Solute–Solvent Interactions Determine the Effect of External Electric Field on the Intensity of Molecular Absorption Spectra

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Received: September 04, 2008; Revised Manuscript Received: November 10, 2008

The study of the electronic absorption spectra of 4-aminoazobenzene subjected to an external electric field in nonpolar and polar solvents shows that the field-induced change in the absorption intensity is dominated by the solvent–solute interaction. Moreover, solvent can determine the sign of the change of the absorption intensity. These experimental observations are supported by ab initio electronic structure calculations and are rationalized by analytic theory. The results carry particular importance for the numerous fundamental and practical applications of electric fields to understanding and design of new materials and biological systems.

1. Introduction

Applied external electric fields are often used to probe fundamental properties of matter and to create new types of materials. Molecular response to an electric field provides important information about molecular structure,1 conformational and tautomeric equilibria,2 molecular dynamics3–5 and optical properties.6 The Stark effect7–9 was among the first to be applied for this purpose. The Stark absorption, or electro-absorption spectroscopy is widely used in the studies of polymer film properties.10,11 Luminescence spectra also show significant dependence on the applied electric field.12 NMR spectroscopy in the presence of strong electric fields allows one to determine the degree of alignment of polar molecules13 that form new types of electro-optic materials.14–16 External electric fields applied perpendicular to a surface have an important effect on the orientation and bonding of surface molecules.17 Electric fields generated in biological environments are explored to create spectroscopic biological probes.18

The studies of the electric field influence on transition dipole moments (DM), which determine intensities of absorption and emission lines, has a long history.19 Early measurements have shown that the effect is usually small, although it cannot be neglected.20 Ground state DMs are commonly used for characterization of electronic charge distributions in molecules21,22 and solute–solvent interactions.23–25 DMs of molecules in excited electronic states are more difficult to obtain. For this purpose one can use the dependence of optical absorption lines on the external electric field.20 In addition to the changes in the ordinary and transition DMs, the field produces an anisotropic distribution of molecular orientations, creating electrical dichroism, and alters excited-state energies. Theoretical analysis of the experimental data can separate these effects and produce the magnitudes and directions of excited-state DMs and transition DMs.20

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The presence of a surrounding medium, such as a solvent, complicates the situation. The reaction field generated by the solvent screens the applied field27 and alters the energy and intensity of absorption bands. The effect of the solvent on the field-induced changes in the molecular electronic absorption spectra constitutes the focus of the current study. By investigating the absorption spectrum of the 4-aminoazobenzene (AAB) molecule in several solvents subjected to an applied electric field, we show that field-induced changes in the absorption intensity are greatly influenced by interaction with the solvents. We find that solvent can qualitatively change the variation of the absorption intensity with applied field. AAB is chosen as one of the azobenzene derivatives, which are widely used in photoisomerization reactions.28–30 The experimental observations are supported further by ab initio electronic structure calculations and are rationalized by analytic theory.

2. Experimental Procedure

AAB (Aldrich) was recrystallized several times from ethanol (orange needles mp 126 °C). The following solvents were used in the subsequent spectroscopic studies: CCl4, hexane (Fluka), benzene (Merck) and CH2Cl2 (POCh). The AAB concentration varied from 3 × 10−5 to 4 × 10−5 mol/dm3.

The electron-vibrational absorption spectra of the solutions of AAB were studied with the two-beam absorption spectrophotometer Specord M500 (Carl Zeiss, Germany). The high-voltage source ABK 45A (ZMAR, Poland) was used to investigate the influence of the external electrical field on the spectra. The measurements were carried out in a homemade absorption cell. The angle between the directions of the external electric field and the propagation of light was 90°. The electrode surface equaled to 1 cm2, and the distance between the electrodes was 1 cm. The voltage applied to the electrodes ranged from 0 to 30 kV. The maximum electric field obtained with this setup equaled to 3 × 107 V/cm. The measurements were carried out at room temperature.
The intensity of the higher energy absorption band arising due to absorption band with AAB in hexane, Figure 3. The intensity of the lowest energy band in the difference spectrum of AAB with concentration of 4 × 10^{-5} mol/L solution of 4-aminoazobenzene in CCl4 for different strengths of the applied electric field (E, V/cm): (a) 0; (b) 0.5 × 10^4; (c) 1 × 10^4; (d) 1.5 × 10^4; (e) 2 × 10^4; (f) 2.5 × 10^4; (g) 3 × 10^4.

Figure 2. Same as Figure 1, but for the 4 × 10^{-5} mol/L solution in n-C6H14 and fields (E, V/cm): (a) 0; (b) 0.5 × 10^4; (c) 1 × 10^4; (d) 1.5 × 10^4; (e) 2 × 10^4.

3. Experimental Results

The absorption spectra of the solution of AAB in CCl4 with concentration of 3 × 10^{-5} mol/L are shown in Figure 1 for different strengths of the external electric field, ranging from 0 to 3 × 10^4 V/cm. The intensity of the lowest energy absorption band with \( \lambda_{\text{max}} = 366 \) nm, associated with the nπ*-type transition, increased from \( A = 0.80 \) to \( A = 1.50 \) with increasing field. Similar dependence was observed for the solution of AAB in benzene with concentration of 4 × 10^{-5} mol/L, Figure 2. The intensity of the same absorption band, now with \( \lambda_{\text{max}} = 375 \) nm, grew from \( A = 0.77 \) to \( A = 0.94 \) as the voltage increased from \( U = 0 \) to \( U = 20 \) kV. The smallest effect for the three nonpolar solvents was observed with the solution of AAB in hexane, Figure 3. The intensity of the lowest energy absorption band with \( \lambda_{\text{max}} = 362 \) nm did not change appreciably as the voltage increased from \( U = 0 \) kV to \( U = 25 \) kV. The intensity of the higher energy absorption band arising due to ππ* transitions grew in all three cases. In particular for the hexane solution, the band maximum at \( \lambda_{\text{max}} = 234 \) nm increased from \( A = 0.4 \) to \( A = 1.4 \) as the voltage increased from \( U = 0 \) kV to \( U = 25 \) kV, Figure 3.

The maximum voltage that could be applied to the solution of AAB with concentration of 4 × 10^{-5} mol/L in the polar solvent CH2Cl2 could not exceed \( U = 10 \) kV. Electrical breakdown of the system occurred at higher voltages. The change in the absorption intensity of the lowest energy band was minor between \( U = 0 \) kV and \( U = 10 \) kV. The maximum grew from \( A = 0.675 \) in the absence of the field to \( A = 0.700 \) at \( U = 10 \) kV.

These experimental results show that the changes in the absorption intensity induced by the external electric field depend drastically on the solvent, even for similar, nonpolar solvents. The same compound surrounded by different condensed phase media exhibits very different behavior; compare Figures 1 and 3.

To eliminate the effect of the solvent, the following experiment was carried out, producing a striking result. The absorption spectrum of the solution of AAB in CCl4, which showed the largest dependence on the electric field, was measured simultaneously with the spectrum of the pure solvent. The measurements were performed with two identical cuvettes in parallel. Identical voltages were applied, and the difference in the absorption spectra of the two cuvettes was obtained, Figure 4. In contrast to Figure 1 showing the solution spectrum, the intensity of the lowest energy band in the difference spectrum decreased with increasing field from \( A = 0.99 \) at \( U = 0 \) kV to \( A = 0.86 \) at \( U = 30 \) kV. By eliminating the effect of the solvent by this measurement, we find that the influence of the external electric field alone on the absorption intensity is small, as predicted in ref 20. Moreover, the solvent not only drastically amplifies the effect but also changes its sign. Note that the second band in the difference spectrum in Figure 4 grew with the field, in a manner similar to the original solution, Figure 1. Thus, the solvent has substantially different effects on the nπ*- and ππ* type transitions in AAB.

The data presented in Figures 1−4 are summarized in Figure 5, which shows the change in the integrated absorption intensity (ΔA) of the lowest energy band as a function of the applied field.

4. Electronic Structure Calculations

To establish the electric field dependence of the absorption intensity of AAB in the absence of a surrounding medium and to confirm the experimental result shown in Figure 4, we performed ab initio electronic structure calculations using time-dependent density functional theory with the B3LYP functional and 6-31g* Gaussian basis. The calculations were performed using the Gaussian suite of programs.31 The results are sum-
5. Theoretical Analysis

The analysis detailed in the Supporting Information shows that the transition DM of a molecular transition is modified in condensed phase \( \bar{\mu}_{eg} \) relative to gas phase \( \bar{\mu}_{eg}^0 \) according to the following expression

\[
\bar{\mu}_{eg}^f(q) = \frac{\bar{\mu}_{eg}^0(q)}{m} \left[ 1 + f' \frac{\bar{\mu}_{eg}^0 - \bar{\mu}_{eg}^0}{2mv_{eg}^2} + \frac{f_2(\alpha_e - \alpha_g)}{hv_{eg}} \right]
\]

Here, \( m, f' \) and \( f_2 \) are functions of the internal field of the medium, \( \bar{\mu}_{eg}^0 \) and \( \alpha_e, \alpha_g \) are molecular DMs and polarizabilities for the ground and excited electronic states, respectively, \( v_{eg} \) is the excitation frequency, and \( h \) is Planck’s constant. The absorption intensity depends on the square of the transition DM, eq 1.

Equation 1 shows that the medium induced change in the transition DM can be both positive and negative depending, to the lowest order in the perturbation theory, on the difference in the molecular DMs and polarizabilities for the excited and ground electronic states. Because AAB is a strongly polar molecule, the \( \bar{\mu}^2 \) term dominates the solvent effect in this case. The absolute magnitude of the solvent effect on the field-induced change in the transition DM is determined by the values of the functions \( m, f' \) and \( f_2 \), which describe the solute–solvent interaction. Generally, the solvent effect increases with solvent polarity. Even for CCl4 with the refractive index \( n = 1.446 \), a simple estimate discussed in the Supporting Information gives \( m \approx 0.7 \). This factor alone, present in the denominator of eq 1, changes the transition dipole moment by 50%.

The Supporting Information shows that the change in the absorption intensity is a linear function of the applied field both in solution and in gas phase, as determined experimentally, Figure 5, and computationally, Table 1.

6. Conclusions

External electric fields polarize solvents and by doing so alter the properties of dissolved molecules. The indirect, solvent-mediated influence of the external field on the molecular absorption spectra is huge. It is much more significant than the direct effect of the field. The reason for this phenomenon becomes clear if one compares the strengths of the external field (\( E \sim 10^3 \) to \( 10^5 \) kV/cm) with the strength of the internal field of the solvent (\( E \sim 10^7 \) kV/cm).\(^{32} \) The latter is orders of magnitude greater than the former. The solute–solvent interaction controls not only the magnitude of the field-induced change in the absorption spectra, but also its sign.

The above conclusions have been confirmed by experimental measurements, collaborated by ab initio electronic structure calculations and rationalized by theoretical analysis. The results indicate that solute–solvent interactions must be explicitly taken into account in the numerous studies of field-induced changes of molecular properties in condensed phase environments.

Acknowledgment. The research was supported by grants from NSF CHE-0701517 and ACS-PRF 46772-AC6.

Supporting Information Available: Theoretical considerations of the effect of a condensed phase medium on the intensity of a molecular electronic absorption spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


