New strategies for new organic molecules with large second order hyperpolarizabilities

M. C. Magnoni, P. Mondini, M. Del Zoppo, C. Castiglioni and G. Zerbi*

*Dipartimento di Chimica Industriale, Politecnico di Milano, Piazza L. da Vinci 32,
20133 Milano, Italy*

Received (in Cambridge) 25th February 1999, Accepted 26th May 1999

Using data from computed observables of vibrational spectroscopy (frequency, infrared, Raman and hyper Raman intensities) we derive structural criteria necessary to design new organic conjugated molecules with enhanced non linear optical responses. In this work, in particular, we focus on second order hyperpolarizability (γ) and extract from our analysis the structural requirements necessary to reach large negative γ values.

Introduction

In the search for new organic materials with extended π electron delocalization to be used in non linear optics, a new class of molecules presently being considered is that of polycyclic aromatic compounds with very low band gap. Among these systems we are particularly interested in oligo and polyacenes that can be considered as model systems which exhibit a 2-D network of π conjugated electrons. It is known that, in spite of the existence of a long delocalization path, oligoacenes do not exhibit particularly large third order polarizabilities[1,2] (second order polarizabilities are vanishing for symmetry reasons, *i.e.* centrosymmetry); it is then interesting to consider which structural modifications, if any, may be feasible to produce enhanced non linear optical (nlo) responses.[3] Depending on the chemical nature and structure of the molecules considered the values of molecular non linear optical responses can be positive or negative. While much attention has been given to molecules which show positive values, negative hyperpolarizabilities are presently becoming of interest for several technological applications.

The purpose of this work is to find the chemical, structural and electronic conditions which may make polyacenes good non linear optical materials possibly with negative hyperpolarizabilities. The knowledge gained in this work may be generalized to form the conceptual background which may lead the synthesis of new materials with specifically desired optical properties.

In the study of the origin, at the molecular level, of molecular optical non linearities we make use of the vibrational method for the evaluation of molecular hyperpolarizabilities of conjugated systems. This method relies on the possibility of expressing the nuclear relaxation contribution to molecular hyperpolarizabilities in terms of spectroscopic observables, *i.e.* vibrational frequencies and absolute intensities. We have recently proposed[4,5] this method which has been successfully tested on a variety of molecular systems.[6–9] In the case of polyconjugated systems the hyperpolarizability values that can be obtained with this method turn out to be very large and correlate nicely with those obtained with traditional techniques. In this work we focus on second order hyperpolarizability (γ), which, within the model adopted, is given by eqn. (1), where ν_k

$$\gamma^{v}_{nmps} = \frac{1}{4\pi^2 c^2} \Sigma_k \left(\frac{1}{\nu_k^2}\right)(I + II)$$

$$I =$$

$$\left(\frac{\partial\mu_n}{\partial Q_k}\right)\left(\frac{\partial\beta_{mps}}{\partial Q_k}\right) + \left(\frac{\partial\mu_m}{\partial Q_k}\right)\left(\frac{\partial\beta_{nps}}{\partial Q_k}\right) + \left(\frac{\partial\mu_p}{\partial Q_k}\right)\left(\frac{\partial\beta_{nms}}{\partial Q_k}\right) + \left(\frac{\partial\mu_s}{\partial Q_k}\right)\left(\frac{\partial\beta_{nmp}}{\partial Q_k}\right)$$

$$II = \left(\frac{\partial\alpha_{nm}}{\partial Q_k}\right)\left(\frac{\partial\alpha_{ps}}{\partial Q_k}\right) + \left(\frac{\partial\alpha_{np}}{\partial Q_k}\right)\left(\frac{\partial\alpha_{ms}}{\partial Q_k}\right) + \left(\frac{\partial\alpha_{ns}}{\partial Q_k}\right)\left(\frac{\partial\alpha_{mp}}{\partial Q_k}\right) \qquad (1)$$

is the vibrational frequency of the k-th normal mode Q_k and the quantities $\partial\mu_n/\partial Q_k$, $\partial\alpha_{nm}/\partial Q_k$, and $\partial\beta_{nms}/\partial Q_k$, where n, m, s and p indicate the Cartesian components, can be obtained from infrared intensities, Raman and hyper Raman cross sections, respectively.

One of the advantages of this method is that it makes it possible to identify the contribution to molecular hyperpolarizabilities in terms of the normal modes of vibration and in terms of their local or collective character. This advantage cannot be overlooked. We wish to emphasize that the vibrational method offers the possibility to disentangle the contributions to molecular nlo properties originating from "chromophores" (or functional groups) which chemists can introduce at various sites of the molecule. One can then establish directly and quantitatively a correlation between chemical structure and molecular nlo properties.

In our previous calculation of γ^{v} we omitted term *I*. We were justified in this simplification by the fact that we have always considered molecular systems characterized by very strong Raman activities and a rather weak infrared spectrum, thus assigning a leading role to term *II*.[1,10] In this work we re-address the question of the relative importance of the two contributions and we discuss the conditions under which the contribution of term *I* becomes important. It must be noticed that negative values of γ can be expected only when term *I* becomes dominant. If we are able to extract from the physics of the process the necessary requirements to obtain large negative γ values we can offer some guidelines to the synthesis of new materials for new devices. The evaluation of term *I* is not straightforward. Experimentally it is impossible to obtain absolute hyper Raman cross sections; moreover very few quantum mechanical programs are available which routinely calculate these quantities.

Calculations

The molecules considered in this work are shown in Figs. 1 and 2. First we considered the series of oligoacenes, from benzene ($N = 1$) through pentacene ($N = 5$) (see Fig. 1). We then turned our attention to some model compounds suitably devised (see Fig. 2) in order to study the influence of π electron distribution and polarization on infrared and Raman intensities and hence on molecular hyperpolarizabilities. This approach allows the modulation of the relative importance of terms *I* and *II*.

The strategy adopted was that of modeling π electron polarizability with the introduction of suitable polar groups. We wish to stress that our main aim is to get an insight into the relationship between the electronic charge distribution, the intensity pattern and the non linear molecular optical response. To attain this result we decided to consider suitably devised molecules irrespective of their actual chemical availability and/or stability.

Once the basic concepts are understood, applications to realistic molecules may follow. As polarizing groups we have considered C=O functional groups and we have devised three types of substitutions: A: centrosymmetric introduction of two C=O groups (C_{2h} point group); B: centrosymmetric introduction of four C=O groups (D_{2h} point group); C: non centrosymmetric introduction of two C=O groups (C_{2v} point group). In the following the notation X/*n* indicates the number of condensed rings in the molecule X (X = A, B and C).

Geometry optimization of all the systems considered and the calculation of their vibrational spectra (IR and Raman), both in frequency and intensity, were performed with the "*ab initio*" quantum chemical program GAUSSIAN92[11] using the 3-21 G basis set.

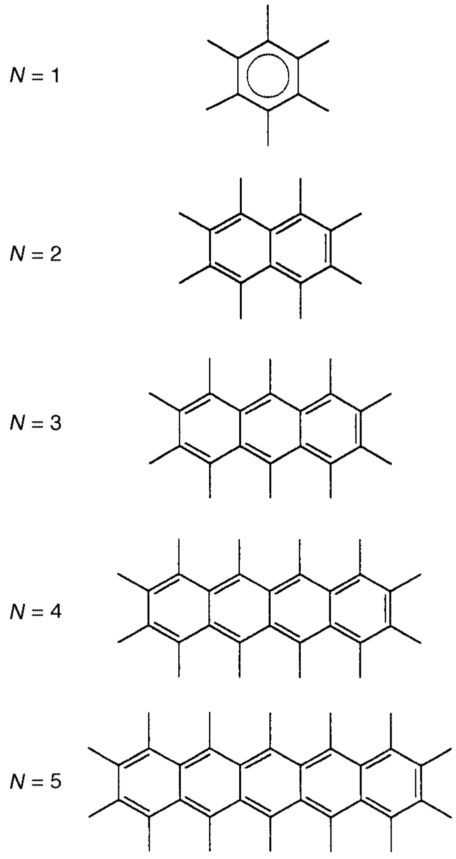

Fig. 1 The molecules studied: oligoacenes.

Theoretical results

Following the kind of calculations previously made[1,6,10] we have calculated at first γ^v by using only term *II* which can be rewritten to yield the average γ value as eqn. (2), where $\bar{a}_k$ and $\gamma^2{}_k$ are the invariants of the tensor $\boldsymbol{\partial a/\partial Q_k}$, eqn. (3).

$$\langle\gamma^{v}_{\text{calc}}\rangle = \frac{1}{15}\left(\frac{1}{4\pi^2c^2}\right)\Sigma_k\left(\frac{1}{\nu_k^2}\right)[45\bar{a}_k{}^2 + 4\gamma_k{}^2] \qquad (2)$$

$$\begin{aligned}\bar{a}_k &= 1/3\ \mathrm{Tr}(\boldsymbol{\partial a/\partial Q_k})\\ \gamma^2{}_k &= \tfrac{1}{2}\{(\partial a_{xx}/\partial Q_k - \partial a_{yy}/\partial Q_k)^2 + (\partial a_{xx}/\partial Q_k - \partial a_{zz}/\partial Q_k)^2 +\\ &\quad \{(\partial a_{yy}/\partial Q_k - \partial a_{zz}/\partial Q_k)^2 + 6\,[(\partial a_{xy}/\partial Q_k)^2 + (\partial a_{yz}/\partial Q_k)^2 +\\ &\quad (\partial a_{xz}/\partial Q_k)^2]\}\end{aligned} \qquad (3)$$

The results obtained in the case of molecules of series 1 (oligoacenes) are reported in Table 1 where we compare theoretical and (when available) experimental γ^v previously measured in our laboratory.[1] The agreement both in value and trend with *N* is very good. Moreover, a comparison with electronic γ values obtained with derivative "*ab initio*" calculations[12] shows a good agreement with our determinations of γ obtained by the vibrational method through only eqn. (2). These results confirm that also in the case of oligoacenes the approximation of using only term *II* in the calculation of γ^v is a good one. It must be noted that the γ values of oligoacenes are rather low especially if compared with other systems such as oligorylenes[1] and the law of growth with *N* is not very steep especially if one considers the large number of delocalized π electrons in the systems considered.

In order to obtain larger γ^v values it is then necessary to

Table 1 Comparison of experimental (from solutions) and "*ab initio*" $\langle\gamma^v\rangle$ of oligoacenes from term *II* in eqn. (2)

	Experimental		*Ab initio*[a]	
N^b	γ^v (esu)	γ^v/N (esu)	$\gamma^v{}_{\text{calc}}{}^c$ (esu)	$\gamma^v{}_{\text{calc}}{}^b/N$ (esu)
1	$9.85 \times 10^{-37\,d}$	$9.85 \times 10^{-37\,d}$	8.90×10^{-37}	8.90×10^{-37}
2	$1.88 \times 10^{-36\,e}$	$9.38 \times 10^{-37\,e}$	1.62×10^{-36}	8.10×10^{-37}
3	$5.45 \times 10^{-36\,e}$	$1.82 \times 10^{-36\,e}$	5.08×10^{-36}	1.69×10^{-36}
4	Insoluble	Insoluble	1.47×10^{-35}	3.68×10^{-36}
5	Insoluble	Insoluble	3.11×10^{-35}	6.22×10^{-36}

[a] GAUSSIAN92—Basis Set: 3-21G. [b] N = number of conjugated rings. [c] $\gamma^v{}_{\text{calc}} = 1/15\ (1/4\pi^2c^2)\ \Sigma_k\ (1/\nu_k{}^2)\ [45\ (\bar{a}_k)^2{}_{\text{av}} + 4\ (\gamma_k)^2{}_{\text{anis}}]$. [d] CCl_4 solution. [e] CH_2Cl_2 solution.

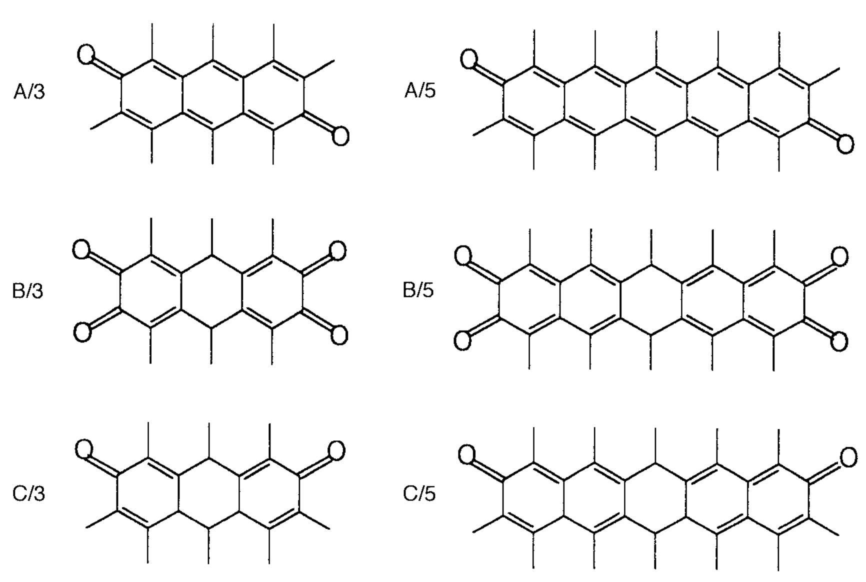

Fig. 2 The model compounds of substituted polyacenes studied.

Table 2 *Ab initio* $\langle \gamma^v \rangle$ values from term *II* in eqn. (2)

Centrosymmetrically substituted oligoacenes	N	γ^v (esu)
Model A/3	3	3.12×10^{-35}
Model A/5	5	3.09×10^{-34}
Model B/3	3	1.89×10^{-34}
Model B/5	5	2.15×10^{-33}
Non centrosymmetrically substituted oligoacenes		
Model C/3	3	4.22×10^{-33}
Model C/5	5	1.20×10^{-33}

introduce suitable structural modifications in the molecules in order to enhance IR and/or Raman intensities.

First we focus on Raman spectra.

In general, Raman spectra of polyconjugated systems are characterized by few and extremely strong lines. The large intensities of these Raman active modes have been rationalized in terms of a totally symmetric collective coordinate[13–15] (usually referred to as $\mathcal{A}$) which enters with very large contributions in these normal modes. The theory which sustains such an interpretation (effective conjugation coordinate, ECC, theory) made it possible to give a physical meaning to this coordinate. It has been shown that the related force constant can be made to correspond to a "measure" of the extent of π electron delocalization and the intensity of the normal modes involving this coordinate is strictly related to the existence of a strong electron–phonon coupling.[13]

In the case of the oligoacenes, object of this work, the normal mode analysis shows that there are no totally symmetric normal modes with exceptionally large Raman intensities and the definition of a preferential collective coordinate is not so obvious. It follows that for these systems there is not much hope of gaining contributions to γ^v from Raman spectra.

Since we cannot generate and use large Raman intensities in order to optimize γ^v values for the molecules studied it might be more profitable to turn our attention to infrared intensities.

It is well known that when polar groups are introduced to the molecule large dipole changes are generated with consequent strong absorption bands in the infrared. In order to fully exploit the infrared activation it is necessary that the polarizing effect is not localized on the functional group, but it must take advantage of electron delocalization throughout the whole molecular framework. These requirements would be met by an infrared active $\mathcal{A}$ mode.

Provided that we are able to induce large infrared intensities, terms of type *I* in eqn. (1) become competitive with terms of type *II* and can no longer be neglected.

The effect of the introduction of polar end groups on term *II* can be seen in Table 2. The first general observation is that in each case the observed effect carries an increase in the Raman intensities which obviously yields an increase of γ^v. The largest increase is observed for molecules of series C (non centrosymmetric), but, on the whole, γ^v values are lower than what would be desirable.

More striking is the behavior of infrared intensities. The introduction of two C=O groups makes some of the normal modes extremely strong in the infrared. The spectral pattern is completely different if the substitution introduced is centrosymmetric or non centrosymmetric. In the former case (series A/*n*) the polarizing effect is very localized, no intramolecular charge transfer takes place and the only normal mode with a really outstanding intensity is the C=O stretching. On the contrary, in the case of molecules of series C several skeletal modes become very strong and the polarizing effect has a collective character. This last statement is proven by the fact that the strongest IR bands in going from $N = 3$ to $N = 5$ show a more than additive enhancement. The normal mode analysis shows that the extremely large intensities are obtained, corresponding with collective normal modes which can be described in terms of stretchings and shrinkings of CC double and single bonds (the strongest normal modes are shown in Fig. 3).

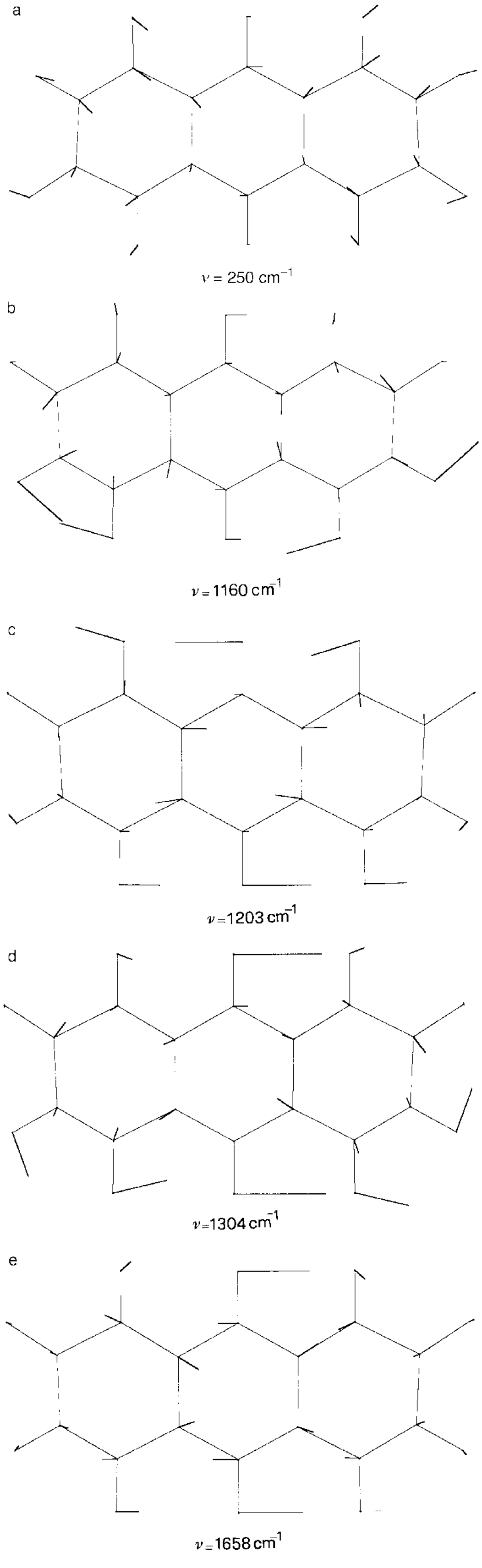

Fig. 3 Calculated vibrational displacements of the five normal modes (Q_k) of the molecule C/3 which show very strong IR intensities (see text).

Table 3 Contributions to term *I* (IR–hyper Raman) and *II* (Raman) in eqn. (2) calculated "*ab initio*" for five relevant normal modes Q_k of molecule C/3

ν_k/cm^{-1}	$\langle\gamma^{\mathrm{v}}\rangle^k{}_I{}^a$ (esu)	$\langle\gamma^{\mathrm{v}}\rangle^k{}_{II}{}^a$ (esu)	$\langle\gamma^{\mathrm{v}}\rangle^k{}_{\mathrm{tot}}{}^b$ (esu)
250	-5.70×10^{-33}	3.92×10^{-34}	-5.31×10^{-33}
1160	-1.74×10^{-34}	1.95×10^{-35}	-1.55×10^{-34}
1203	-2.78×10^{-34}	1.38×10^{-35}	-2.64×10^{-34}
1304	-1.22×10^{-34}	1.71×10^{-36}	-1.20×10^{-34}
1658	-1.83×10^{-34}	1.04×10^{-36}	-1.82×10^{-34}

[a] $\langle\gamma\rangle = 1/5[(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz}) + 2\,(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})]$. [b] $\langle\gamma\rangle^k{}_{\mathrm{tot}} = \langle\gamma\rangle^k{}_{\mathrm{Raman}} + \langle\gamma\rangle^k{}_{\text{IR-hyper Raman}}$.

In this situation it is no longer possible to neglect term *I* in eqn. (1). The calculation of term *I* in eqn. (1) requires the knowledge of the hyper Raman scattering cross section which, so far, cannot be found experimentally for the kind of molecules treated in this paper and, in general, for polyconjugated systems. The problem to be faced is the "*ab initio*" calculation of hyper Raman intensities, *i.e.* of the elements of the tensor $\partial\boldsymbol{\beta}/\partial Q_k$. In order to calculate these quantities we can apply the finite differences method using a finite distortion procedure, eqn. (4),

$$\gamma^{\mathrm{v}^{\mathrm{hyper}}_{mmps}} = \frac{1}{4\pi^2 c^2}\left(\frac{1}{\nu_k^2}\right)\left[\left(\frac{\Delta\mu_n}{\Delta Q_k}\right)\left(\frac{\Delta\beta_{mps}}{\Delta Q_k}\right) + \left(\frac{\Delta\mu_m}{\Delta Q_k}\right)\left(\frac{\Delta\beta_{nps}}{\Delta Q_k}\right) + \left(\frac{\Delta\mu_p}{\Delta Q_k}\right)\left(\frac{\Delta\beta_{nms}}{\Delta Q_k}\right) + \left(\frac{\Delta\mu_s}{\Delta Q_k}\right)\left(\frac{\Delta\beta_{nmp}}{\Delta Q_k}\right)\right] \quad (4)$$

where ΔQ_k is the finite distortion of the normal coordinate (in our calculations $\Delta Q_k = 0.05$ bohr amu$^{1/2}$), $\Delta\beta$ and $\Delta\mu$ are respectively the variation of first hyperpolarizability and dipole moment after the distortion of the molecular structure. A similar method has already been used by Kirtman *et al.* for the evaluation of vibrational hyperpolarizabilities of polyenes.[16]

In order to estimate the contribution to γ of terms of type *I* we have selected the five most intense IR bands of molecule C/3 and have calculated the quantity given by eqn. (4). In Table 3 are reported the contributions to $\langle\gamma\rangle$ from terms of type *I* and *II* for these normal modes. In each case the contribution from term *I* is one or even two orders of magnitude larger than that from term *II* and is negative.

The large γ^{v} value obtained as: $\langle\gamma^{\mathrm{v}}\rangle = \langle\gamma^{\mathrm{v}}\rangle^{\mathrm{Raman}} + \langle\gamma^{\mathrm{v}}\rangle'^{\text{ hyper Raman}} = -2.24 \times 10^{-33}$ esu should be compared with $\langle\gamma^{\mathrm{e}}\rangle = -3.64 \times 10^{-34}$ esu (γ^{e} has been obtained directly from GAMESS program). Also in the case of electronic γ we find a negative value even though it is much smaller than the vibrational counterpart. We think it satisfactory to find sign agreement. The reason for the rather large discrepancy in absolute value should be the focus of further study. However, this result indicates that the calculation of term *I* can not be neglected whenever relevant IR intensities are expected.

Conclusions

First we wish to derive from the above analysis the conditions which are required for obtaining large negative γ values. A negative contribution to vibrational second hyperpolarizabilities can only come from term *I*. This means that large IR intensities are required. Moreover this contribution must be larger than that of type *II* which is necessarily positive and hence may compensate for *I*. This makes it necessary to seek systems which have large IR intensities, but not necessarily huge Raman intensities. Raman intensities of conjugated systems have been rationalized in terms of a collective, totally symmetric, Raman active normal coordinate (Я mode).[13] In centrosymmetric materials no Raman active normal mode can be simultaneously IR active. This rules out all centrosymmetric compounds as candidates for systems with large IR intensities.

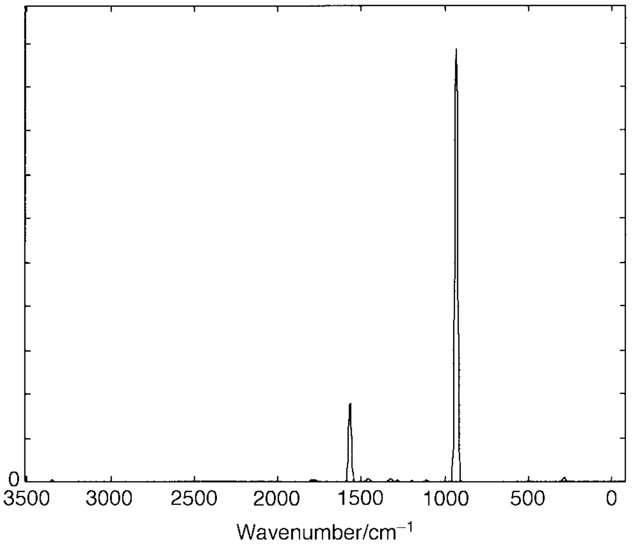

Fig. 4 "*Ab initio*" calculated (3-21G) IR spectrum of $C_{21}H_{23}{}^+$ showing the very strong absorption associated to the normal mode Я.

On the contrary when the electrical symmetry is removed and intramolecular charge transfer is induced along the chain axis, as in the case of push-pull systems, we have Я modes with large activities both in IR and Raman spectra.[7,8] Finally, in the case of lower symmetry point groups (*e.g.* C_{2v}) there can be a non total symmetric collective Я vibration which is active both in the Raman and infrared spectra, but with appreciable intensity only in the IR.

The first suggestion derived from the rules stated above is that good candidates for obtaining large negative γ values are molecular systems such as symmetric cyanines which belong to the correct point group and have an extended delocalization path along the chain. We have made preliminary calculations on very short molecules and found that these systems have negative second order hyperpolarizabilities; longer chains are being considered in order to obtain large $\langle\gamma\rangle$ values.

A second important consequence of the above rules brings into the field of nlo materials the whole class of doped and photoexcited conjugated materials. Indeed the same symmetry requirements of the molecules previously considered are met by positively charged polyenes (C_nH_{n+2}, with *n* odd) which mimic charged solitons which, in their turn, are the charge carriers in doped electrically conducting or photoexcited polyene chains. It is interesting to point out the well known fact that doped conjugated molecules show extremely strong doping induced IR bands. As expected, the calculations on $C_{21}H_{23}{}^+$ show a selective enhancement of IR active Я modes which show the strongest intensities ever seen or calculated (Fig. 4).

The *I* contribution to $\langle\gamma^{\mathrm{v}}\rangle$ of the strongest IR band ($\nu = 930$ cm^{-1}) for $C_{21}H_{23}{}^+$ is found to be $\langle\gamma^{\mathrm{v}}\rangle_{Я}{}^{\text{hyper Raman}} = -1.189 \times 10^{-32}$ esu, to be compared with $\langle\gamma^{\mathrm{v}}\rangle^{\mathrm{Raman}}$ value 8.90×10^{-33} esu. This last value is obtained by summing over all the Raman active normal modes. We find here very large vibrational γ values. This finding seems to be in agreement with the idea obtained on the basis of theoretical[17,18] and experimental[19] works which indicate a substantial enhancement of the nlo response of doped molecules or of molecules in their excited state.[18] Also in this case care must be taken in drawing any conclusion, since the calculation and the experimental measuring of the quantities of interest are very subtle and no clear understanding of the physics has yet been reached; moreover the choice of an odd charged polyene to model the charge defect may also be a matter for discussion. Anyway we feel that the vibrational approach can add some understanding to this problem.

References

1 M. C. Rumi, G. Zerbi, K. Müllen and M. Rehahn, *J. Chem. Phys.*, 1997, **106**, 24.

2 Y.-J. Lu and S.-L. Lee, *Chem. Phys.*, 1993, **179**, 431.

3 S. R. Flom, G. C. Walker, L. E. Lynch, L. L. Miller and P. F. Barbara, *Chem. Phys. Lett.*, 1989, **154**, 193.

4 C. Castiglioni, M. Gussoni, M. Del Zoppo and G. Zerbi, *Solid State Commun.*, 1992, **82**, 13.

5 C. Castiglioni, M. Del Zoppo and G. Zerbi, *Phys. Rev. B*, 1996, **53**, 13319.

6 M. Del Zoppo, C. Castiglioni, M. Rui, M. Gussoni and G. Zerbi, *Synth. Met.*, 1992, **51**, 135.

7 M. Del Zoppo, C. Castiglioni, P. Zuliani and G. Zerbi, *Synth. Met.*, 1997, **85**, 1043.

8 P. Zuliani, M. Del Zoppo, C. Castiglioni, G. Zerbi, S. R. Marder and J. W. Perry, *J. Chem. Phys.*, 1995, **103**, 9935.

9 C. Castiglioni, M. Del Zoppo, P. Zuliani and G. Zerbi, *Synth. Met.*, 1995, **74**, 171.

10 M. Del Zoppo, C. Castiglioni, M. Veronelli and G. Zerbi, *Synth. Met.*, 1993, **55**, 3919.

11 GAUSSIAN92 (revision c), M. J. Frish, G. W. Trucks, M. Head-Gordon, P. M. Gill, M. W. Wong, J. B. Foresman, B. G. Jonson, H. B. Schlegel, M. A. Robb, E. S. Repogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, Gaussian Inc., Pittsburg, PA, 1992.

12 P. Norman, D. Jonsson, N. Ågren, P. Dahle, K. Ruud, T. Helgaker and N. Koch, *Chem. Phys. Lett.*, 1996, **253**, 1.

13 M. Gussoni, C. Castiglioni and G. Zerbi, in *Vibrational Spectroscopy of New Materials*, ed. R. J. H. Clark and R. E. Hester, Wiley, New York, 1991, p. 251.

14 C. Castiglioni, M. Del Zoppo and G. Zerbi, *J. Raman Spectrosc.*, 1993, **24**, 485.

15 V. Hernandez, C. Castiglioni, M. Del Zoppo and G. Zerbi, *Phys. Rev. B*, 1994, **50**, 9815.

16 B. Kirtman, B. Champagne and J.-M. André, *J. Chem. Phys.*, 1996, **104**, 4125.

17 B. Champagne, E. Deumens and Y. Öhrn, *J. Chem. Phys.*, 1997, **107**, 5433.

18 Y. Luo, P. Norman, D. Jonsson and H. Ågren, *Mol. Phys.*, 1996, **89**, 1409.

19 (*a*) D. C. Rodenberger, J. R. Heflin and A. F. Garito, *Nature*, 1992, **359**, 309; (*b*) D. C. Rodenberger, J. R. Heflin and A. F. Garito, *Phys. Rev. A*, 1995, **51**, 3234; (*c*) C. W. Spangler, in *Handbook of Conducting Polymers. II Edition*, ed. T. Skotheim, Dekker, New York, 1998, p. 743.

Paper 9/01539F