

Comparison between semiempirical and experimental force fields of oligothiophenes as an approach for the calculations of the vibrational spectrum of the polymer

V. Hernández, F.J. Ramírez and J.T. López Navarrete

Departamento de Química Física, Facultad de Ciencias, Universidad de Málaga, 29071-Málaga, SPAIN

The vibrational spectra of oligomers of thiophene are treated theoretically with the main purpose to derive information for the interpretation of the spectra of polythiophene and isotopic derivatives. In the present work, we first compare the calculated MNDO Pulay scaled force field of thiophene molecule with an experimental harmonic force field that we have obtained by least-square refinement on nine isotopic derivatives. The scaling factors were transferred from thiophene for the computation of the vibrational spectrum of polythiophene.

1. INTRODUCTION

In the field of polyconjugated conducting polymers, the assignment of the vibrational spectra in an essential step in elucidating the molecular structure of these materials. It is known that such assignment depends largely on the force field employed. However, the experimental approach to the determination of the harmonic force field for a relatively large molecule is very difficult without a very extensive work involving many isotopic species. On the other hand, vibrational spectra and force constants calculated by both semiempirical or *ab initio* quantum chemical methods deviate systematically from the observed values. Consequently, various scaling processes acting on the force constants have been proposed in order to reduce the discrepancies between calculated and experimental data [1].

In the last years [2] we have shown that from the study of the electronic and dynamical properties of large oligomers of organic conducting polymers one can derive different parameters to be satisfactorily transferred to the study of the dynamics of these polymers taken as one dimensional crystal. In this way, the use of semiempirical quantum chemical

methods, as MNDO, has allowed us to obtain ground state geometries, electronic and vibrational properties in a easy and systematic way. In the present work we wish to show that MNDO Pulay scaled force field of elemental monomers could be directly used for the calculations of the dynamical properties of the polymer when we have not experimental data of larger oligomers. Moreover, the scaled force field found for monomers and polymers could be used as starting set for a least-squares refinement to the experimental data. We wish to analyze here the case of the polythiophene and its isotopic derivatives, which show good electrical conductivity and chemical stability.

2. CALCULATIONS

Our work is organized in the following way: since we aim at the interpretation of the vibrational spectrum of the polymer, we have carried out lattice dynamis calculations deriving the vibrational force constants from semiempirical MNDO calculations on the monomer. For the scaled process works we have always followed the method of scaling proposed by Pulay et al. [1]. This method is very known and has been succesfully used for the determination of the

force field of many conjugated and aromatic molecules. To compute the force field the molecular geometry of thiophene has been optimized to guarantee a minimum of potential energy in the force constant calculation. The MNDO harmonic force constant matrix has been computed in cartesian coordinates and then transformed to a space of non-redundant group coordinates following the Pulay formalism [1]. All computations were performed in a VAX 8530 computer.

3. RESULTS AND DISCUSSION

3.1. Monomer: Thiophene.

Although the vibrational spectra of thiophene and several deuterated derivatives have been the subject of a thorough experimental work [3], it is surprising how few information on its force field is available up to date from both experimental and theoretical works. Scott [4] has carried out normal coordinate calculations by a least-squares fitting to experimental frequencies of the thiophene and deuterated derivatives determining a reduced valence force field for the molecule.

In this work, we have carried out dynamical MNDO calculations on this molecule with a two-fold purpose, namely to find the Pulay scaling factors acting on the force constants required to bring dynamical calculations on the other oligomers and the polymer closer to experiments, and also examine the ability of the proposed method in predicting frequencies and vibrational descriptions and the possibility to use the scaled force field as a starting point to further refinement.

In Table 1 we report a comparison between the experimental frequencies and the calculated ones based on the scaled and refined force constants for the in-plane modes. The fitting between experimental and scaled frequencies can be considered very good in the light of the fact that no least-square adjustment of

the force constants has been made. Moreover, the descriptions of the modes always agree very well with the proposed experimental assignments. We have also calculated the normal frequencies of C_{2v} deuterated derivatives which experimental data are available. The average deviations between experimental and calculated frequencies, 16.5 cm^{-1} or 2.1%, show a systematic behaviour and confirm the stability of the scaled force field.

To check the validity of our scaled MNDO force field it has been used as the initial set to carry out a refinement to fit the experimental frequencies of thiophene and eight deuterated derivatives. The ratio between the total number of experimental data and the number of force constants under refinement has been of 119:55 for the in-plane modes and 45:14 for the out-of-plane ones. The agreement between observed and refined frequencies is now obviously very good in all the cases with a average deviation of 3.2 cm^{-1} or 0.3 %. However the description of the normal modes remains practically unchangeable to the corresponding one when the scaled force field was used. The results for the in-plane modes of C_{2v} derivatives are also included in Table 1.

Comparing scaled MNDO and refined force constants, Table 2, we can see that diagonal force constants are very close in all the cases with the exception of the two in-plane ring deformations which should be increased by 30 % respect to the scaled values. Off-diagonal force constants refine to values very closed to the ones calculated by MNDO and their signs are always correctly predicted with very few exceptions when the absolute value is very small. Refined force constants also compare well with the experimental values reported by Scott and are always evaluated with lower errors.

The scaling factors found for thiophene can be transferred to bithiophene and larger oligomers to predict the vibrational spectra of these molecules. For the dimer, experimental data are available from

TABLE 1
Observed^a, MNDO scaled and refined modes (in cm⁻¹) for thiophene and C₂v-deuterated derivatives.

| Thiophene | | | Thiophene-d ₄ | | | Thiophene-3,4-d ₂ | | | Thiophene-3,4-d ₂ | | | P. E. D. (greater 10%) |
|------------------------|------------------|------------------|--------------------------|------------------|------------------|------------------------------|------------------|------------------|------------------------------|------------------|------------------|------------------------------|
| v _{sca} | v _{ref} | v _{exp} | v _{sca} | v _{ref} | v _{exp} | v _{sca} | v _{ref} | v _{exp} | v _{sca} | v _{ref} | v _{exp} | |
| A ₁ species | | | | | | | | | | | | |
| 3130 | 3131 | 3126 | 2336 | 2339 | 2343 | 3125 | 3130 | 3123 | 3094 | 3098 | 3101 | 100v(CH) |
| 3095 | 3097 | 3098 | 2302 | 2300 | 2306 | 2306 | 2309 | 2314 | 2310 | 2330 | 2336 | 100v(CH) |
| 1419 | 1419 | 1409 | 1401 | 1364 | 1376 | 1416 | 1394 | 1389 | 1404 | 1398 | 1398 | 76v(C=C) |
| 1349 | 1364 | 1360 | 1279 | 1249 | 1248 | 1313 | 1318 | 1322 | 1324 | 1305 | 1310 | 54v(C-C)+20δ(CH) |
| 1091 | 1081 | 1083 | 921 | 895 | 896 | 1059 | 1038 | 1034 | 1087 | 1051 | 1046 | 75δ(CH) |
| 1068 | 1033 | 1036 | 772 | 785 | 785 | 895 | 875 | 876 | 899 | 883 | 884 | 92δ(CH) |
| 857 | 841 | 839 | 723 | 730 | 731 | 749 | 750 | 750 | 736 | 753 | 754 | 84v(CS) |
| 601 | 607 | 607 | 587 | 584 | 585 | 598 | 601 | 593 | 590 | 589 | - | 85δ _{ring} |
| B ₁ species | | | | | | | | | | | | |
| 3139 | 3130 | - | 2330 | 2337 | - | 3120 | 3127 | - | 3090 | 3100 | 3088 | 100v(CH) |
| 3094 | 3096 | 3098 | 2295 | 2291 | 2290 | 2308 | 2313 | - | 2302 | 2316 | - | 100v(CH) |
| 1511 | 1508 | 1507 | 1477 | 1455 | 1459 | 1488 | 1476 | 1480 | 1501 | 1488 | 1490 | 65v(C=C) |
| 1209 | 1258 | 1256 | 1010 | 1029 | 1034 | 1141 | 1176 | 1178 | 1183 | 1223 | 1218 | 94δ(CH) |
| 1075 | 1085 | - | 812 | 844 | 846 | 946 | 913 | 918 | 908 | 923 | 918 | 88δ(CH) |
| 900 | 877 | 872 | 773 | 754 | 752 | 820 | 846 | 849 | 781 | 766 | - | 55v(CS)+47δ _{ring} |
| 713 | 751 | 751 | 685 | 710 | 711 | 686 | 716 | 713 | 713 | 745 | - | 48δ _{ring} +40v(CS) |

^a Data from Ref. 3.

TABLE 2
Diagonal Force constants (in mdyn/Å⁻¹ or mdyn.rad/Å⁻²) and scaled factors obtained for thiophene.

| Coord. | MNDO | Refined | Experimental ^a | Factor |
|--------------------------|-------|---------------|---------------------------|--------|
| v(CH) _α | 5.290 | 5.346 (0.005) | 5.314 (0.013) | 0.796 |
| v(CH) _β | 5.265 | 5.218 (0.004) | 5.193 (0.010) | 0.796 |
| v(CS) | 4.378 | 4.177 (0.016) | 4.794 (0.067) | 0.755 |
| v(C=C) | 8.053 | 7.923 (0.014) | 8.704 (0.125) | 0.804 |
| v(CC) | 6.418 | 5.437 (0.036) | 6.574 (0.097) | 0.869 |
| δ(CH) _α | 0.395 | 0.408 (0.002) | 0.418 (0.005) | 0.854 |
| δ(CH) _β | 0.417 | 0.431 (0.002) | 0.435 (0.005) | 0.854 |
| δ _{ring} (sym) | 1.428 | 2.150 (0.022) | - | 0.978 |
| δ _{ring} (asym) | 1.271 | 1.767 (0.009) | - | 0.978 |
| γ(CH) _α | 0.336 | 0.327 (0.002) | 0.333 (0.002) | 0.749 |
| γ(CH) _β | 0.351 | 0.399 (0.002) | 0.400 (0.002) | 0.749 |
| γ _{ring} (1) | 0.430 | 0.447 (0.004) | - | 1.381 |
| γ _{ring} (2) | 0.387 | 0.418 (0.002) | - | 1.381 |

^a Data from Ref. 4.

the infrared and Raman spectra of the normal derivative [5] and in our calculations no new scaling factors are introduced in order to take into account the inter-rings modes. The proposed assignments are in good agreement with early works where we have used a complete set of scaling factors built also using the experimental data of large oligomers [6]. On the other hand, recently, vibrationally resolved fluorescence and fluorescence excitation spectra has been measured for solid and solvated thiophene [7] founding six strong fundamental modes of vibrations which also are in good agreement with our theoretical data.

TABLE 3

Calculated $k=0$ out-of-plane modes (in cm^{-1}) of polythiophene (PTh), deuterated-polythiophene (DPTh) and $2,5\text{-}^{13}\text{C}$ -polythiophene ($^{13}\text{CPTh}$).

| PTh | DPTh | $^{13}\text{CPTh}$ | P.E.D. |
|------------------------------------|------|--------------------|---|
| B_{2g} species | | | |
| 893 | 890 | 825 | 100 γ (CH) |
| 642 | 627 | 559 | 64 γ (CC)+33 γ (CH) |
| 393 | 388 | 345 | 39 γ_{ring} +35 γ (CC) |
| B_{3g} species | | | |
| 793 | 788 | 697 | 95 γ (CH) |
| 612 | 594 | 525 | 83 γ (CC) |
| 137 | 136 | 136 | 61 γ_{ring} |
| A_u species | | | |
| 884 | 883 | 805 | 100 γ (CH) |
| 581 | 575 | 469 | 83 γ_{ring} |
| 154 | 150 | 148 | 90 γ (CC) |
| B_{1u} species | | | |
| 772 | 771 | 619 | 100 γ (CH) |
| 490 | 477 | 461 | 100 γ_{ring} |
| 43 | 43 | 41 | 40 τ (CC)+35 γ (CC) |

3.2. Polymer: polythiophene

Before the study of the polymer we have transferred the scaling factors derived from the work on thiophene to the case of the tetrathiophene. Also in this case the scaling factors applied are the same to the monomer and no adjustment on them has been made. Then the MNDO scaled force field for the inner part of the tetramer has been used for the calculation of the phonon dispersion curves of the in-plane and out-of-plane modes of polythiophene. In this paper we restrict our discussion to the out-of-plane modes. In Table 3 we propose a vibrational assignment for the out-of-plane mode which have been calculated here for the first time and although there is experimental evidence only for the infrared active CH deformation [8] mode the values are close for the three isotopic derivatives.

REFERENCES

- 1 P.Pulay, G.Fogarasi, G.Pongor, J.E.Boggs and A.Vargha, J.Am.Chem.Soc., 105, (1983) 7037.
- 2 J.T.López Navarrete and G.Zerbi, Synth.Metals, 32, (1989) 151.
- 3 M.Rico, J.M.Orza and J.Morcillo, Spectrochim.Acta, 21, (1965) 689.
- 4 D.W.Scott, J.Mol.Spectrosc., 31, (1969) 451.
- 5 G.Zerbi, B.Chierichetti and O.Ingãnas, J.Chem. Phys., 94, (1991) 4637.
- 6 J.T.López Navarrete and G.Zerbi, J.Chem.Phys., 94, (1991) 957.
- 7 D.Birnbaum and B.E.Kohler, J.Chem.Phys., 95, (1991) 4783.
- 8 M.Akimoto, Y.Furukawa, H.Takeuchi, I.Harada, Y.Soma and M.Soma, Synth.Metals, 15, (1986) 353.