Large Enhancement of the Nonlinear Optical Response of Reduced Fullerene Derivatives

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Abstract: The third-order nonlinear optical properties of fulleropyrrolidine and its salt as well as their reduced forms are investigated. Upon reduction, the response increases by up to, and sometimes more than, three orders of magnitude, giving values comparable to the largest ever reported. Calculations and experiments provide a coherent picture for the nonlinear optical properties of these new materials.

Keywords: fullerenes • hyperpolarizability • nonlinear optics • quantum chemistry

Introduction

A key parameter for photonic applications is the nonlinear optical response of materials. Within this context, fullerenes have been shown to possess good nonlinear optical properties though, perhaps, not entirely outstanding.[1] Chemical modifications of the fullerenic cage can tune the photophysical properties,[2] while oxidation/reduction can change electronic states in a drastic way, making doped fullerene superconducting.[3] C_{60} reduction can also increase its second-order hyperpolarizability by nearly two orders of magnitude.[4] In this work, we investigate the nonlinear optical response of a C_{60} derivative, namely the prototypical fulleropyrrolidine, its fulleropyrrolidinium salt and their reduced forms and show that increases of up to and sometimes exceeding three orders of magnitude, with respect to the neutral molecule, can be achieved. Z-scan and the optical Kerr effect (OKE) techniques, along with a combination of semiempirical and density function theory (DFT) quantum chemical calculations provide a coherent picture; they indicate that extensive modification of the signal is caused by the lowering of the electronic transitions and this affects both the real and the imaginary part of the response.

Experimental Section

Two different techniques were employed for the characterization of the third-order nonlinear response. The Z-scan technique[5] was used for the determination of the nonlinear absorption and refraction in the case of the transient response of the molecules (upon nanosecond excitation), whereas the optical Kerr effect (OKE)[6] was employed for the determination of the modulus of $\chi^{(3)}$ of the instantaneous response (upon femtosecond excitation).

The Z-scan is a well-known and efficient technique for the determination of the nonlinear optical parameters of a material, providing simultaneously the magnitude of the nonlinear absorption and the magnitude and the sign of the nonlinear refraction of the material under study. This technique is based essentially on the measurement of the transmission of a focused laser beam through the sample, as a function of the sample position with respect to the focal plane of the focusing lens.

In our Z-scan experiments the second harmonic of an Nd YAG laser at 532 nm or 2.33 eV, with pulse duration of 10 ns and a repetition rate of 5 Hz was employed. The laser beam, after being focused by a 15 cm focal length lens into the sample, was passed through a large-area 50% beam splitter. That part of the beam transmitted through the splitter beam was passed through an aperture in the far field and then measured by a photomultiplier. The portion of the beam reflected by the beam splitter was collected by a large aperture lens (ensuring collection of the total light transmitted through the sample) and then measured by a photomultiplier. The variation of the transmission of the focused laser beam in these two cases, as a function of the sample distance from the focal plane, gives rise to what are called closed- and open-aperture Z-scan measurements, respectively. The beam radius at the focus was determined to be about 40 μm, and the sample position in respect to the focal plane of the laser beam was

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controlled by a computer-controlled stepper motor. The details of the determination of the nonlinear absorption and refraction parameters, β and γ' respectively, have been given elsewhere.[7]

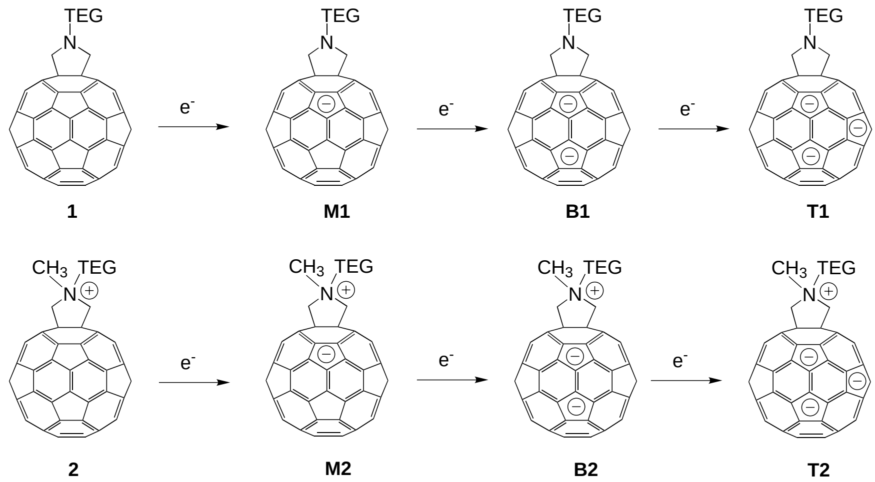

Figure 1. Reduction scheme (TEG $= -C_2H_4OC_2H_4OC_2H_4OCH_3$).

The OKE technique has been used extensively for the determination of the response time of the electronic third-order nonlinear optical response of materials and the magnitude of the same component of the susceptibility $\chi^{(3)}$ as that measured with Z-scan. For the OKE measurements, a standard delay-line Mach – Zehnder interferometer was employed. A Spectra Physics Tsunami Ti:Sapphire laser, operating at 800 nm, 100 fs with a repetition rate of 81 MHz was used as the excitation source. The laser beam was split into two parts, the pump and the probe beams; the intensity of the probe beam was kept 100 times less than that of the pump beam, and both beams were linearly polarized with a 45° difference in their polarization state. A variable delay was introduced into the probe beam; this was also modulated by means of a chopper at a frequency of 1 kHz. The two beams were combined in the sample using a 10 cm focal length lens, the beam diameters at the focal plane being around 60 μm. The transmitted probe beam was passed through an analyzer (Glan Thomson), while the pump beam was dumped. The probe beam was collected with a photomultiplier and measured by means of a lock-in amplifier. For determination of the third-order susceptibility and the corresponding second hyperpolarizability of the materials, CS_2 was used as a reference material.[8]

Materials: Fulleropyrrolidines are fullerene derivatives synthesized through 1,3-dipolar cycloaddition of azomethine ylides to C_{60}.[9] Depending on the the reaction time, a monoadduct (compound **1**), or eight bisadduct isomers are obtained.[10] Reaction of fulleropyrrolidine(s) with excess of methyliodide produces the fulleropyrrolidinium salt(s) (compound **2**). All the compounds can be reduced by Rb. Single reduction is indicated with **M**, double reduction is labelled with **B**, triple reduction is labelled with **T**. The singly reduced form of fulleropyrrolidine, **M1**, is a radical anion, the singly reduced form of fulleropyrrolidinium salt, **M2**, is a neutral radical, the doubly reduced form of fulleropyrrolidine, **B1**, is a dianion, etc (Figure 1).

The compounds **1** and **2** were prepared following the synthetic method described elsewhere.[9, 10] Rb (99.9 %) and anhydrous benzonitrile were purchased from Aldrich and used without further purification. In a glove box, stoichiometric amounts of Rb and compounds **1** and **2**, respectively, were introduced inside flasks containing benzonitrile (5 mL) and the mixtures were left to stir overnight at room temperature so that compounds **1** and **2** were reduced. After the reduction, the color of the solution of singly- and doubly-reduced species changed from dark brown to dark brown-green, while in the case of the triple reduction, a dark red color was obtained. Compound **1** was dissolved in toluene and compound **2** in DMSO, while their reduced forms were soluble in benzonitrile. For **1** and **2**, the concentration was 1 mm. For the reduced forms, solutions of 1 mm were used for the transient response and 0.05 mm for the electronic response measurements. These solutions of the reduced forms were prepared inside the glove box and introduced to special airtight quartz cuvettes of 1 mm path length. The nonlinear optical response was measured directly after preparation to ensure that no chemical modification of the compounds had occurred. The absorption spectra of the compounds were recorded with a Perkin – Elmer spectrophotometer and were examined before and after the irradiation to ensure that no photodegradation of the compounds had been induced.

Computational methods: Two quantum chemical models were used. The first was based on density functional theory (DFT) and is identified by the acronym B3LYP/6-31G*.[11, 12] The Gaussian 98 suite of programs[13] allows the introduction of an electric field along one or more directions. The calculated energies can be use to obtain, by numerical differentiation, the field dependent derivatives up to the second hyperpolarizability, γ. The model provides the zero-field, zero-frequency polarizabilities, which are expected to underestimate the real values since in reality neither field nor frequency is zero.

The second model was based on the complete neglect of differential overlap/spectroscopic parameterization (CNDO/S),[14] which has been highly successful in the description of both linear and nonlinear optical properties of fullerenes.[15] The calculation of the hyperpolarizabilities was performed by using all the Orr – Ward diagrams[16] whereby the generalised second-order hyperpolarizability is given by Equation (1):

$$\begin{aligned}\gamma^{S_n}_{ijkl}(-\omega_4;\omega_1,\omega_2,\omega_3) = K(-\omega_4;\omega_1,\omega_2,\omega_3)\left(\frac{e^4}{\hbar^3}\right) I_{1,2,3}\Bigg[\sum{}'_{abc}\Bigg(&\frac{r^i_{nc}\bar{r}^l_{cb}\bar{r}^k_{ba}r^j_{an}}{(\omega_{cn}-\omega_4)(\omega_{bn}-\omega_1-\omega_2)(\omega_{an}-\omega_1)} + \frac{r^l_{nc}\bar{r}^i_{cb}\bar{r}^k_{ba}r^j_{an}}{(\omega^*_{cn}+\omega_3)(\omega_{bn}-\omega_1-\omega_2)(\omega_{an}-\omega_1)}\\ &+\frac{r^j_{nc}\bar{r}^k_{cb}\bar{r}^i_{ba}r^l_{an}}{(\omega^*_{cn}+\omega_1)(\omega^*_{bn}+\omega_1+\omega_2)(\omega_{an}-\omega_3)} + \frac{r^j_{nc}\bar{r}^k_{cb}\bar{r}^l_{ba}r^i_{an}}{(\omega^*_{cn}+\omega_1)(\omega^*_{bn}+\omega_1+\omega_2)(\omega^*_{an}+\omega_4)}\Bigg) - \sum{}'_{ab}\Bigg(\frac{r^i_{nb}r^l_{bn}r^k_{na}r^j_{an}}{(\omega_{bn}-\omega_4)(\omega_{bn}-\omega_3)(\omega_{an}-\omega_1)}\\ &+\frac{r^i_{nb}r^l_{bn}r^k_{na}r^j_{an}}{(\omega_{bn}-\omega_3)(\omega^*_{an}+\omega_2)(\omega_{an}-\omega_1)} + \frac{r^l_{nb}r^i_{bn}r^j_{na}r^k_{an}}{(\omega^*_{bn}+\omega_4)(\omega^*_{bn}+\omega_3)(\omega^*_{an}+\omega_1)} + \frac{r^l_{nb}r^i_{bn}r^j_{na}r^k_{an}}{(\omega^*_{bn}+\omega_3)(\omega_{an}-\omega_2)(\omega^*_{an}+\omega_1)}\Bigg)\Bigg]\end{aligned} \quad (1)$$

In Equation (1) i, j, k are the Cartesian axes, $K(-\omega_4;\omega_1,\omega_2;\omega_3)$ describes the nature of the technique used to investigate the NLO properties; $I_{1,2,3}$ denotes all possible permutations of the three indices, and r represents the transition dipole moment. Our set of experiments measured $\gamma(\omega;\omega,-\omega;\omega)$. For both models, direct comparison with experiment was possible through $\langle\gamma\rangle$ [Eq. (2)]:

$$\langle\gamma\rangle = (\gamma^2_{\mathrm{R}} + \gamma^2_{\mathrm{I}})^{1/2} \quad (2)$$

whereby γ_{R} and γ_{I} are the real and the imaginary components which are given by Equation (3) in which s is either the real or the imaginary part of the response.

$$\gamma_{\mathrm{s}} = {}^1\!/_5[{}^1\!/_3\{\sum_{i \neq j}(\gamma_{iijj} + \gamma_{ijji} + \gamma_{ijij})\} + \gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz}] \quad (3)$$

To make the presentation of the results more pleasing to the eye, the stick spectrum obtained from the calculations, that is, energies and cross sections, was then broadened by multiplying it by a function $G(\nu)$ [Eq. (4)]:

$$\mathrm{G}(\nu) = \frac{\mathrm{e}^{-(\nu-\nu_0)^2/\mathrm{a}^2}}{(a\sqrt{\pi})} \qquad (4)$$

in which ν is the wavenumber of the incident radiation (in $\mathrm{cm^{-1}}$), ν_0 is the wavenumber at which the NLO calculation was performed (in $\mathrm{cm^{-1}}$), and "a" is a constant, which was here taken to be $1000\ \mathrm{cm^{-1}}$.

Results and Discussion

The first issue to address is the existence of the six reduced species, **M1**, **B1**, **T1**, **M2**, **B2**, **T2**, in the experiments when one, two, or three equivalents of Rb are dissolved in the solutions.[17] The major peaks of the absorption spectra, presented in Figure 2, show that after addition of the first equivalent of Rb to **1**, the spectrum of **M1** (Figure 2 top) appears, giving a peak at 1000 nm in agreement with reference [18]. Further addition of Rb does not alter these spectra, indicating that either the spectra of **B1** and **T1** are less intense than that of **M1** or that these reduced forms are not formed. After the addition of the first equivalent of Rb to **2**, the spectrum of **M2** (Figure 2 bottom) presents a peak at 1020 nm, in agreement with reference [18]. Addition of a second equivalent of Rb leaves the band centered at 1020 nm unchanged and produces a second band at 890 nm; therefore, it is possible that **M2** and **B2** co-exist in solution. Addition of a third equivalent of Rb retains the bands centered at 1020 nm and 890 nm, and produces a third band at 740 nm; thus, it is possible that **M2**, **B2**, and **T2** co-exist in solution. Although co-existence of some of the reduced species can occur, for simplicity in the following we shall refer to the solutions obtained by the use of the different equivalents of Rb with the **M1** to **T2** nomenclature.

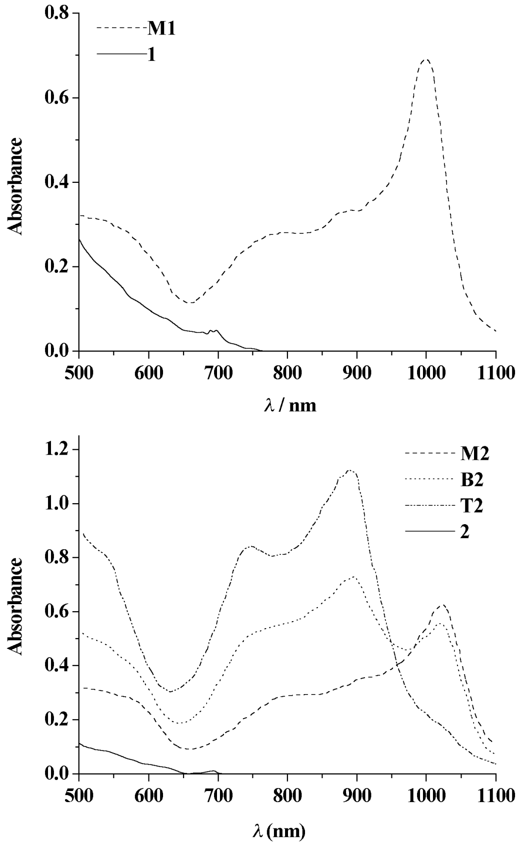

Figure 2. Absorption spectra of the reduced forms of fulleropyrrolidine (top) and fulleropyrrolidinium salt (bottom) (see text).

Z-scan measurements were performed for solutions of 1 mM in concentration, irradiated at 532 nm, 10 ns laser radiation, with 60–200 $\mathrm{MW\,cm^{-2}}$ intensities. In this regime, the solvent response was found to be negligible. Under these experimental conditions, the response of the compounds depends on the population of the excited states; therefore a transient response is expected. All systems were observed to exhibit significant nonlinear absorption and refraction, the latter having a negative sign. The nonlinear refraction was slightly larger in the derivatives of the fulleropyrrolidinium salt and was maximal for T2. Table 1 summarizes the linear absorption, the real and imaginary parts of the third-order susceptibility, and the second hyperpolarizability of **1**, **2**, **M1**, **M2**, **B2**, and **T2**. Reduction enhances the linear absorption and the real part of the third-order susceptibility. In contrast, the nonlinear absorption and the corresponding imaginary part of the third-order susceptibility decreases with reduction, the decrease becoming stronger for compound **T2**. Interestingly, the ratio $\mathrm{Re}\chi^{(3)}/\mathrm{Im}\chi^{(3)}$ increases as a function of the reduction and varies between 3 for **2** to 48.5 for **T2**. In passing, it should be mentioned that the optical limiting activity of the reduced forms was tested and found to be low, because of their large linear absorption.

Table 1. Nonlinear optical parameters of the compounds studied with 10 ns, 532 nm laser radiation. All solutions are 1 mM.

Sample	Species	α_0 [$\mathrm{cm^{-1}}$]	$\mathrm{Im}\chi^{(3)}$ [10^{-12} esu]	$\mathrm{Re}\chi^{(3)}$ [10^{-12} esu]	γ [10^{-29} esu]
monoadduct	**1**	2.9	16.21	37.26	1.6
monoadduct + 1 Rb	**M1**	5.0	9.39	39.92	1.6
salt of monoadduct	**2**	2.1	10.51	32.08	1.4
salt of monoadduct + 1 Rb	**M2**	7.2	8.76	45.83	1.8
salt of monoadduct + 2 Rb	**B2**	11.0	5.63	44.35	1.7
salt of monoadduct + 3 Rb	**T2**	18.8	1.25	60.62	2.3

OKE measurements were performed on 1 mM solutions of the pristine fulleropyrrolidine **1** and 0.05 mM solutions of the reduced species **M1**. They were irradiated at 800 nm, with 100 fs pulses and a repetition rate of 81 MHz. The technique measures the purely electronic response. Figure 3 shows the intensity dependence of the signal for **1**, **M1**, benzonitrile, toluene, and the reference material $\mathrm{CS_2}$. The response of **1** is similar to that of the solvents and to that reported for $\mathrm{C_{60}}$.[19] By using the value for $\mathrm{CS_2}$ and the appropriate formalism,[7, 20] the nonlinear refractive index of compound **1**, n_2, is approximately 0.55×10^{-13} esu. The signal of **M1** is, on the other hand, very strong. If one accounts for the lower concentration, n_2 is estimated to be 3.52×10^{-10} esu, that is 6400 times larger

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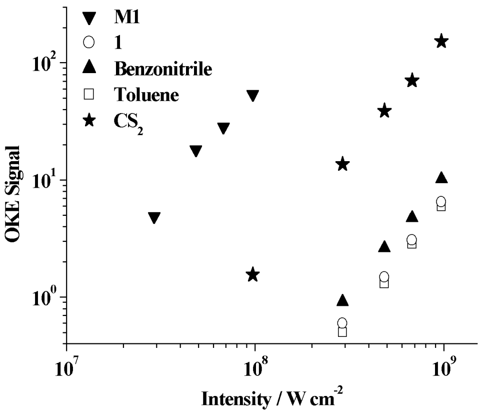

Figure 3. Signal for fulleropyrrolidine, its reduced form, benzonitrile, toluene, and reference compound CS_2.

than in the neutral species. Figure 4 shows the intensity dependence of the signal of **2**, **M2**, benzonitrile, DMSO, and CS_2. Methylation of **1** to give **2** increases the nonlinearity 14-fold. Upon reduction, however, n_2 becomes 1.00×10^{-10} esu, that is, n_2(**M1**):n_2(**M2**) = 3.52:1.00 and reduction of **2** increases its nonlinearity by 130 times only. Figure 5 shows the response obtained by further reductions of **2**. Both the doubly reduced **B2** and the triply reduced **T2** species have a slightly smaller n_2 than **M1**, which is estimated to be 3.20×10^{-10} esu.

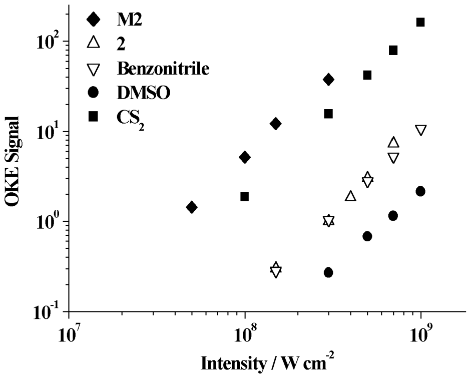

Figure 4. Signal for fulleropyrrolidinium salt, its reduced form, benzonitrile, DMSO, and reference compound CS_2.

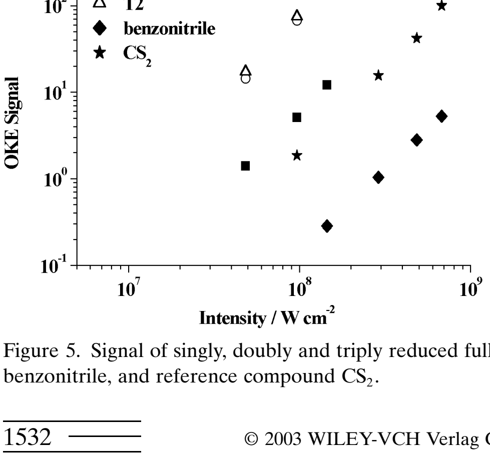

Figure 5. Signal of singly, doubly and triply reduced fulleropyrrolidinium, benzonitrile, and reference compound CS_2.

Reduction of the monoadduct of fulleropyrrolidine and its salt greatly increases their purely electronic second-order hyperpolarizability. Further investigations were carried out computationally. B3LYP/6-31G* density functional theory based calculations of the static second hyperpolarizability, $\gamma(0;0,0,0)$, were performed for **1**, **M1**, **2**, and **M2**. For **1**, $\gamma(0;0,0,0) = 3.33 \times 10^{-35}$ esu, while for **2**, $\gamma(0;0,0,0) = -3.43 \times 10^{-35}$ esu. These values are rather low and in line with previous calculations for C_{60} (for a summary of previous calculations: see Table 1 of reference [15b]). Chemical reduction enhances $\gamma(0;0,0,0)$ of **M1** by 30% to 4.34×10^{-35} esu, and increases $\gamma(0;0,0,0)$ of **M2** by nearly an order of magnitude bringing it to -2.33×10^{-34} esu. This is far from the three orders of magnitudes observed experimentally at 800 nm. The B3LYP/6-31G* results imply that some near-resonant contributions are present. Following a previously used approach, $\gamma(\omega;\omega,-\omega,\omega)$ was then calculated as a function of the incident photon frequency, ω. This is the microscopic counterpart of the OKE experiment. To avoid the difficulty of the calculation of a configuration interaction with an open shell, the systems considered were **1**, **2**, **B1**, and **B2**. Figure 6 shows the dispersion profiles of calculated dispersion from 885 to 590 nm (from 1.4 to 2.10 eV). The experimental measurements were performed at 800 nm. The rationale for investigating a range of wavelengths is twofold: 1) the calculated electronic states energy may not match perfectly

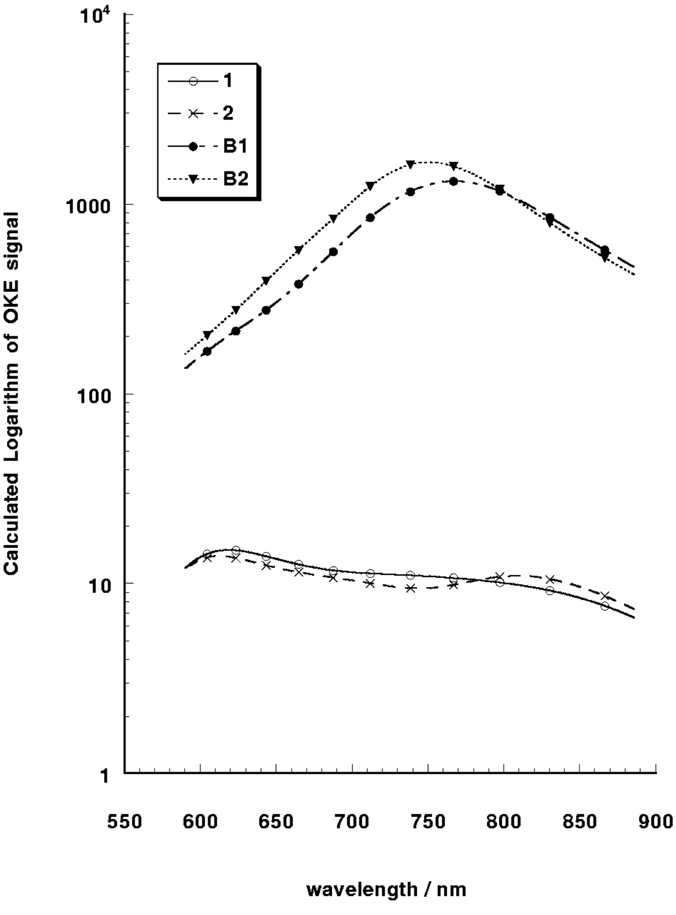

Figure 6. Dispersion of the calculated OKE (or DFWM) response. The experiments were performed at 800 nm.

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the experimental ones and some shift may be in order;[15b] and 2) knowledge that the dispersion profile is nearly constant over a certain range of wavelengths excludes strong resonance effects.

The calculations show that this is the region of the experiments in which the nonlinear optical response for the reduced species is largest. Moreover, the rather smooth profiles exclude sudden, spurious resonances. Also notice that throughout the region, the calculated signal for **1** and **2** is nearly constant and up to ~ 3 orders of magnitude smaller than that of the reduced molecules. A further factor of agreement with the experiment is the calculated absorption, which is rather low, see Table 2. Importantly, the oscillator strength (f_0)[21] never exceeds 0.2.

Table 2. Calculated electronic state wavelengths, λ [nm], and oscillator strengths, f_0, of **B1** and **B2**.

B1		**B2**	
λ	f_0	λ	f_0
4335	0.00	5275	0.00
2798	0.00	2755	0.00
1233	0.00	1418	0.01
1100	0.18	1243	0.00
1059	0.01	1143	0.17
995	0.18	1068	0.17
780	0.09	798	0.00
776	0.01	793	0.00
776	0.03	755	0.04
770	0.00	739	0.05
751	0.08	730	0.02
725	0.03	729	0.03
616	0.01	667	0.02
522	0.00	528	0.00
495	0.00	507	0.00
490	0.00	498	0.00
484	0.00	498	0.00
480	0.00	484	0.00
474	0.00	481	0.00
472	0.00	478	0.00
470	0.00	474	0.00
465	0.00	471	0.00
463	0.00	460	0.00
459	0.00	460	0.00
453	0.00	457	0.00
452	0.00	456	0.00
451	0.00	452	0.00

To ascertain the nature of the response and the contribution of the low-lying electronic states, a missing state analysis (MSA)[22] was performed. MSA allows us to establish the contribution $\sigma(\mathrm{r})$ of an electronic state (r) to a nonlinear optical process simply by eliminating it from the summation of Equation (2); this leads to Equation (5):

$$\sigma(\mathrm{r}) = \frac{\gamma_{\mathrm{tot}} - \gamma_{\mathrm{r}}}{\gamma_{\mathrm{tot}}} \tag{5}$$

in which γ_{tot} is the full response and γ_{r} is the response without the contribution of state r. MSA was applied to the most intense part of the dispersion of the response shown in Figure 6. Only one state at a time was removed for systems **B1** and **B2**. This is in agreement with a similar procedure used for fullerenes, whereby only a few electronic states were found to give a dominant contribution in the description of the nonlinear optical properties of the lower isomers.[15b] In each system, a single electronic state gives a large contribution: they are the state located at 751 nm for **B1**, and the state located at 739 nm for **B2**. The corresponding values were $\sigma_{\mathbf{B1}}(751\ \mathrm{nm}) = 0.61$ and $\sigma_{\mathbf{B2}}(739\ \mathrm{nm}) = 0.68$. The contributions of all the other states were much smaller. MSA therefore shows that the response is one photon; however, the elimination of the resonant state does not even change its order of magnitude. The conclusion of the analysis is that the "few-state picture" that describes the NLO properties of C_{60}[15b] does not hold for the reduced forms of the fulleropyrrolidine adducts and that their large response is due to many small and medium size contributions. Peculiarly, this is similar to the case of the response of higher fullerenes.[15b]

Conclusion

While fulleropyrrolidines and their salts have a second hyperpolarizability comparable to that of C_{60}, their reduced forms show an enhancement of the signal of up to and sometimes exceeding three orders of magnitude. Experimental and computational investigations provide a coherent picture of this response. A second hyperpolarizability three orders of magnitude higher than in C_{60} is not routinely observed. In fact, in a recent compilation of four-wave mixing and optical Kerr effect data,[1a] only one set of experiments in solution gave a similar value for laser wavelength (1064 nm) in this range.[20] According to the authors, however, the response in their materials is considerably resonance-enhanced. Reduced fulleropyrrolidines, with their relatively low absorption and their remarkably high response, therefore, emerge as extremely interesting systems worth of systematic investigation to tune their nonlinear optical properties.

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