First-order hyperpolarizabilities and pKₐ of weak organic acids in protic solvents are linearly related

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Second-order nonlinearities (β) of weak organic acids in protic solvents have been measured by the double-quantum Rayleigh scattering (DRS) technique. β is found to bear a linear relationship to the pKₐ of these compounds in those solvents. A direct implication of this observation is that the DRS technique can be used to determine the pKₐ of weak organic acids in any solvent.

It has been generally recognized that donor–acceptor-substituted organic compounds such as benzenes, stilbenes, azo dyes and polyenes possess large molecular second-order nonlinear optical (NLO) susceptibilities (β). However, ionic compounds and high dielectric constant solvents were avoided, thus far, for measurements since the electric-field-induced second-harmonic generation (EFISHG) technique, commonly used for determination of β, involves a high-voltage DC field to align the molecules in the direction of the field in solution. An alternate technique, the double-quantum Rayleigh scattering (DRS), rediscovered recently allows determination of β without the above constraints. Also, the DRS technique yields an average value of β whereas the EFISH technique gives the component of β projected along the direction of alignment (normally, the dipole direction) of the molecules in solution. In this communication, we report the β values of a few amino benzoic acids and sulphonylic acids in some polar protic solvents and demonstrate that β bears a linear relationship with the pKₐ of these weak acids in those solvents.

Compounds a–e were purchased from Aldrich and their β values measured by the DRS technique at 1.064 μm in methanol and other protic solvents. The fundamental IR light from a Q-switched Nd: YAG laser was focused on a 4 × 4 × 2 cm³ cell containing the solution of compounds. The second-harmonic light was collected using a large-diameter and short-focal-length aspherical condenser lens and other imaging optics at the photocathode of a uv-visible photomultiplier tube (PMT) after separating the fundamental by a 532 nm interference filter of 4 nm bandwidth. The output signal from the uv-visible PMT was integrated and averaged over 10,000 laser shots in a Boxcar signal averager (SRS 250). The experiments were carried out at laser powers below the threshold for stimulated Raman and Brillouin scattering and for self-focusing and self-defocusing.

The intensities of the second-harmonic scattered light, Iₑₑ, and the incident beam, I₀, are related by

\[ Iₑₑ = G B^2 I₀^2 = G \sum \beta_k I₀^2 \]

where G depends upon the scattering geometry and contains the average of the products of the direction cosines and the local field corrections and also the instrumentation factor. Nₑₑ is the number density of the kth specie with second-order polarizability βₑₑ. For a two-component system,

\[ B^2 = N_{\text{solute}} \beta^2_{\text{solute}} + N_{\text{solvent}} \beta^2_{\text{solvent}} \]

Since low concentrations (10⁻⁴–10⁻⁶ M) of solute were used, we assume that its presence does not change the number density of the solvent molecules, N_{solvent} significantly. Measurements at different number densities of the solute show a linear dependence of GB² on N_{solute}.

From the intercept and slope we calculated β_{solute} and G since β_{solute} is known. Chloroform was calibrated with respect to carbon tetrachloride by the method described in detail by Zyss et al., and in a similar fashion we obtained β for water, methanol, ethanol and isopropanol as 0.05, 0.52, 0.61 and 0.65, respectively, in units of 10⁻⁸ esu.

The β values of a–e obtained from DRS experiments in methanol, ethanol, isopropanol and water are listed in Table 1. All these compounds have an electron donor

<table>
<thead>
<tr>
<th>Compound</th>
<th>β_{calc.} (× 10⁻⁸ esu)</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>Isopropanol</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>2.0</td>
<td>6.8</td>
<td>7.2</td>
<td>7.8</td>
<td>9.0</td>
</tr>
<tr>
<td>b</td>
<td>4.2</td>
<td>10.2</td>
<td>11.0</td>
<td>11.6</td>
<td>13.0</td>
</tr>
<tr>
<td>c</td>
<td>5.5</td>
<td>15.8</td>
<td>16.6</td>
<td>17.2</td>
<td>18.5</td>
</tr>
<tr>
<td>d</td>
<td>5.2</td>
<td>14.8</td>
<td>16.1</td>
<td>17.2</td>
<td>20.0</td>
</tr>
<tr>
<td>e</td>
<td>6.1</td>
<td>20.8</td>
<td>22.9</td>
<td>23.4</td>
<td>26.2</td>
</tr>
</tbody>
</table>
and an electron acceptor group. As a result, the contribution from the canonical quinonoid structure in the ground state is high. Since delocalization of electrons is most favoured when the donor–acceptor are para to each other, the para-compounds show large nonlinearities and the order is para > meta > ortho for a fixed pair of donor–acceptor substituents. For the common amino donor we expect the sulfonic-acid-substituted derivative to exhibit higher \( \beta \) values than analogous carboxylic acid derivatives since the former is a better electron acceptor than the latter. This is actually observed experimentally (see Table 1). We have also computed finite-field \( \beta \) for these compounds using the PM3 parametrization within the MOPAC package with full geometry optimization. The calculated \( \beta \) values are purely gas phase numbers and do not include the solvent effects. But the experimental trend in \( \beta \) is nicely reproduced in the calculation although the calculated results are always lower. This may be explained by recalling the well-established notion that in solution specific interactions with solvent molecules may alter the NLO characteristics (i.e. \( \beta \)) and we can write various components of \( \beta \) as

\[
\beta = \beta_q + \beta_m + \beta_i ,
\]

where \( \beta_q \) is the quadratic polarizability of the molecules in the gas phase (i.e. isolated) and \( \beta_m \) and \( \beta_i \) correspond to hydrogen bonding (intermolecular and intramolecular) and intermolecular interaction (dipole–dipole, ion–dipole, ion–ion, etc.) contributions to \( \beta \), respectively. For different solvents these components of \( \beta \) will be different and the stability of the solvated conjugate base (anion) will determine the dissociation constant in solution. For acids with low \( pK_a \) values in solution the amino group will be protonated and the concentration of the zwitterionic specie will influence the equilibrium constant. Insofar as the trend in \( \beta \) is concerned, it is not at all surprising that we find that water > isopropanol > ethanol > methanol, although their polarity varies as water > methanol > ethanol > isopropanol. We also find that \( pK_a \) (ref. 19–21) of a–e (which are weak acids) in these solvents correlates linearly with their \( \beta \) in solution (Figure 1). This indirectly points out that the driving forces which lead to a higher degree of dissociation and improvement on the quadratic polarizability (since the slope of all the plots in Figure 1 is negative) in solution are the same. Thus, we propose that the DRS technique may be used as a probe for measuring \( pK_a \) of weak organic acids.

In conclusion, we have demonstrated that \( pK_a \) and \( \beta \) of weak organic acids in solution are linearly connected. Since we have chosen the solvents and NLO chromophores randomly, we believe that this inference is general. Currently, we are developing a more generalized model for describing this dependence quantitatively.

7. The experimental apparatus will be described elsewhere in detail.
RESEARCH COMMUNICATIONS

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