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

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Second-order nonlinearities (β) of five 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 pK_a of these compounds in those solvents. A direct implication of this observation is that the DRS technique can be used to determine the pK_a of weak organic acids in any solvent.

It has been generally recognized[1,2] 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[3], 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[4–6] 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 sulphonic acids in some polar protic solvents and demonstrate that β bears a linear relationship with the pK_a of these weak acids in those solvents.

Compounds a–e were purchased from Aldrich and their β values measured by the DRS technique[7] 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 $4 \times 4 \times 2\ \text{cm}^3$ 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, I_{2w}, and the incident beam, I_0, are related by[8,9]

$$I_{2w} = GB^2 I_0^2 = G \sum_k N_k \,|\beta_k|^2\, I_0^2, \qquad (1)$$

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. N_k is the number density of the kth specie with second-order polarizability β_k. For a two-component system,

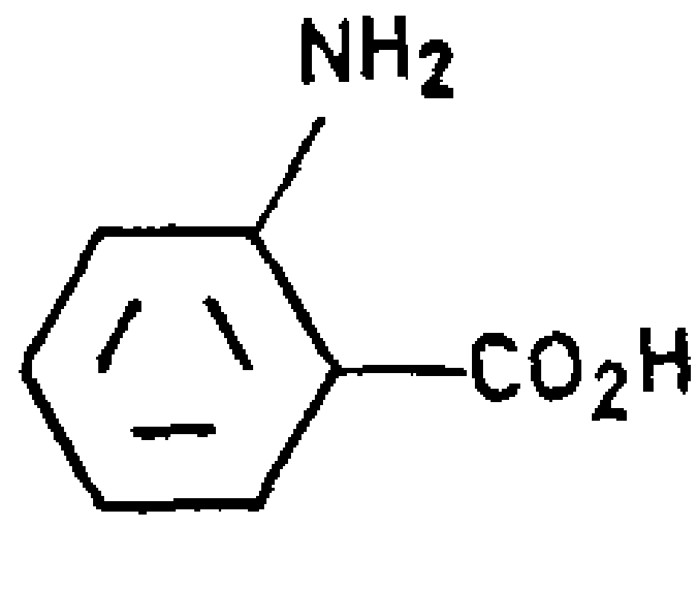
$$B^2 = N_{\text{solvent}}\ \beta^2_{\text{solvent}} + N_{\text{solute}}\ \beta^2_{\text{solute}}. \qquad (2)$$

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 GB^2 on N_{solute}. From the intercept and slope we calculated β_{solute} and G since β_{solvent} is known. Chloroform was calibrated with respect to carbon tetrachloride by the method described in detail by Zyss *et al.*[10], 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^{-30} esu.

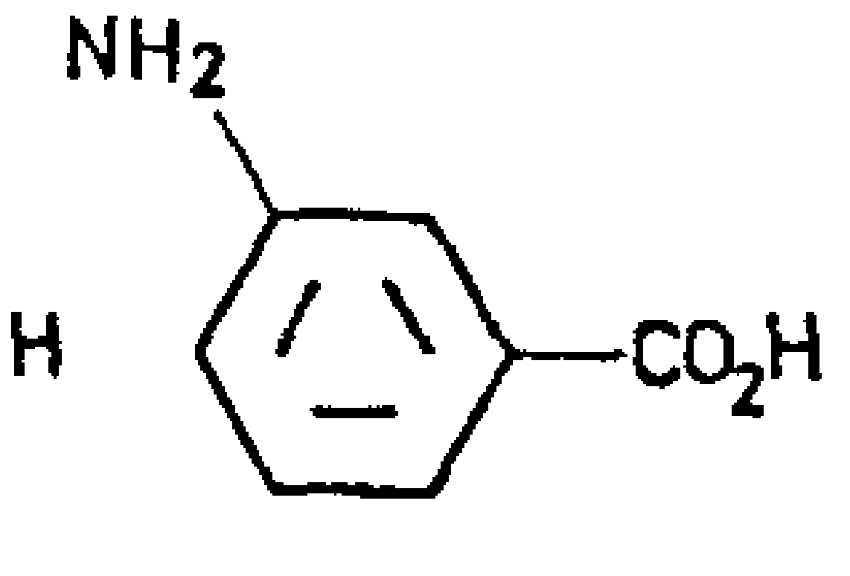
The β values of a–e obtained from DRS experiments in methanol, ethanol, isopropanol and water are listed in Table 1. All these compounds have an electron donor

Table 1. Quadratic hyperpolarizabilities ($\beta_{\text{DRS}} \times 10^{30}$ esu) of compounds a–e in different solvents and their calculated β ($\beta_{\text{calc}} \times 10^{30}$ esu) values

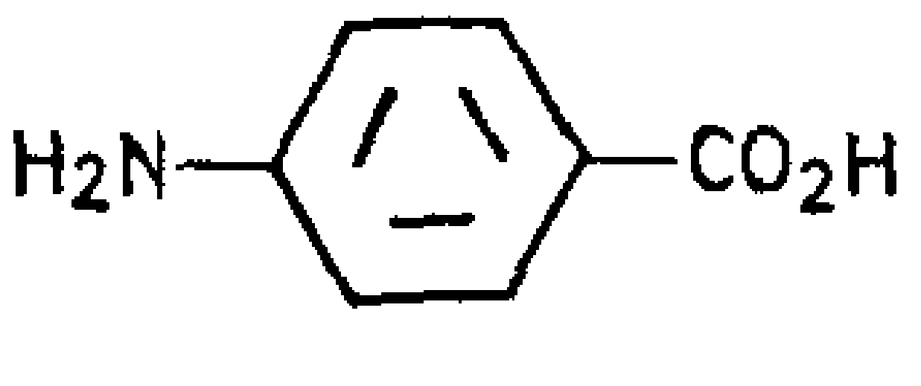
		β_{DRS}			
Compound	$\beta_{\text{calc.}}$	Methanol	Ethanol	Isopropanol	Water
a	2.0	6.8	7.2	7.8	9.0
b	4.2	10.2	11.0	11.6	13.0
c	5.5	15.8	16.6	17.2	18.5
d	5.2	14.8	16.1	17.2	20.0
e	6.1	20.8	22.9	23.4	26.2



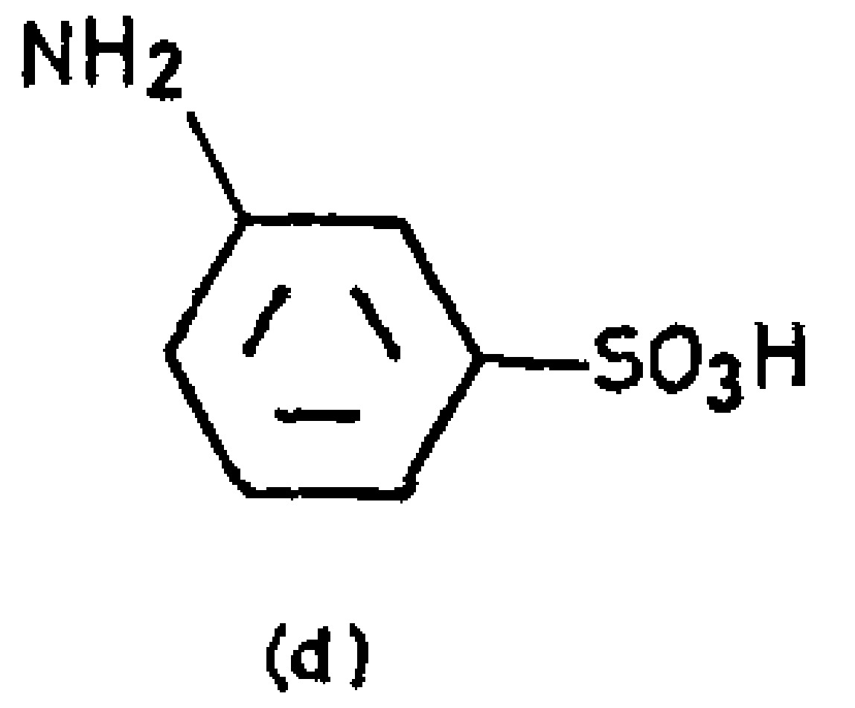
(a)



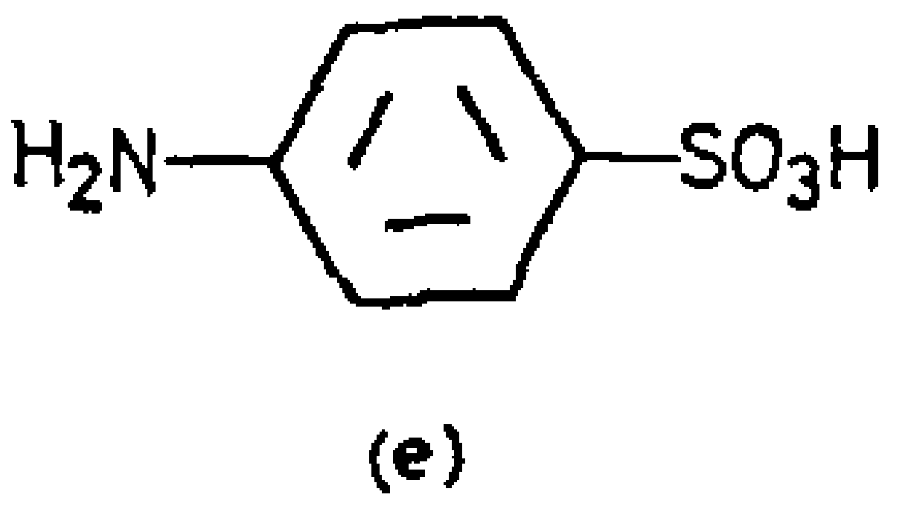
(b)



(c)



(d)



(e)

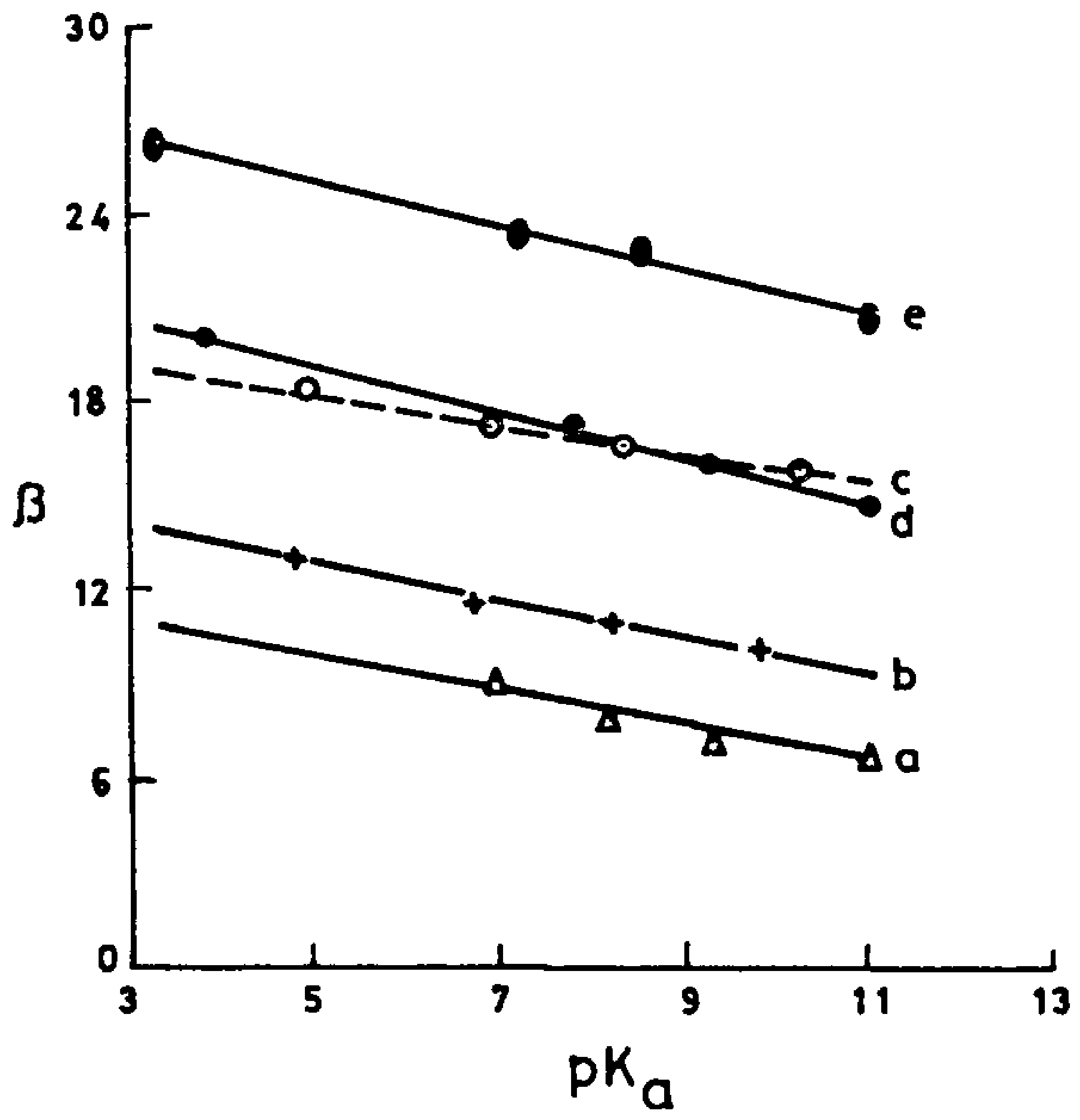


Figure 1. pK_a vs β_{DRS} ($\times 10^{-30}$ esu) plot for compounds a–e. The straight line is a linear least-squares fit through the experimental points. The intercepts (at pK_a = 3.0) and slopes are: *a*, 10.6, −0.53; *b*, 14.0, −0.55; *c*, 22.7, −0.72, *d*, 20.4, −0.65; and *e*, 28.4, −0.68, respectively.

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[11,12]. For the common amino donor we expect the sulfonic-acid-substituted derivative to exhibit higher β 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 β for these compounds using the PM3 parametrization within the MOPAC[13,14] package with full geometry optimization. The calculated β values are purely gas phase numbers and do not include the solvent effects. But the experimental trend in β 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[15–18] may alter the NLO characteristics (i.e. β) and we can write various components of β as

$$\beta = \beta_g + \beta_{hb} + \beta_{int}, \qquad (3)$$

where β_g is the quadratic polarizability of the molecules in the gas phase (i.e. isolated) and β_{hb} and β_{int} correspond to hydrogen bonding (intermolecular and intramolecular) and intermolecular interaction (dipole–dipole, ion–dipole, ion–ion, etc.) contributions to β, respectively. For different solvents these components of β 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 β 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 β 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 β 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.

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1. Chemla, D S. and Zyss, J., *Nonlinear Optical Properties of Organic Molecules and Crystals*, Academic Press, New York, 1987, vols 1 and 2; see the references therein.
2. Marder, S. R., Sohn, J. E., Stucky, G. D. (eds), *Materials for Nonlinear Optics: Chemical Perspectives*, American Chemical Society Symposium Series 455, American Chemical Society, Washington DC, 1991.
3. Levine, B. F. and Bethea, C. G., *J. Chem. Phys.*, 1975, **63**, 2666–2673.
4. Clays, K. and Persoon, A., *Phys. Rev. Lett.*, 1991, **66**, 2980–2983.
5. Clays, K. and Persoon, A., *Rev. Sci Instrum.*, 1992, **63**, 3285–3289.
6. Laidlaw, W. M., Denning, R. G., Verbiest, T., Chauchard, E. and Persoon, A., *Nature*, 1993, **363**, 58–60.
7. The experimental apparatus will be described elsewhere in detail.
8. Terhune, R. W., Marker, P. D. and Savage, C. M, *Phys. Rev. Lett*, 1965, **17**, 681–684.
9. Bersohn, R., Pao, Y. H and Frisch, H. L., *J. Chem Phys.*, 1966, **45**, 3184–3199.
10. Zyss, J., Van, T. C., Dhenaut, C. and Ledoux, I., *Chem. Phys*, 1993, **177**, 281–296.
11. Cheng, L. T., Tam, W., Meredith, G. R, Rikken, G. L. J. A. and Meijer, E W., in *Nonlinear Optical Properties of Organic Materials II* (eds Khanarian, G), SPIE Proceedings, 1989, vol. 1147, pp. 61–72.
12. Matsuzawa, N. and Dixon, D. A, *J. Phys. Chem*, 1992, **96**, 6232.
13. Stewart, J. J P., *J. Comput Chem*, 1989, **10**, 221–264.
14. Kurtz, H. A, Stewart, J J. P. and Dieter, K. M, *J. Comput Chem.*, 1990, **11**, 82–67.
15. Zyss, J. and Ledoux, I, *Chem. Phys*, 1982, **73**, 203–213
16. Singer, K D. and Garito, A F, *J Chem. Phys*, 1981, **75**, 3572–3580

17. Clark, T and Chandrasekhar, J., *Isr J Chem.*, 1993, 33, 435–448
18 Sen, R., Majumdar, D. and Bhattacharyya, S P, *Chem Phys. Lett.*, 1992, 190, 443–446
19 *CRC Handbook of Chemistry and Physics*, 61st edition
20. *Lange's Handbook of Chemistry*, 13th edition, McGraw-Hill
21. Lurie, Ju, *Handbook of Analytical Chemistry*, Mir Publishers, Moscow.

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