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Vibrational Stark Effect Spectroscopy

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The effects of electric fields on vibrational spectra are of fundamental importance for understanding the anharmonicity of chemical bonds. Furthermore, the sensitivity of vibrational transitions to electric fields can provide a local probe of electrostatic fields in ordered systems such as proteins, where many infrared studies are in progress. Despite this potential utility and a significant amount of theoretical work,[1] there are almost no experimental data.[2] In this Communication we describe a method for obtaining vibrational Stark effect (VSE) spectra under quite general conditions and report the results for a simple CN stretching vibration.

The basic method is essentially identical to that used for electronic Stark spectroscopy on condensed phase systems,[3] modified by changing the light source and detector for measurements in the infrared. Light from a Nernst glower (Ayers Eng., CA) was chopped, passed through a 0.25 m single monochromator (grating blazed at 4.0 μm, 150 grooves/mm, Ag-coated mirrors, resolution 3.5 cm^{-1}), passed though the sample, and detected with a liquid nitrogen-cooled InSb detector (Grasby Infrared, 1 mm^2, sapphire window). An optical filter was placed before the detector to minimize light due to higher order reflections from the grating. The sample cell was constructed from two Ni-coated (~60 Å thick Ni) sapphire windows separated by a 25 μm Teflon spacer. The cell is under vacuum and in contact with a liquid nitrogen-cooled cold finger. A KRS-5 grid polarizer was inserted between the monochromator and the Dewar for polarization measurements. To minimize rotation of the polarization of light by the birefringent sapphire window, the o-ray (or e-ray) axis of the window and the polarization direction of the light were always kept in the same plane (horizontal).

We have chosen the CN stretching vibration of anisonitrile because it is in a convenient wavelength region, it has a moderately strong IR absorption, and the band is simple. Figure 1 shows the IR spectrum of anisonitrile in a toluene glass at 77 K (top panel) and the VSE spectrum in the middle panel. It is evident that a good signal-to-noise ratio can be obtained.

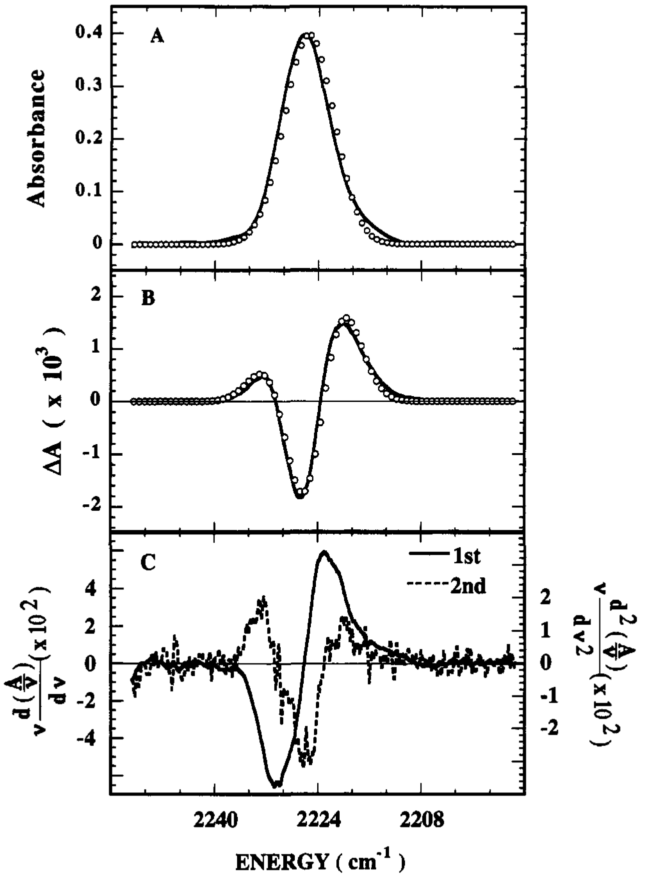

Figure 1. (A) IR absorption spectrum of anisonitrile in toluene at 77 K in the CN stretching region (solid line). (B) Vibrational Stark effect spectrum for a field strength of 1.0 MV/cm, χ = 90° (solid line). Decomposition of the VSE spectrum into first (—) and second (- - -) derivatives of the absorption spectrum. The open circles on the absorption and VSE spectra are the simultaneous best fits using a single Gaussian for the absorption in the (A) and the derivative contributions in the (C), respectively.

Figure 2 shows the amplitude of the VSE as a function of the applied electric field strength, demonstrating the expected quadratic dependence (see below). The shape of the VSE spectrum for anisonitrile was independent of field over the range shown in Figure 2 (data not shown). Figure 3A shows the effect of varying the experimental angle χ between the applied field direction and the electric vector of the polarized light used to probe the VSE. It is evident that the line shape of the VSE spectrum is independent of χ and that the effect, corrected for pathlength,[3] is larger for χ = 62° than for χ = 90°.[4]

The change in transition frequency, $\Delta\nu$, due to an externally applied field **F**, is given by

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

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(1) (a) Bishop, D. M. *Rev. Mod. Phys.* **1990**, *62*, 343. Bishop, D. M.; Kirtman, B. *J. Chem. Phys.* **1991**, *95*, 2646. Bishop, D. M. *J. Chem. Phys.* **1993**, *98*, 3179. Marti, J.; Bishop, D. M. *J. Chem. Phys.* **1993**, *99*, 3860. (b) Hush, N. S.; Williams, M. L. *J. Mol. Spectrosc.* **1974**, *50*, 349. (c) Dykstra, C. E. *J. Chem. Educ.* **1988**, *65*, 198. The paucity of data has limited the development of this area.

(2) (a) Most early experiments were limited to studying the electric field effect on IR transitions in liquids or on defects in solids; see, e.g.: Handler, P.; Aspnes, D. E. *J. Chem. Phys.* **1967**, *47*, 473. Bridge, N. J.; Haner, D. A.; Dows, D. A. *J. Chem. Phys.* **1968**, *48*, 4196. Hayes, W.; Macdonald, H. F. *Proc. R. Soc. London* **1967**, *A297*, 503. Jones, D. E. H. *J. Chem. Soc., Faraday Trans. 2* **1976**, 1397. Experiments performed in the liquid phase have limitations due to partial molecular alignment, and only very weak fields can be applied. (b) Rumyantzev and Blinov reported changes in the IR transmission spectra of two organic films deposited on an Al surface (Rumyantzev, V. G.; Blinov, L. M. *Opt. Spectrosc. (Engl. Trans.)* **1972**, *32*, 675). (c) VSE studies of the type described in this manuscript are mainly limited to CO and CN adsorbed on metal in ultrahigh vacuum or in an electrochemical environment; see, e.g.: Lambert, D. K. *Phys. Rev. Lett.* **1983**, *50*, 2106. Lambert, D. K. *J. Chem. Phys.* **1988**, *89*, 3847. Kötz, R.; Yeager, E. *J. Electroanal. Chem.* **1981**, *123*, 335. Bagus, P. S.; Nelin, C. J.; Müller, W.; Philpott, M. R.; Seki, H. *Phys. Rev. Lett.* **1987**, *58*, 559. There is a recent report of an IR hole burning spectrum of matrix-isolated NaCN in the presence of an external electric field: Spitzer, R. C.; Sievers, A. J.; Silsbee, R. H. *J. Opt. Soc. Am. B* **1992**, *9*, 978.

(3) Boxer, S. G. In *The Photosynthetic Reaction Center*; Deisenhofer, J., Norris, J. R., Eds.; Academic Press: New York, 1993; Vol. 2, pp 179−220.

(4) There are some parallels between the methods used to measure Stark spectra and those developed for vibrational circular dichroism (VCD; see, e.g.: Nafie, L. A.; Diem, M. *Appl. Spectrosc.* **1979**, *33*, 130. Kiederling, T. A. *Appl. Spectrosc. Rev.* **1981**, *17*, 189). The most significant difference is that in VCD the polarization is modulated at a much higher frequency (typically 50 kHz) than is possible for very large AC electric fields (typically less than 500 Hz). Also, VSE is detected at twice the field modulation frequency, whereas VCD is detected at the modulation frequency. VSE experiments were performed using single (field only at 350 Hz) or double (field at 485.3 Hz and light at 77.7 Hz) demodulation; however, it was found that substantially better signal-to-noise ratios could be obtained using single demodulation with a high dynamic reserve digital lock-in amplifier (Stanford Research SRS850). This approach requires that absorption and VSE spectra be obtained separately; however, this is no problem given the long-term stability of the experimental setup. For example, the peak absorbance for two absorption spectra taken one after another varies by less than 2%.

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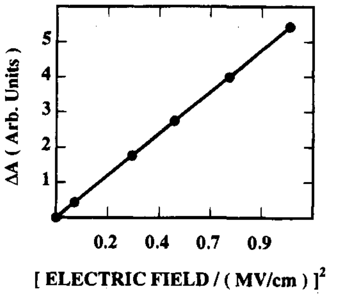

Figure 2. Intensity of the Stark signal as a function of the square of the applied electric field.

where $\Delta\boldsymbol{\mu}$ and $\Delta\alpha$ are the changes in dipole moment and polarizability, respectively, between the states involved. For an isotropic, immobilized sample, an applied electric field will broaden an isolated transition due to $\Delta\boldsymbol{\mu}$, giving rise to a Stark effect line shape which is approximately the second derivative of the absorption line shape. If $\Delta\alpha$ is significant, the Stark effect line shape is approximately the first derivative of the absorption line shape. Quantitatively, when $\Delta\nu$ is smaller than the inhomogeneous line width, the change in absorbance under the influence of an external field can be written as[3]

$$\Delta A(\nu) = (f\mathbf{F})^2\{A_\chi A(\nu) + (B_\chi \nu/15hc)\,\mathrm{d}[A(\nu)/\nu]/\mathrm{d}\nu + (C_\chi \nu/30h^2c^2)\,\mathrm{d}^2[A(\nu)/\nu]/\mathrm{d}\nu^2\} \quad (2)$$

where A_χ depends on the transition polarizability and hyperpolarizability, $B_\chi = {}^1/_2\{5\mathrm{Tr}(\Delta\alpha) + (3\cos^2\chi - 1)[3(\mathbf{p}\cdot\Delta\alpha\cdot\mathbf{p}) - \mathrm{Tr}(\Delta\alpha)]\}$ (neglecting the contribution from the transition polarizability), and $C_\chi = |\Delta\boldsymbol{\mu}|^2[5 + (3\cos^2\zeta - 1)(3\cos^2\chi - 1)]$. ζ is the molecular angle between $\Delta\boldsymbol{\mu}$ and the transition moment $\mathbf{p}$. ζ is obtained from the second derivative coefficients of the Stark spectra (C_χ) obtained at different values of χ, the experimental angle between $\mathbf{F}$ and the electric vector of the linearly polarized light used to probe ΔA. f is the local field correction.[5]

As shown in the lower panel of Figure 1, the VSE spectrum of anisonitrile can be decomposed into a sum of first and second derivative contributions using fitting methods described in detail elsewhere.[3] This gives $|\Delta\boldsymbol{\mu}| = 0.05 \pm 0.02D/f$, and $\mathrm{Tr}(\Delta\alpha) = 3.0 \pm 2.0$ Å$^3/f^2$, where f is the local field correction factor.[5] The contribution from the zeroth derivative of the absorption spectrum is small compared to that from the first and second derivatives, which means that the change in intensity of this band in the applied field is very small. If the field were applied along the CN bond direction, the observed $|\Delta\boldsymbol{\mu}|$ would give rise to a Stark tuning rate of $(0.8 \pm 0.3) \times 10^{-6}$ cm^{-1}/(V/cm). This is on the same order of magnitude as that observed for CO and CN on different surfaces.[2c] To our knowledge, there have been no previous measurements of the magnitude of $\Delta\alpha$ for molecular vibrations. Our observation is that the difference polarizability for an infrared transition is small. This is reasonable since both of the vibrational levels involved in the transition are in the same electronic state. Figure 3B shows the ratios of the second derivative contributions at $\chi = 62°$ and 70° to that at $\chi = 90°$ plotted against χ. The solid line is the best fit to the expected angle dependence of C_χ, giving $\zeta = 0°$ for the angle between the transition dipole and the difference dipole moment. Although the angle between the transition dipole and $\Delta\boldsymbol{\mu}$ can have any value and is often different from 0° for electronic transitions, it is reasonable that its value is approximately 0° for vibrations which are approximately one-dimensional oscillators, such as the CN vibration considered here.

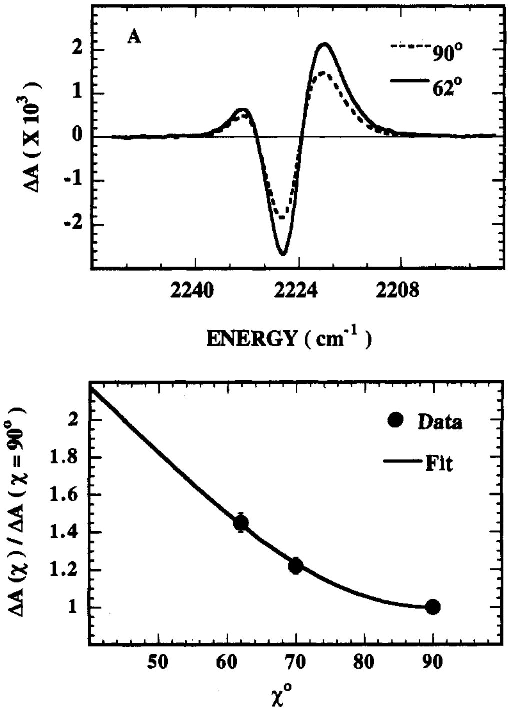

Figure 3. (A) Vibrational Stark effect spectra as in Figure 1B at two different experimental angles between the applied electric field direction and the probe light polarization direction, $\chi = 90°$ (- - -) and $\chi = 62°$ (—) for the same absorbance (pathlength corrected) and a field strength of 1.0 MV/cm. (B) Second derivative contributions to the Stark effect spectra at different experimental angles (χ) divided by the contribution at $\chi = 90°$. The best fit of the χ dependence of C_χ (see eq 2) to the data gives a value of $\zeta = 0°$ for the angle between the transition dipole and the difference dipole.

In order to be able to observe the vibrational Stark effect, the external electric field must change the relative spacings of the vibrational energy levels of a molecular electronic state. This is possible only when the oscillator is anharmonic.[1c] The anharmonicity may arise from mechanical vibrations or electrical properties of the molecule or both.[1a] The results obtained in our experiments show that the CN stretching vibration in anisonitrile is considerably anharmonic. A detailed study involving a series of related molecules is in progress to obtain quantitative information on mechanical and electrical contributions, as well as to extend these measurements further into the infrared.

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[5] f is in general a tensor and is not known precisely; however, it is expected to be between 1.1 and 1.3 for simple solvents. See, e.g.: Böttcher, C. J. F. *Theory of Electric Polarization*; Elsevier: Amsterdam, 1993; Vol. 1. VSE may ultimately prove to be a sensitive means for determining f.