappa_i}\right) \tag{34}$$

To first order, there is no difference polarizability. Not surprisingly, the difference dipole given in eq 34 is similar to its single mode analogue in eq 14. As before, the first term represents the mechanical contribution, from the force of the field on charged atoms combined with anharmonicity in the potential energy surface. Because the shift of equilibrium positions (the distortion of the molecule) is typically not along a single normal coordinate, this term involves a sum over the vibrational modes. The second term, representing electronic interactions, is the dipole moment vector associated with electron cloud rearrangements that occur upon vibrational excitation. Although it is generally expected that the vectors in eq 34 that are parallel to $\boldsymbol{\mu}_i$ will dominate the expression, yielding $\Delta\boldsymbol{\mu}$ parallel to $\mathbf{M}$, it can be seen how other terms may contribute as well. Equation 33 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 $\Delta\boldsymbol{\mu}$ and $\Delta\boldsymbol{\alpha}_{||}$, to the higher-order theory used in the previous section.

Multi-mode transition dipoles are computed, as before, with the dipole operator

$$\begin{aligned} \hat{\mathbf{M}}(Q,\mathbf{F}) &= -\nabla_{\mathbf{F}}V(Q,\mathbf{F}) \\ &= \boldsymbol{\mu}_iQ_i - 2\mathbf{v}''_i\mathbf{F}Q_i - \mathbf{v}'_{ij}Q_iQ_j \end{aligned} \tag{35}$$

The operator is re-expressed in the shifted and rotated coordinate system so the position factors, q_i, can be replaced by raising and lowering operators.[28] First-order perturbations to the quantum states, using the k_i and k_{ijk} terms as the perturbations, are also found. Combining the dipole operator with the perturbed initial and final states yields equations for field dependent transition dipoles, which are separated into terms for **M**, **A**, and **B**, although **B** is found to be zero to first order. For an excitation of one level in the i'th mode

$$\mathbf{M}_{n_i-1\rightarrow n_i} = \boldsymbol{\mu}_i\sqrt{\frac{\hbar\omega_in_i}{2\kappa_i}} \tag{36}$$

$$\mathbf{A}_{n_i-1\rightarrow n_i} = \sqrt{\frac{\hbar\omega_in_i}{2\kappa_i}}\left[-\frac{3\boldsymbol{\mu}_i\upsilon_{iij}\boldsymbol{\mu}_j^{\mathrm{T}}}{2\kappa_i\kappa_j} - \frac{\boldsymbol{\mu}_i\mathbf{v}'^{\mathrm{T}}_{ii}}{2\kappa_i} - 2\mathbf{v}''_i - \frac{2\mathbf{v}''_{ij}\boldsymbol{\mu}_j^{\mathrm{T}}}{\kappa_j} + \sum_{k\neq i}\boldsymbol{\mu}_k\frac{2\kappa_j\mathbf{v}'^{\mathrm{T}}_{ik} + 6\upsilon_{ijk}\boldsymbol{\mu}_j^{\mathrm{T}}}{\kappa_j(\kappa_i - \kappa_k)}\right] \tag{37}$$

The $^{\mathrm{T}}$ symbols in eq 37 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 36), the transition dipole is parallel to the dipole gradient. In the transition polarizability equation, most terms were found in the single mode analogue, eq 17, whereas the others arise from the coordinate rotation and the corresponding mixing of normal modes.

Excitation by two quantum levels, yielding either overtone absorption or combination mode absorption, is forbidden for a simple harmonic oscillator but is possible in real molecules and for the systems considered here. These transition dipoles are calculated as well

$$\mathbf{M}_{n_i-2\rightarrow n_i} = -\frac{\hbar\sqrt{n_i(n_i-1)}}{2\omega_i}\left[\mathbf{v}'_{ii} + \frac{3\boldsymbol{\mu}_j v_{iij}}{2\omega_j}\left(\frac{1}{2\omega_i+\omega_j} - \frac{1}{2\omega_i-\omega_j}\right)\right] \quad (38)$$

$$\mathbf{M}_{\substack{n_i-1\rightarrow n_i\\ n_j-1\rightarrow n_j}} = -\frac{\hbar\sqrt{n_in_j}}{2\sqrt{\omega_i\omega_j}}\left[\mathbf{v}'_{ij} + \frac{3\boldsymbol{\mu}_k v_{ijk}}{\omega_k}\left(\frac{1}{\omega_i+\omega_j+\omega_k} - \frac{1}{\omega_i+\omega_j-\omega_k}\right)\right] \quad (39)$$

Transition polarizabilities for overtone and combination transitions are zero to first order. Because the molecular parameters in eq 38 are the same as those in the expression for $\Delta\boldsymbol{\mu}$ (eq 34), knowledge of one quantity can aid in the prediction of the other. A couple terms worth noting in eqs 38 and 39 are ones with frequency differences in the denominators, which give rise to strong intensity sharing between nearby transitions, an aspect of Fermi resonance. Because nondegenerate perturbation theory was used, the equations are progressively less accurate as frequencies approach each other.

Resonant Transitions. So far, it has been assumed that the energy levels are nondegenerate. 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 (e.g., the bending vibrations of CO_2), 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 eigenvector elements given in eq 24 that would become singular due to multiple λ_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. In particular, eqs 34 and 37 give the Stark effects for degenerate modes, as well as for nondegenerate modes.

More generally, it is often desirable to consider a normal mode vibration as a linear combination of basis state vibrations. Examples include the degenerate systems presented above and situations in which Stark effects are known for an isolated probe which is then attached to a protein, where it couples with protein vibrations. In these cases, it is useful to be able to calculate the Stark effects of the resonant modes from a knowledge of the Stark effects of the basis states. This is demonstrated here with a two level model system. The vibrationally excited basis states are taken to be $|A\rangle$ and $|B\rangle$ which mix to form superposition states $|A'\rangle$ and $|B'\rangle$, with a mixing coefficient c

$$|A'\rangle \equiv \sqrt{1-c^2}|A\rangle + c|B\rangle \; |B'\rangle \equiv -c|A\rangle + \sqrt{1-c^2}|B\rangle \quad (40)$$

The transition dipoles and transition polarizabilities of excitations to the superposition states are found with a general transition dipole operator (from eq 2), resulting in expressions that include the same linear combinations as in the quantum states. Using M_Ψ and $\mathbf{A}_\Psi$ as the transition dipole and transition polarizability for excitation to excited state $|\Psi\rangle$

$$M_{A'} = \sqrt{1-c^2}M_A + cM_B \; M_{B'} = -cM_A + \sqrt{1-c^2}M_B \quad (41)$$

$$\mathbf{A}_{A'} = \sqrt{1-c^2}\mathbf{A}_A + c\mathbf{A}_B \; \mathbf{A}_{B'} = -c\mathbf{A}_A + \sqrt{1-c^2}\mathbf{A}_B \quad (42)$$

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

$$\Delta\boldsymbol{\mu}_{A'} = (1-c^2)\Delta\boldsymbol{\mu}_A + c^2\Delta\boldsymbol{\mu}_B - 2c\sqrt{1-c^2}\frac{\hbar}{\omega_{A'}}\left(\frac{3v_{ABj}\boldsymbol{\mu}_j}{\kappa_j} + \mathbf{v}'_{AB}\right) \quad (43)$$

$$\Delta\boldsymbol{\mu}_{B'} = (1-c^2)\Delta\boldsymbol{\mu}_B + c^2\Delta\boldsymbol{\mu}_A + 2c\sqrt{1-c^2}\frac{\hbar}{\omega_{B'}}\left(\frac{3v_{ABj}\boldsymbol{\mu}_j}{\kappa_j} + \mathbf{v}'_{AB}\right) \quad (44)$$

For example, if a molecule has an intense absorption band with a large Stark effect near a weak band with no Stark effect, small amounts of quadratic coupling will transfer about the same fraction of absorption band area and $\Delta\boldsymbol{\mu}$ value from the strong band to the weak band (it is assumed that the final term in eqs 43 and 44 are smaller than the others despite the larger coupling factor, which is expected because both v_{ABj} and $\mathbf{v}_{AB}'$ are off-diagonal terms and thus typically very small). This example explains the Stark effect spectrum measured for ^{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. These data, which are the best experimental data currently available, include both magnitudes and available orientational information for $\Delta\boldsymbol{\mu}$,$\Delta\boldsymbol{\alpha}$, and $\mathbf{A}$. Only the components of the parameters that are parallel to the transition dipole are considered in this section, leaving some of the other components for the multi-mode analysis, below. 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,[33] the carbon has a partial positive charge, whereas 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.

Although 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 by a Fermi resonant interaction, so the analysis uses a frequency which has been corrected for Fermi resonance.[34] The reduced masses of the nitrile stretch modes were calculated from a normal coordinate analysis of the molecules[33] using a 6-31G* ab initio calculation for acetonitrile and an AM1 semiempirical 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. Because 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 spectroscopic data of HCN.[35] These values are for

TABLE 1: Single Mode Results for Acetonitrile and 4-Chloro-benzonitrile

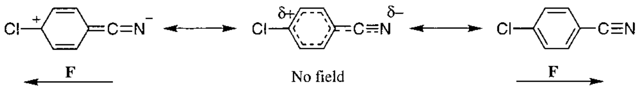
variable	unit	Acetonitrile		4-Cl-benzonitrile		source
		parameters used by theory[a]				
$\bar{\nu}$	cm^{-1}	2270.6		2230.6		ref 34; ref 1
M	10^{-3} aC Å	−1.94	±0.02	−2.97	±0.03	ref 1
$\Delta\boldsymbol{\mu}$	10^{-3} aC Å	−0.965	±0.005	−1.277	±0.012	ref 1
$\Delta\boldsymbol{\alpha}_{\|}$	10^{-3} aC Å^2 V^{-1}	−8.1	±1.8	−2.7	±2.9	ref 1
$A_{\|}$	10^{-3} aC Å^2 V^{-1}	9.67	±0.76	13.34	±0.89	ref 1
m	10^{-28} kg	108.7		109.0		note *b*
υ_3	aJ Å^{-3}	−20.99	±0.23	−20.99	±0.23	ref 35
υ_4	aJ Å^{-4}	24.2	±1.2	24.2	±1.2	ref 35
		calculated results[c]				
ω	fs^{-1}	0.4323	±0.0003	0.4252	±0.0003	eq 13
κ	aJ Å^{-2}	20.32	±0.02	19.70	±0.03	$m\omega^2$
q	aC	−0.0541	±0.0006	−0.0829	±0.0009	eq 16; note *d*
υ_2'	aC Å^{-1}	0.262	±0.003	0.296	±0.007	eq 14
υ_1''	aC Å V^{-1}	−0.143	±0.011	−0.196	±0.013	eq 17
$\Delta\boldsymbol{\mu}$ term 1[e]	10^{-3} aC Å	−0.376	±0.005	−0.603	±0.009	eq 14
$A_{\|}$ term 3[f]	10^{-3} aC Å^2 V^{-1}	9.61	±0.76	13.22	±0.89	eq 17
$\Delta\boldsymbol{\alpha}_{\|}$ term 7[g]	10^{-3} aC Å^2 V^{-1}	1.99	±0.16	2.85	±0.19	eq 15
$\Delta\boldsymbol{\alpha}_{\|}$ terms 2,3[h]	10^{-3} aC Å^2 V^{-1}	−10.1	±1.8	−5.6	±2.9	eq 15
$B_{\|}/M$	Å^2 V^{-2}	−0.18	±0.06	−0.03	±0.09	eq 18

[a] Uncertainties for M, $\Delta\boldsymbol{\mu}$, $\Delta\boldsymbol{\alpha}_{\|}$, and $A_{\|}$ were calculated from the original data; uncertainties for υ_3 and υ_4 are those published in ref 35. [b] Masses are from normal mode calculations, as described in the text. [c] Uncertainties were found as described in the text. [d] This calculation requires υ_2' and υ_3', as minor corrections. υ_3' was taken from ref 10. Table 1 was first calculated with an approximate value for υ_2', allowing υ_2' to be calculated from eq 14; the table was then iteratively improved until a consistent value of υ_2' was achieved. [e] Anharmonicity contribution to $\Delta\boldsymbol{\mu}$ from eq 14. [f] Electronic polarizability contribution to $A_{\|}$ from eq 17. [g] Seventh term of $\Delta\boldsymbol{\alpha}_{\|}$ from eq 15. [h] Sum of second and third terms of $\Delta\boldsymbol{\alpha}_{\|}$ from eq 15.

HCN rather than the molecules analyzed here and they represent just the anharmonicity of the nitrile bond rather then the anharmonicity of the normal mode. However, they are expected to be good approximations of the correct values because nitrile bond force constants have been shown to be transferable among a large collection of benzonitriles[36,37] and the normal mode of interest is highly localized to the nitrile bond.[38] For acetonitrile, more anharmonicity data is available, yielding results in good agreement with these, as shown below, 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,[35] but are lower limits for this application because of the these limitations. Finally, the sign of υ_2' was chosen to be in agreement with theoretical calculations[10] and with the resonance structure model presented below.

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 D = 0.033 36 aC Å, 1 Å^3 of polarizability volume = 0.011 13 aC Å^2/V, 1 cm^{-1} of energy = 1.9865 × 10^{-5} aJ, 1 MV/cm = 0.01 V/Å, and 1 mdyne = 1 aJ/Å.

It is seen that anharmonicity accounts for about 39% of $\Delta\boldsymbol{\mu}$ for acetonitrile and about 47% of $\Delta\boldsymbol{\mu}$ 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 $\Delta\boldsymbol{\mu}$ 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 $\Delta\boldsymbol{\mu}$ term arises from υ_2', which represents the effect of the electric field on the harmonic force constant. Its value implies a 0.026% and a 0.030% increase in the harmonic force constant upon application of a 1 MV/cm field parallel to the nitrile bond for acetonitrile and 4-chloro-benzonitrile, respectively. The origin of this effect is most easily understood by considering charge-separated resonance structures of 4-chloro-benzonitrile, which are stabilized or destabilized in an electric field. The field influences the harmonic force constant because it changes the relative importance of the different resonant structures, which have different nitrile bond strengths.



Although $\Delta\boldsymbol{\mu}$ arises from a combination of anharmonicity and the effect of the field on the harmonic force constant, these account for less than 1% of $A_{\|}$. Instead, $A_{\|}$ arises almost exclusively from υ_1'', which represents the field dependence of the effective charge, due to electronic polarizability. In the same 1 MV/cm field, υ_1'' yields about a 2.5% increase in the effective charge for both molecules (the effective charge becomes less negative). Returning to qualitative arguments with the 4-chloro-benzonitrile resonance structures shown above, this υ_1'' calculation is in agreement with the expected charge distribution on the nitrile group.

The physical origin for $\Delta\boldsymbol{\alpha}_{\|}$ is less intuitive, but can be considered in terms of the relative sizes of the seven terms in eq 15. Using results from $\Delta\boldsymbol{\mu}$ and $A_{\|}$, the first, fourth, fifth, and sixth terms of $\Delta\boldsymbol{\alpha}_{\|}$ each contribute insignificantly to the measured result, leading to a total contribution of less than 3%.[39] Because the first and fourth terms are the only terms that include just mechanical effects, this origin of $\Delta\boldsymbol{\alpha}_{\|}$ is ruled out, leaving electronic effects as the dominant source. The seventh term ($\propto\upsilon_3\upsilon_1''$) yields a significant positive contribution to $\Delta\boldsymbol{\alpha}_{\|}$ which must be offset by the second and third terms ($\propto -\upsilon_3'$ and $\propto -\upsilon_2''$, respectively) because $\Delta\boldsymbol{\alpha}_{\|}$ was determined to be negative; the sum of the second and third terms is calculated to be about -10^{-2} aC Å^2 V^{-1}. Although the values of these final two terms cannot be separated with the available information, it can be seen that they significantly contradict results from ab initio theory. Calculations[10] find that υ_2'' is about −0.023 aJ V^{-2} and υ_3' is about 0.032 aJ Å^{-2} V^{-1}, leading to a combined contribution to $\Delta\boldsymbol{\alpha}_{\|}$ of only 10^{-6} aC Å^2 V^{-1}. It is not presently known whether this discrepancy arises from approximations made in the analysis of experimental data to yield $\Delta\boldsymbol{\alpha}_{\|}$,[1,40] or from those made in the ab initio calculations.

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 18 and found to change the transition dipole by up to about 1 part in 10^5, for molecules oriented parallel to a 1 MV/cm field. These values could be

TABLE 2: Potential Energy Matrix Components (eq 3) for Mononitriles[a]

compound	κ aJ Å^{-2}	q [b] aC	v_2' aC Å^{-1}	v_1'' aC Å V^{-1}	$\Delta\alpha_{\|\|}$ terms 2,3[c] 10^{-3} aC Å^2 V^{-1}
acetonitrile	20.32[d]	−0.0543	0.254	−0.096	−12.3
propionitrile	19.85	−0.0517	0.284	−0.093	−11.0
butyronitrile	19.90	−0.0529	0.291	−0.095	−7.9
valeronitrile	19.78	−0.0602	0.239	−0.041	1.2
hexanenitrile	19.84	−0.0522	0.286	−0.045	−7.7
acetonitrile-d3	19.87	−0.0582	0.258	−0.107	−17.0
benzonitrile	19.43	−0.0858	0.295	−0.178	−11.5
2-Cl-benzonitrile	19.73	−0.0652	0.286	−0.157	−7.1
3-Cl-benzonitrile	19.74	−0.0666	0.301	−0.148	−5.3
4-Cl-benzonitrile	19.70	−0.0830	0.296	−0.175	−6.2
4-methoxybenzonitrile	19.58	−0.1153	0.428	−0.17	−1.6

[a] Computed using Stark effect data from ref 1, anharmonicity data from ref 35, masses from AM1 calculation, and using the single mode theory (eqs 13−18). [b] See note *d* of Table 1. [c] Sum of second and third terms of $\Delta\alpha_{\|\|}$ expression in eq 6. [d] Fermi resonance corrected frequency from ref 34.

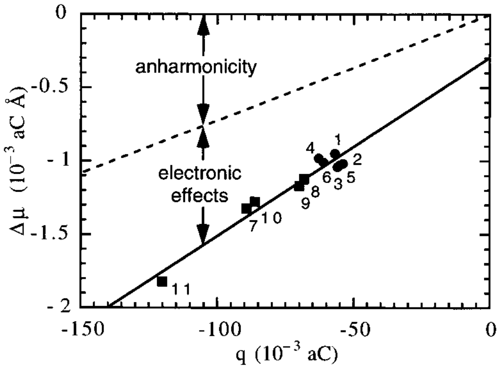


Figure 1. Correlation of difference dipoles with effective charges for mononitriles. Difference dipole data are from ref 1 and assume a local field correction value of 1.1; effective charge data are calculated from the transition dipole data in ref 1, using the single mode theory. Circles represent aliphatic 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-methoxybenzonitrile. 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.

substituted back into the data analysis to further refine all the values, but the improvement would be well within the experimental uncertainty.

Analysis of Mononitriles. A single mode analysis of a variety of aliphatic and aromatic mononitriles, results of which are shown in Table 2, yields the same overall picture as that found above. Because the experimental data for most of the molecules[1] was collected without varying the angle between the applied electric field and the light polarization, similar data were used for acetonitrile and 4-chloro-benzonitrile to allow meaningful comparisons. Figure 1 shows the correlation of $\Delta\boldsymbol{\mu}$ with q for all the nitriles, along with the least squares best fit line, which has a slope of 0.012 Å and an intercept of -3.2×10^{-4} aC Å. The dashed line shows the anharmonicity contribution of $\Delta\boldsymbol{\mu}$; it has a slope of 0.0072 Å, computed from the first term of eq 14 and anharmonicity data for HCN.[35] As before, anharmonicity accounts for roughly 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.[41] For the nitrile stretch mode (mode 2), the dipole gradient was calculated from our experimental results because this is more accurate for the environment in which the Stark data were taken, whereas the published dipole gradients[41] were used for the other modes. The experimental nitrile dipole gradient was 17% larger than the corresponding published value, indicating that 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 $\Delta\boldsymbol{\mu}$ arises from anharmonicity in the nitrile mode. Anharmonic coupling to the other modes (v_{iij} in eq 34) 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. As a result, the value for $\mathbf{v}_{22}'$ (denoted v_2' in the single mode theory) is somewhat less than previously calculated; it is still parallel to the z-axis but has a corrected value of 1.9×10^{-3} Å V^{-1} fs^{-2} in mass-weighted coordinates, and 0.21 aC Å^{-1} in physical coordinates.

TABLE 3: (A) Multi-mode Analysis of Acetonitrile[a] (B) Vector and Matrix Components of Acetonitrile Stark Effects

parameter	unit	mode 1 CH stretch	mode 2 CN stretch	mode 3 CH bend	mode 4 CC stretch
(A) multi-mode analysis of acetonitrile					
$\bar{\nu}$ [b]	cm^{-1}	2292.7	2270.6	1390	915.4
ω_i	fs^{-1}	0.5505	0.4277	0.2618	0.1724
$\boldsymbol{\mu}_i$	10^{11} aC kg$^{-1/2}$	−7.14 [b]	−5.53 [c]	−8.78 [b]	−0.32 [b]
v_{ii2}	10^{-3} aJ$^{-1/2}$ fs^{-3}	−0.179	−17.38	−0.706	−3.66
$\Delta\boldsymbol{\mu}$ term 1[d]	10^{-6} aC Å	−3.13	−388.5	−66.9	−29.1
(B) vector and matrix components of acetonitrile stark effects					
$\Delta\boldsymbol{\mu}$ term 1[e]	10^{-6} aC Å		x: 0	y:0	z: −487.6
$\mathbf{v}_{22}'$	Å V^{-1} fs^{-2}		x: 0	y: 0	z: 0.00192
$\mathbf{v}_1''$ [f]	10^{11} aC Å V^{-1} kg$^{-1/2}$		xx: −5.4	yy: −5.4	zz: −13.7

[a] Computed using Stark effect data from ref 1. Note that normal coordinates are used here for molecular parameters. To convert to physical coordinates, multiply $\boldsymbol{\mu}_i$ and $\mathbf{v}_i''$ by $m_i^{1/2}$, $\mathbf{v}_{ij}'$ by $m_i^{1/2}m_j^{1/2}$, and v_{ijk} by $m_i^{1/2}m_j^{1/2}m_k^{1/2}$, where m_i is the reduced mass of mode i. m_2 has a value of 108.7×10^{-28} kg. [b] Ref 41. [c] Computed from data in ref 1, as described in text. [d] Anharmonicity contribution to $\Delta\boldsymbol{\mu}$ from coupling to each normal mode, using eq 34. [e] Total anharmonicity contribution to $\Delta\boldsymbol{\mu}$. [f] Off-diagonal elements are zero, by symmetry.

The physical origin of the transition polarizability was also investigated using the multi-mode theory. Several small terms were ignored in this calculation, including terms involving v_{ijk} where $i \neq j \neq k$ and $\mathbf{v}_{ij}'$ with $i \neq j$. These values cannot be calculated from our data, are unavailable in the literature, and are also expected to be even smaller than v_{iij} and $\mathbf{v}_{ii}'$, terms which are available and which provide extremely small contributions to $\mathbf{A}$. Ignoring these probably negligible corrections yields the result that over 99% of the transition polarizability arises from $\mathbf{v}_2''$, as found with the single mode theory.

It was found experimentally that the transition polarizability has a significant perpendicular component[1], which was initially attributed to a nonconserved line shape arising from interaction with the Fermi resonant band 50 cm^{-1} to higher energy. Although this is possible, it was rationalized on the incorrect understanding 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 expected that the polarizablility perpendicular to the symmetry axis changes slightly with motion in the nitrile stretch mode.

A final equation which can be checked experimentally is the transition dipole of the overtone absorption, eq 38. It was measured by taking the infrared spectrum of a neat sample of acetonitrile at room temperature, integrating absorption peak areas for both the fundamental and overtone bands, and calculating the ratio of the areas divided by frequencies ($\mathbf{M}^2 \propto$ band area/ω). Multiplying the square root of this ratio by the transition dipole for the fundamental mode given in Table 1 yields the experimentally determined overtone transition dipole moment, with a value of 0.42×10^{-3} aC Å. Because it is only the ratio of the room temperature peak areas that is used, this method is expected to account reasonably well for the sample being neat and at room temperature, rather than dilute and at low temperature like the rest of samples considered here. Using eq 38 and values from Table 3, the calculated overtone transition dipole is 0.43×10^{-3} aC Å, in remarkably good agreement with experiment.

Conclusions

Previous experimental results[1,3] inspired many questions on the physical origins of vibrational Stark effects, which are addressed in this paper. Using the classic “balls and springs” model, a detailed set of equations are derived for the Stark effects of a single vibrational mode and a less detailed set are derived for multiple vibrational modes. Comparison with experiment yields insight into which molecular parameters account for the different Stark effects and also yields numeric values for several parameters which have not been measured previously.

It is found that the dominant Stark effect, $\Delta\boldsymbol{\mu}$, which represents the linear Stark tuning rate, arises from about half mechanical effects and half electronic effects for a wide range of nitriles. Mechanical effects are from bond anharmonicity (υ_3 or $\mathbf{v}_{ijk}$) whereas electronic effects are from the effect of an electric field on chemical bond strengths (υ_2' or $\mathbf{v}_{ij}'$). In acetonitrile, where a multi-mode analysis is possible, 40% of $\Delta\boldsymbol{\mu}$ arises from anharmonicity in the nitrile mode and 10% arises from anharmonic coupling to other modes.

The transition polarizability, **A**, arises almost exclusively from the gradient of the molecular electronic polarizability (υ_1'' or $\mathbf{v}_i''$), a term which can also be interpreted as the field effect on the effective charge. Because an electric field affects the electron cloud distribution, and hence the partial charges on the atoms, it also affects vibrational transition dipole moments. In acetonitrile, an electric field perpendicular to the molecular axis is found to affect the nitrile effective charge by 40% as much as a field parallel to the bond axis. Although the value for **A** is significant (and has a large effect on Stark spectral line shapes), the higher order transition hyperpolarizability, **B**, is shown to be much smaller and can be neglected for electric fields of 1 MV/cm.

The quadratic Stark shift, $\Delta\boldsymbol{\alpha}$, is found to be a sum of terms arising from mechanical and electronic effects. Because all terms are either high-order components of a Taylor expansion (eq 3) or are products of low-order components, $\Delta\boldsymbol{\alpha}$ is expected to be small; this is in agreement with experiment, where $\Delta\boldsymbol{\alpha}$ was found to have a minimal effect on Stark spectra. $\Delta\boldsymbol{\alpha}$ depends to a significant extent on the product of the cubic anharmonicity and the polarizability gradient, ($\upsilon_3\upsilon_1''$). It also depends on two other terms involving electronic perturbations (υ_3' and υ_2''), whose effects cannot be separated but are shown to contrast ab initio results.

The theories make several predictions for multiple transitions and resonant transitions, of which only a couple can be analyzed without more data. Stark effects for resonant transitions are predicted to be dominated by linear combinations of the effects for the uncoupled states, plus a minor coupling term for difference dipoles, in good agreement with experimental results for ^{15}NO bound to myoglobin.[42] It is also possible to calculate overtone vibrational intensities from the same molecular parameters that contribute to $\Delta\boldsymbol{\mu}$ (υ_{ijk} and $\mathbf{v}_{ij}'$); a prediction made in this way for the nitrile overtone vibration of acetonitrile is nearly identical to the experimental value. Although there are no experimental data yet, it is predicted that difference dipoles are additive for multiple transitions. For degenerate transitions, Stark effects should be identical to those for nondegenerate transitions if a normal mode representation is chosen which is not coupled by an electric field.

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 that have not been verified, and for which experimental data are needed.

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