

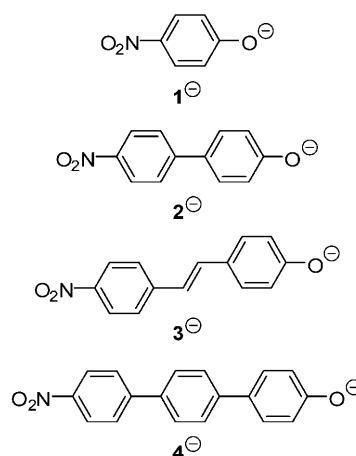
## Absorption Spectra of 4-Nitrophenolate Ions Measured *in Vacuo* and in Solution

Maj-Britt Suhr Kirketerp,<sup>[c]</sup> Michael Åxman Petersen,<sup>[b]</sup> Marius Wanko,<sup>[a]</sup> Leonardo Andres Espinosa Leal,<sup>[a]</sup> Henning Zettergren,<sup>[c]</sup> Francisco M. Raymo,<sup>[d]</sup> Angel Rubio,<sup>\*,[a]</sup> Mogens Brøndsted Nielsen,<sup>\*,[b]</sup> and Steen Brøndsted Nielsen<sup>\*,[c]</sup>

Hyperpolarizable organic molecules that display intramolecular charge transfer (ICT) transitions are important building blocks for advanced optical materials.<sup>[1]</sup> One such class of species is the *p*-nitrophenolates that serve as donor–acceptor molecules, or so-called push–pull chromophores, since an electron is transferred from the negatively charged phenolate to the nitro group upon photoexcitation, with a significant change in the charge distribution. The  $\pi\pi^*$  transition is not purely CT in character due to the highly delocalized donor and acceptor orbitals. Both the phenolate and nitro group oxygen atoms are strong hydrogen-bond acceptors and the nitro group has an additional tendency to coordinate with metal centers—properties successfully employed for engineering of nonlinear optical (NLO) materials.<sup>[2]</sup> In this regard, it is advantageous to know the intrinsic absorption of the isolated molecule or ion to shed light on the electronic perturbation by a microenvironment and, not least, to provide a reference to benchmark theory. An approximate approach is to characterize molecules spectroscopically in solvents of varying polarity and thereafter to extrapolate to vacuum. Several scales have been developed based on the energy of inter- or intramolecular CT transitions, such as the Dimroth–Reichard  $E_T(30)$ ,<sup>[3]</sup> the Z-scale,<sup>[4]</sup> the  $\pi\pi^*$ -scale,<sup>[5]</sup> and taking into account H-bond interactions.<sup>[6]</sup> The situation is more complicated when one wants to correlate the

ICT of anionic nitrophenolates with solvent polarity. Ionophores are not easily dissolved in nonpolar solvents and even then there are field effects from counter ions. In polar solvents, the ground and excited states are stabilized to different extents, which results in solvatochromic shifts.

To determine the intrinsic optical properties, it is necessary to carry out experiments on bare molecular ions *in vacuo*. Herein we report gas-phase absorption spectra of four *p*-nitrophenolates, **1**<sup>−</sup>, **2**<sup>−</sup>, **3**<sup>−</sup>, and **4**<sup>−</sup> (Figure 1).<sup>[7]</sup> The ions are charac-



**Figure 1.** Phenylgous nitrate ions (**1**, **2**, **4**) and a combination of a phenylgous and a vinylogous nitrate ion (**3**) chosen for study.

terized by different  $\pi$ -conjugated spacers between the donor and acceptor groups and were chosen to elucidate the influence of the number of phenylene spacers and deviations from planarity. Results are compared to advanced quantum-chemical calculations and solution-phase measurements.

Gas-phase spectroscopy on molecules that are easily evaporated is routinely done whereas experiments on ions require specialized instrumentation. An inherent problem in the latter case is the presence of too few chromophores to cause a measurable decrease in the incoming light intensity, implying that conventional spectroscopy does not work. Instead, gas-phase UV/Vis absorption spectra are derived from the photo-induced homolytic dissociation of the chromophore and by monitoring one or more of its photoproducts. We use the electrostatic ion storage ring in Aarhus, ELISA (Figure 2), which, when combined with lasers, work as a gas-phase optical cell.<sup>[8]</sup> Ions are produced by electrospray ionization, stored in a 22-pole pretrap, accelerated as a bunch to 22 keV energies and in-

[a] Dr. M. Wanko, L. Andres Espinosa Leal, Prof. A. Rubio  
NanoBio Spectroscopy Group and ETSF Centre for Scientific Development  
Centro Mixto CSIC-UPV/EHU "Física de Materiales"  
University of the Basque Country  
UPV/EHU Centro Joxe Mari Korta  
Avenida de Tolosa, 72, E-20018 Donostia-San Sebastian (Spain)  
Fax: (+34) 943018390  
E-mail: Angel.Rubio@ehu.es

[b] Dr. M. Åxman Petersen, Prof. M. Brøndsted Nielsen  
Department of Chemistry  
University of Copenhagen, Universitetsparken 5  
DK-2100 Copenhagen Ø (Denmark)  
Fax: (+45) 3532 0212  
E-mail: mbn@kiku.dk

[c] M.-B. Suhr Kirketerp, Dr. H. Zettergren, Prof. S. Brøndsted Nielsen  
Department of Physics and Astronomy  
Aarhus University, Ny Munkegade  
DK-8000 Aarhus C (Denmark)  
Fax: (+45) 8612 0740  
E-mail: sbn@phys.au.dk

[d] Prof. F. M. Raymo  
Department of Chemistry  
University of Miami, 1301 Memorial Drive  
Florida, 33146-0431 (USA)

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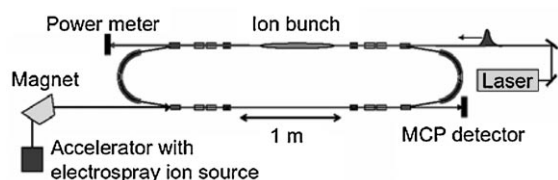


Figure 2. Instrumental setup for gas-phase spectroscopy.

jected into the ring. Here they circulate until they change their kinetic-energy-to-charge ratio by dissociation. After tens of milliseconds, the ions are irradiated by light at one side of the ring. If ionic dissociation occurs at the opposite side to the laser interaction region, the neutrals formed move undisturbed and hit the MCP detector at the end of the track, which gives rise to counts. A spectrum of the neutrals yield is obtained as a function of excitation wavelength.<sup>[9,10]</sup>

The dominant reaction after photoexcitation of nitrophenolates is loss of NO, occurring on a  $\mu\text{s}$  to ms time scale, and identified by operating ELISA as a mass spectrometer.<sup>[11]</sup> The number of photoexcited ions as a function of  $\lambda$  was obtained from exponential fits to time decay spectra and normalized by the photon flux and ion beam intensity (Figure 3). The lowest-energy absorption maxima are at 392, 541, 660, and 775 nm for  $1^-$ ,  $2^-$ ,  $3^-$ , and  $4^-$ , respectively. Thus, our data show that  $\lambda_{\text{max}}$  red-shifts along the progression

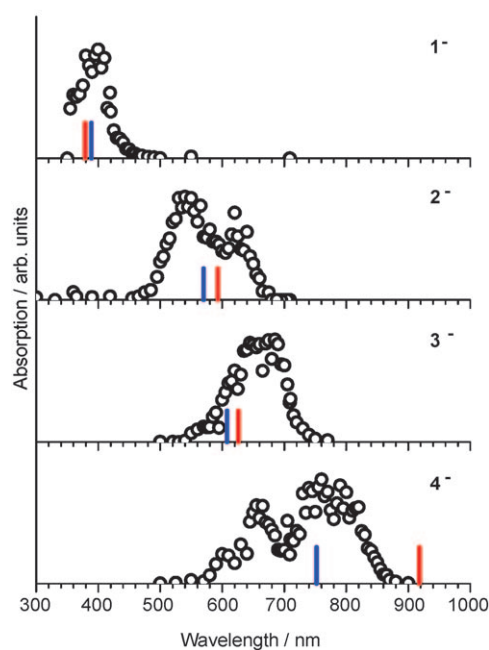


Figure 3. Gas phase absorption spectra. The vertical lines are calculated  $\lambda_{\text{max}}$  values, in blue CC2 and in red TDDFT.

$1^-$ ,  $2^-$ ,  $4^-$ . The absorption of the stilbene derivative  $3^-$  is found intermediate that of  $2^-$  and  $4^-$ .

Theoretical results were obtained with time-dependent density functional theory (TDDFT) and the CC2 coupled-cluster linear response methods.<sup>[12]</sup> The dipole-allowed  $\pi\pi^*$  transition is to the  $2^1A_1$  excited state, which is lowest in energy. The frontier orbitals are of  $B_1$  symmetry ( $C_{2v}$ ), and the transition dipole moment is along the long axis of the molecule. CC2 transition energies (Figure 3 and Table 1) are in excellent agreement with the experiments. TDDFT performs as well for  $1^-$ ,  $2^-$ ,  $3^-$  but less so for  $4^-$  (Table 1).

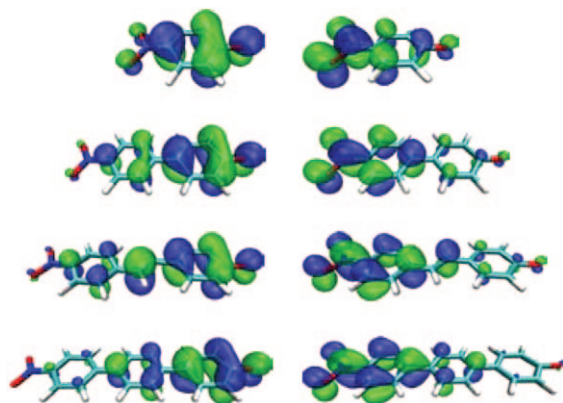
Table 1. Longest-wavelength absorption maxima ( $\lambda_{\text{max}}$ ) of *p*-nitrophenolates<sup>[a]</sup> in different solvents and in the gas phase. The values of  $\lambda_{\text{max}}$  are in nm.

Compound	H <sub>2</sub> O	Solution			Exp	Gas phase	
		MeOH	Toluene (+ 18C6)	MeCN		CC2	TDDFT
$1^-$	402 <sup>[7d]</sup>	387	408	430	392	389	379
$2^-$	400 <sup>[7c]</sup>	406	472	507	541	570	593
$3^-$		435	504	543	660	608	626
$4^-$		377	445	466	775	752	918

[a] As sodium phenolate in solution (obtained by deprotonation of corresponding phenol by NaOMe).

Both DFT and MP2 predict non-planar geometries for  $2^-$  and  $4^-$  but a nearly flat potential energy surface. The planar transition state for  $2^-$  is 0.02 eV above the minimum (MP2/TZVPP). The dihedral angle between the phenyl rings depends on the method. Hybrid DFT (PBE0/TZVP) predicts rotations of 15–22° and MP2/TZVPP 20.1–28.7°. According to MP2, the angle decreases with the completeness of the basis set. Hence the planar and non-planar geometries represent limiting cases to estimate the fluctuation in the vertical excitation energy at 0.05–0.07 eV and 0.06–0.17 eV for  $2^-$  and  $4^-$ , respectively, (Table S2); an angle of 0° results in a blue-shift. This may explain the sidebands in the spectra as there are no other dipole-allowed transitions in the region. The bands may, however, also be due to vibrational progressions.

The  $\lambda_{\text{max}}$  of the anions in three solvents are given in Table 1. Phenolates were obtained by deprotonation of phenols using NaOMe as base. In MeCN, the  $\lambda_{\text{max}}$  of  $1^-$  is red-shifted by 38 nm compared to vacuum, characteristic for  $\pi\pi^*$  transitions. A significant blue-shift is seen for the other three anions, most pronounced for  $4^-$  (309 nm), in agreement with HOMO and LUMO orbitals (Figure 4). Thus, SORCI<sup>[13]</sup> and CC2 calculations predict a considerable CT from phenolate to nitrophenyl, and that the difference in dipole moment between the ground and the first excited state increases with the length of the molecule, 27 D for  $4^-$ ! (See the Supporting Information, which contains experimental and computational details; calculated vertical excitation energies, oscillator strengths, difference dipole moments, and solvent shifts.) Counter ions and solvent dipoles therefore stabilize the ground state more than the excited state, an effect that increases in the order  $2^- < 3^- < 4^-$ . The CT is slightly enhanced by out-of-plane torsion of the phenyl



**Figure 4.** State-averaged natural orbitals from 2-root DDCI2 calculations. Left: HOMO, right: LUMO.

rings, which again increases in the presence of a counter ion. Nonetheless, the shift is almost the same for the planar and the nonplanar geometries. In water and methanol, the blue-shift is even larger for  $2^-$ ,  $3^-$ , and  $4^-$  owing to H-bonds.

Sodium phenolates are not soluble in toluene, but are brought into solution using the crown ether 18-crown-6 (18C6) that encapsulates  $\text{Na}^+$  in its cavity. While the maxima in this medium are red-shifted relative to those in MeOH, they are in fact all at higher energy than those in the more polar solvent MeCN. Clearly, interactions with the metal ion play an important role in toluene. According to ion-pair calculations and a continuum electrostatic model, H-bonding, structural effects and the shielding of the counter ion by the crown ether in toluene are essential.

In conclusion, we have recorded gas phase absorption spectra of four nitrophenolate anions and found that the CC2 model provides excellent predictions of the maxima. While only a relatively narrow spectral region is covered by the four chromophores in solution, they cover the entire visible region when isolated in vacuo. The large shifts can be explained by the CT character of the electronic transition. Calculations reveal that the solvent shift is mainly a result of counter ion and H-bond interactions. Therefore, it does not seem viable to correlate the data with one of the solvent polarity scales. For setting the reference point for the intrinsic absorptions of the chromophore anions, gas phase results are indeed required.

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