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Scaled Quantum-Mechanical Force Field and Vibrational Spectra of 3-Methylthiophene

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The infrared and Raman spectra of 3-methylthiophene at room temperature have been recorded and measured. A general assignment of its vibrational fundamentals has been proposed on the basis of these experimental data. An *ab initio* quadratic force field calculation at the 6-31G** level was carried out. The optimized molecular structure, frequencies, potential energy distribution, infrared intensities, and Raman activities obtained were in a good agreement with the experimental results.

Introduction

Polyconjugated organic polymers constitute a class of materials which at present has attracted the attention of many researchers because they show very large nonlinear optical responses and become good electrical conductors when suitably doped.[1−3] Among the newly synthesized polymers that present a high degree of processability while maintaining good electrical conductivities is the poly(3-methylthiophene), which has attracted a great deal of attention.

The contributions from vibrational spectroscopy to the field of conducting polymers have been and are relevant and unique since vibrational spectra provide simultaneous and selective information about the structure of a polymer and of its charge distributions. Raman scattering has become a very important tool for analyzing the delocalization of π electrons, helping chemists to synthesize new materials with improved properties. In this sense, it is necessary and important to carry out a careful assignment of the vibrational spectra of the polymer and its corresponding monomer guided by the computation of a suitable force field. The use of a quantum chemical approach has allowed us in past years to evaluate ground state geometries and electronic and vibrational properties on a series of polyconjugated oligomers and polymers which reproduced the experimental trends.[4−7] In the present work we carried out a complete assignment of the vibrational spectrum of 3-methylthiophene (3-MTP) from a combination of our experimental infrared and Raman data with high-level *ab initio* calculations. This work provides us with the necessary spectral information in order to understand the spectra of the polymer and also allows us to find an initial set of *ab initio* scaling factors of the force constants which will apply to the calculations of the phonon dispersion curves of the polymer.

Until recently the vibrational spectrum of 3-MTP has been the subject of very little research. The infrared and Raman spectra of 3-MTP was analyzed for the first time by McCullough *et al.*[8] in 1953 and, several years later, by Akiyama *et al.*,[9,10] who published a general study of several thiophene derivatives involving 3-MTP. More recently, we have reported a first assignment for the fundamental vibrations of this molecule,[6,11] in addition to a semiempirical MNDO force field as the way to obtain the best set of MNDO scaling factors for the polymer.

In the past few years, the interpretation of the vibrational spectra of polyatomic molecules has progressed because *ab initio* Hartree−Fock calculations using moderate size basis sets have been widely applied.[12−14] The purely theoretical force fields combined with empirical scaling factor sets allow for accurate predictions of the fundamental modes of medium-size molecules,[15] thus providing the scaled quantum-mechanical (SQM) *ab initio* force fields. As demonstrated by a great number of compounds, SQM force fields based on double-ζ basis sets usually reproduce experimental frequencies with mean errors of about ± 10 cm^{-1}. Here, we report Raman and Fourier transform infrared (FT-IR) spectra of 3-MTP. The experimental frequencies were first tentatively assigned on the basis of previous vibrational studies on thiophene and thiophene derivatives,[8−10,16−19] involving some methyl derivatives. In order to confirm these assignments, a SQM *ab initio* force field at the 6-31G** level has been performed, and both vibrational frequencies and infrared intensities were compared with the experiments, which allowed for a revision of our prior assignments.

The present work is organized as follows: firstly we give the experimental details and the calculation methods. Secondly we report the infrared and Raman spectra and discuss the assignments. Finally, we present the results from the normal coordinate analysis in terms of theoretical frequencies, potential energy distribution, infrared intensities, and Raman activities. In the last section we will present our conclusions.

Experimental Section

We have used 3-methylthiophene (Aldrich Chemie, 99+% purity) which was distilled several times under vacuum. The infrared spectra from pure liquid samples were obtained by using cells with 0.025 cm path length between potassium bromide windows and those from the gas by using suitable cells with 10 cm path length and sodium chloride windows containing the vapor in equilibrium with the pure liquid. All of the infrared spectra were recorded at room temperature in a Perkin-Elmer 1760X FT-IR spectrophotometer purged with Ar gas. To increase the signal-to-noise ratio a minimum of 20 scans were accumulated for all the cases, with a spectral resolution of 0.5 cm^{-1}. Raman spectra of room temperature liquid samples were recorded on a Jobin Yvon Ramanor U1000 spectrometer using excitation radiation wavelength at 488.0 nm generated by a Spectra Physics argon ion laser working at 100 mW. The best resolution obtained was 1 cm^{-1}.

Computational Methods

The equilibrium geometry for 3-MTP was predicted at the restricted Hartree−Fock (RHF) level of theory. We have used the 6-31G** standard basis set,[20] which includes a set of six second order (d-type) Gaussian primitive functions for the description of each heavy (non-hydrogen) atom and a single
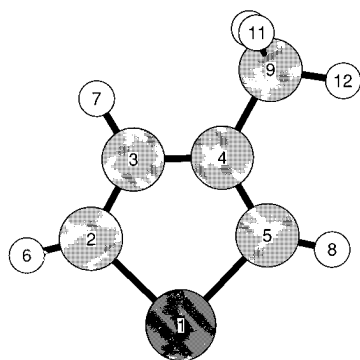
Figure 1. Molecular structure of 3-methylthiophene as predicted by the 6-31G** *ab initio* basis set, with the atomic numbering used in this work.

set of Gaussian p-type functions to each hydrogen atom. This basis set guarantees reasonable accuracy in vibrational frequency calculations for such a molecule. Cartesian force constants were evaluated within the same theoretical scheme used for the geometry optimization, where the second derivatives of the molecular energy were computed analytically. All the *ab initio* calculations were performed using the GAUSSIAN-92 program[21] on a Convex 240 at the CICA Computer Center of Sevilla (Spain). Maximal forces (in atomic units) after geometry optimization were lower than 2.6×10^{-4}. Maximal deviations from ideally zero translation and rotation frequencies were lower than 5.2 cm^{-1}. Frequencies were obtained by means of diagonalization of a mass-weighted Cartesian force constant matrix. Infrared absorption intensities were evaluated from atomic polar tensors,[22] and Raman activities were evaluated from analytical polarizability derivatives, both provided by the GAUSSIAN 92 program[21] using the 6-31G** basis set.

The Cartesian force constants were transformed into a set of nonredundant local symmetrical internal coordinates, defined according to the Pulay method,[23] in order to give a more useful description of the vibrational potential energy and make further calculations easier. The scaling of the 6-31G** force field was performed following the method proposed by Pulay and co-workers,[24] in three steps. First, we used a single scaling factor to get an initial description of the fundamental frequencies to compare them with the observed frequencies. Then, a set of starting scaling factors was built from the ratio between the experimental and theoretical frequencies. Finally, the scaling factors were refined by means of an iterative process until root mean square (rms) deviation of the calculated frequencies was reduced to an acceptable magnitude, obtaining a different factor for every force constant which has a different character. The descriptions of the predicted frequencies during the scaling process were followed by the potential energy distribution (PED) matrix. Frequencies and normal coordinates were calculated by the Wilson FG methodology.[25]

Results and Discussion

The molecule of 3-MTP is composed of 12 atoms, so it has 30 normal vibrational modes. Its molecular structure has not been studied by any diffraction technique; therefore we have taken into account two different symmetries depending on the conformation of the methyl group. If one of the methyl hydrogen atoms is coplanar to the aromatic ring (Figure 1) the molecule is C_s; otherwise, it would belong to the C_1 point group. On the basis of a C_s symmetry, the 30 fundamental vibrations of 3-MTP can be distributed as 20 A′ + 10 A″. But if the molecule were C_1 there would not be any relevant distribution.

(A) Assignment of the Spectra. The FT-IR spectrum of 3-MTP is shown in Figure 2, while Figure 3 displays the

Figure 2. FT-IR spectrum of 3-methylthiophene in the liquid phase: (a) 2800−3200 cm^{-1} region; (b) 400−1800 cm^{-1} region.

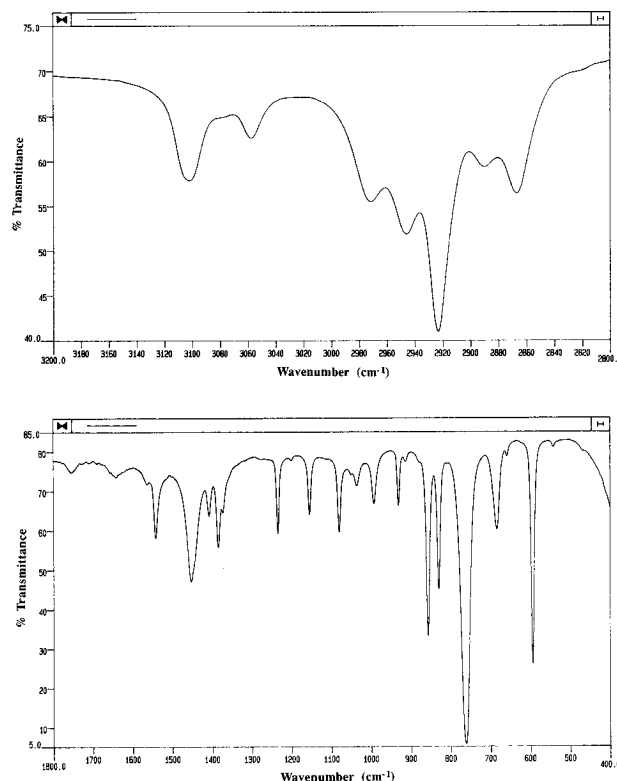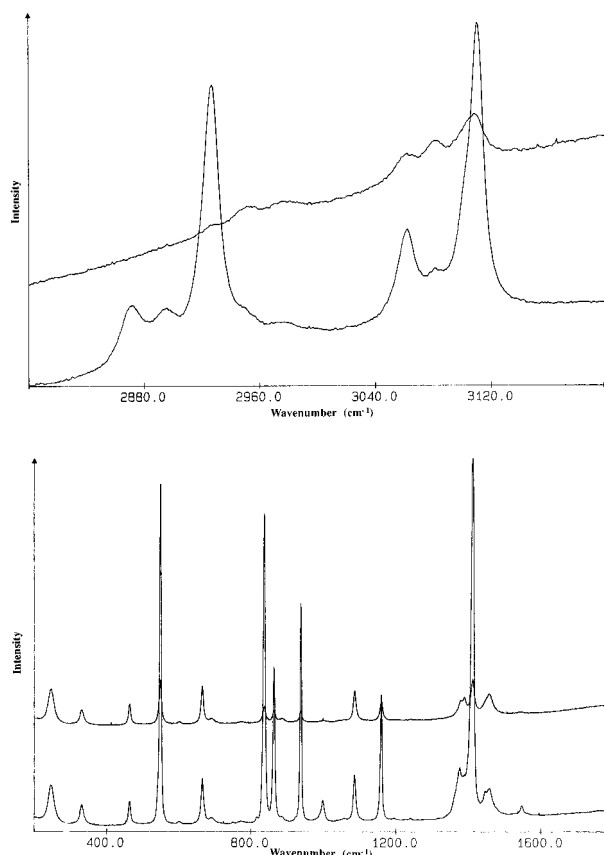**Figure 3.** Polarized Raman spectrum of 3-methylthiophene in the liquid phase: (a) 2800−3200 cm^{-1} region; (b) 200−1800 cm^{-1} region.

polarized Raman spectra. The frequencies, relative intensities, and depolarization ratios measured on these spectra are listed in Table 1, together with the proposed assignments for fundamental and some overtones and combination vibrations.

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TABLE 1: Experimental Frequencies and Proposed Assignments for Bands Measured in the Infrared and Raman Spectra of 3-Methylthiophene

infrared		Raman			
freq[b]	intens[c]	freq[b]	intens[c]	ρ^d	assignment[a]
3101	m	3111	m	p	$\nu(C_\alpha H)$, A'
		3104	sh		$\nu(C_\alpha H)$, A'
3056	w	3062	w	p	$\nu(C_\beta H)$, A'
2971	m	2978	vw		$\nu_a(CH_3)$, A'
2945	m−s	2953	vw		$\nu_a(CH_3)$, A''
2923	s	2927	m	p	$\nu_s(CH_3)$, A'
2890	wv	2897	vw	p	$2\delta_a(CH_3)$, A'
2867	w	2872	vw	p	$2\delta_a(CH_3)$, A'
2732	vw	2733	vw	p	$2\delta_s(CH_3)$, A'
1753	vw				$\delta(CH) + \gamma(CH)$, A''
1642	vw				$2\nu_s(CS)$, A'
1563	vw				$r(CH_3) + \delta(ring)$, A''
1542	m	1543	vw	p	$\nu_a(C=C)$, A'
1452	m	1453	w	dp	$\delta_a(CH_3)$, A''
1447	sh	1442	w	p	$\delta_a(CH_3)$, A'
1408	w	1407	vs	p	$\nu_s(C=C)$, A'
1385	m	1383	vw		$\delta_s(CH_3)$, A'
1373	w	1371	w	p	$\nu(CC)$, A'
1276	vw				$\nu_s(CS) + \gamma(ring)$, A''
1234	m	1233	vw		$\delta(CH)$, A'
1201	vw				$2\gamma(ring)$, A'
1155	m	1154	m	p	$\delta(CH)$, A'
1080	m	1081	w	p	$\delta(CH)$, A'
1036	vw	1039	vw		$r(CH_3)$, A''
993	w−m	993	w	p	$r(CH_3)$, A'
931	w−m	930	s	p	$\nu(CX)$, A'
914	vw	917	vw	p	$2\delta(ring)$, A'
877	sh	874	vw	dp	$\gamma(CH)$, A''
857	s	856	m	p	$\nu_a(CS)$, A'
830	m−s	830	vs	p	$\nu_s(CS)$, A'
762	vs	766	vw		$\gamma(CH)$, A''
685	m	683	vw		$\gamma(CH)$, A''
659	vw	659	w		$\delta(ring)$, A'
594	s	594	vw		$\gamma(ring)$, A''
542	vw	542	vs p	p	$\delta(ring)$, A'
464	vw	457	w	dp	$\gamma(ring)$, A''
		323	w	p	$\delta(CX)$, A'
		238	w	dp	$\gamma(CX)$, A''

[a] See Table 2 for descriptions; s = symmetric; a = antisymmetric. [b] In cm^{-1}. [c] w = weak; m = medium; s = strong; v = very; sh = shoulder. [d] Depolarization ratios: p = polarized; dp = depolarized.

TABLE 2: Description of the Local-Symmetrical Modes Used in the Assignment of the Fundamental Vibrations of 3-Methylthiophene

description	no.	symbol[a]
methyl C−H stretching	3	$\nu(CH_3)$
methyl C−H bending	3	$\delta(CH_3)$
methyl C−H rocking	2	$r(CH_3)$
methyl C−H torsion	1	$\tau(CH_3)$
ring C−H stretching	3	$\nu(CH)$
ring C−H in-plane bending	3	$\delta(CH)$
ring C−H out-of-plane bending	3	$\gamma(CH)$
ring C=C stretching	2	$\nu(C=C)$
ring C−C stretching	1	$\nu(CC)$
ring C−S stretching	2	$\nu(CS)$
ring in-plane bending	2	$\delta(ring)$
ring out-of-plane bending	2	$\gamma(ring)$
ring-methyl stretching	1	$\nu(CX)$
ring-methyl in-plane bending	1	$\delta(CX)$
ring-methyl out-of-plane bending	1	$\gamma(CX)$

To make the assignment task easier, we have adopted a set of local-symmetrical modes[24] that can be correlated with characteristic group frequencies; they are listed in Table 2. The assignment discussion is based on previous vibrational studies reported for thiophene and nine deuterated derivatives, methyl group characteristic frequencies, and depolarization ratios measured from the Raman spectra. We have classified the normal modes into three groups corresponding to (i) thiophene ring vibrations, (ii) methyl group vibrations, and (iii) ring-methyl vibrations.

Thiophene Ring Vibrations. The intensity and width of the absorption recorded at 3101 cm^{-1} in the infrared spectrum of 3-MTP lead us to believe that this band is composed of two overlapped $\nu(C_\alpha H)$ stretching vibrations involving the α-hydrogens of the thiophene ring. In the Raman spectra, one of these fundamental vibrations appears as a medium intensity band at 3111 cm^{-1}, the other vibration being observed as the shoulder measured at 3104 cm^{-1}. The $\nu(C_\beta H)$ mode has been assigned to the infrared band measured at 3056 cm^{-1} and at 3062 cm^{-1} in the Raman spectrum. The importance of these bands comes from the fact that the relationship between the infrared intensities of the $\nu(C_\alpha H)$ and $\nu(C_\beta H)$ vibrations can be an approximate measurement of the polymerization degree. As has been seen before, the fundamental vibrations involving α-atoms give rise to more intense bands than those involving β-atoms; from this fact we can infer data about the chain length distribution of the polymer and about some mislinkings in $\alpha-\beta'$ sites between adjacent rings.

The highest frequency absorption observed below 1800 cm^{-1} has to be assigned to the antisymmetric $\nu_a(C=C)$ stretching vibration. This mode has been measured at 1542 cm^{-1} for 3-MTP, and for thiophene it was assigned by Morcillo et al.[18] at 1504 cm^{-1}. Our proposed assignment for the related symmetric mode, $\nu_s(C=C)$, is very close to that proposed for thiophene. The results reported by Furukawa[26] on several thiophene oligomers and the polymer indicate that the $\nu_a(C=C)$ vibration should shift to lower frequencies when the chain length increases as a consequence of the conjugation, while the intensities should shift to higher values. This fact has been proven in this laboratory from theoretical and experimental studies.[7,27] The relationship between the antisymmetric and symmetric $\nu(C=C)$ infrared intensities can also be used to approach the conjugation length.

We have assigned the $\nu(CC)$ ring vibration of 3-MTP to the weak infrared band at 1373 cm^{-1}, which appears in the Raman spectrum as a polarized peak at 1371 cm^{-1}. This fundamental vibration was assigned at 1358 cm^{-1} in thiophene,[18,19] supporting our results. However, a medium intensity band close to that measured at 1373 cm^{-1} can be observed in 3-MTP, namely, at 1385 cm^{-1}, and it could be assigned to the $\delta_s(CH_3)$ bending vibration, but an extensive coupling with the $\nu(CC)$ vibration would be expected. Their proposed assignments will be revised again in the light of the normal coordinate calculation.

The four $\delta(CH)$ in-plane bending vibrations of thiophene were reported by Morcillo et al.[18] at 1250, 1085, 1080, and 1036 cm^{-1}, where the second one is calculated from the isotopic product rule on several deuterated derivatives. These data also indicated that the two $\delta(C_\beta H)$ modes had to be assigned to the bands at 1250 and 1080 cm^{-1} in the infrared spectrum of liquid thiophene. From these previous data we have assigned the $\delta(C_\beta H)$ vibration of 3-MTP to the medium infrared peak measured at 1234 cm^{-1}, while the bands at 1155 and 1080 cm^{-1} were assigned to the two $\delta(C_\alpha H)$ bending modes. The later were observed in the Raman spectrum as polarized bands at 1154 and 1081 cm1^{-1}, thus supporting their assignments. The former was observed as a very weak band, and therefore its depolarization ratio could not be measured.

The frequencies measured for antisymmetric and symmetric $\nu(CS)$ vibrations in 3-MTP are very similar to those reported by Morcillo for the same vibrations of liquid thiophene,[18] namely, 870 and 834 cm^{-1}, respectively. Thus, the $\nu_a(CS)$ was registered at 857 cm^{-1} in the infrared spectrum and at 856 cm^{-1}
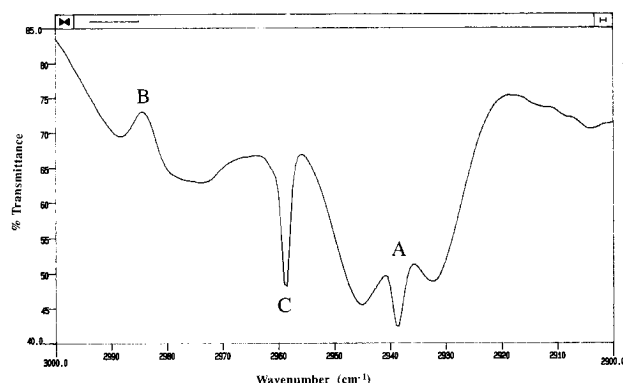
Figure 4. FT-IR spectrum of 3-methylthiophene in the gas phase: methyl stretching region.

TABLE 3: Optimized 6-31G** Structural Parameters Obtained for 3-Methylthiophene[a]

bond[b]	3-MTP	thiophene	angle[c]	3-MTP	thiophene
S_1-C_2	1.724	1.714	$S_1-C_2-C_3$	111.78	111.47
S_1-C_5	1.728	1.714	$C_2-C_3-C_4$	113.18	112.45
C_2-C_3	1.343	1.370	$C_3-C_4-C_5$	111.41	112.45
C_2-H_6	1.071	1.078	$C_4-C_5-S_1$	112.60	111.47
C_3-C_4	1.442	1.423	$C_5-S_1-C_2$	91.02	92.16
C_3-H_7	1.075	1.081	$S_1-C_2-H_6$	120.51	119.85
C_4-C_5	1.346	1.370	$C_2-C_3-H_7$	123.46	123.28
C_4-C_9	1.504		$S_1-C_5-H_8$	120.11	119.85
C_5-H_8	1.072	1.078	$C_3-C_4-C_9$	123.32	
C_9-H_{10}	1.086		$C_4-C_9-H_{10}$	111.00	
C_9-H_{11}	1.086		$C_4-C_9-H_{11}$	111.00	
C_9-H_{12}	1.083		$C_4-C_9-H_{12}$	111.16	
			$H_{10}-C_9-H_{11}$	107.48	
			$H_{10}-C_9-H_{12}$	108.03	
			$H_{11}-C_9-H_{12}$	108.03	

[a] See Figure 1 for atomic numbering. Experimental data of thiophene have been included for comparison. [b] Angstroms. [c] Degrees.

in the Raman one, while ν_s(CS) was assigned at 830 cm^{-1} in the two cases. These two Raman peaks are intense and polarized. The in-plane ring bending vibrations have been observed for 3-MTP at lower frequencies than for thiophene,[18] as the result of the presence of a methyl group instead of a hydrogen atom. The proposed frequencies for these two fundamentals are 659 and 542 cm^{-1}, the last one being a very intense and strongly polarized Raman line.

The γ(CH) vibrations were reported by Morcillo *et al.*[18] at 903, 867, 714, and 688 cm^{-1} for thiophene, and on the basis of these frequencies and our results about depolarization ratios, we have assigned two out-of-plane C−H bending modes to the Raman bands measured at 874 and 683 cm^{-1}. These modes appear with weak intensities and are depolarized. The third γ(CH) was assigned to a strong infrared absorption measured at 762 cm^{-1}, which is usually observed in the infrared spectrum of aromatic rings. Finally, we have assigned the two γ(ring) of 3-MTP at 594 and 457 cm^{-1}, both near the frequencies reported by Morcillo *et al.*[18] for the same vibrations, namely, 567 and 453 cm^{-1}.

Methyl Group Vibrations. Three strong peaks can be observed in the infrared spectrum of 3-MTP between 2900 and 3000 cm^{-1}. This is the usual range of appearance for aliphatic C−H stretching vibrations;[28] therefore they have been assigned to the ν(CH$_3$) modes. The band at 2927 cm^{-1} is strongly polarized, so we have assigned it to the ν_s(CH$_3$), A′ mode. The other two bands correspond to ν_a(CH$_3$) vibrations, and they have very weak intensities in the Raman spectrum, so that their depolarization ratios are not definitive. In order to determine their symmetry species, we have recorded the infrared spectrum of 3-MTP in the gas phase, and Figure 4 shows the band contours for methyl stretching vibrations. Although some overlapping among these bands exists, the band measured at 2945 cm^{-1} in the liquid phase infrared spectrum shows a clear type C contour, with a strong central maximum at 2958 cm^{-1}. This fact means that the change of dipole moment for the corresponding vibration is in the direction of the largest moment of inertia axis (for 3-MTP this is the axis perpendicular to the thiophene ring). Because of that, we have assigned it as an A″ mode in the basis of a C_s symmetry.

The degenerate δ_a(CH$_3$) modes usually give rise to two very close infrared absorptions near 1450 cm^{-1}.[28] These modes produce a broad infrared band with a maximum at 1452 cm^{-1} and a shoulder measured at 1447 cm^{-1} for 3-MTP. In the Raman spectra they appear as two weak bands at 1453 and 1442 cm^{-1}. Data from the polarized Raman spectra indicate that the band at 1453 cm^{-1} is depolarized. Although depolarization ratios for δ(CH$_3$) vibrations are not evidence as strong as those for ν(CH$_3$) in order to confirm the methyl orientation, this

depolarized band agrees with our initial hypothesis about the molecular conformation of 3-MTP.

As was pointed out above, we cannot decide on an unambiguous assignment for the δ_s(CH$_3$) vibration; in the infrared spectrum of 3-MTP we have measured two bands at 1385 and 1373 cm^{-1}, and in our opinion they would have a mixed character involving both δ_s(CH$_3$) and ν(CC) vibrations. The corresponding first overtones of these three methyl bending vibrations were observed at 2890, 2867, and 2732 cm^{-1} in the infrared spectrum of 3-MTP. All of them appear as polarized Raman bands, thus supporting their assignments. Finally, we have assigned the two r(CH$_3$) rocking vibrations, on the basis of previous works on methyl-substituted aromatic compounds,[29,30] at 1036 and 993 cm^{-1} in the infrared spectrum and at 1039 and 993 cm^{-1} in the Raman spectrum, the second one being clearly polarized.

Ring-Methyl Vibrations. Three ring-methyl vibrations can be assigned for 3-MTP, named as ν(CX), δ(CX), and γ(CX) vibrations (see Table 2). The former was assigned to the strong band measured at 931 cm^{-1} in the Raman spectrum, while for the δ(CX) vibration we have chosen the Raman band at 323 cm^{-1}, both of them polarized, therefore corresponding to two A′ vibrations. The γ(CX) vibration has been assigned in the Raman spectrum at 238 cm^{-1}. As expected, the two ring-methyl bending fundamentals have the lowest frequencies in the spectra, with the exception of the methyl torsional vibration, which was not observed because of its extremely low frequency.

(B) Force Field and Normal Coordinate Calculations. A force field calculation requires the previous optimization of the molecular structure until it has a minimal point of energy. The geometrical parameters corresponding to this point are listed in Table 3. No comparison between calculated and observed values has been made because of the unavailability of experimental geometry for this molecule. Nevertheless, we can compare distances and angles from the thiophene ring of this molecule with those reported for unsubstituted thiophene from experimental works,[31] which are included in the Table 3. In general we conclude that the predicted values for 3-MTP are very close to the experimental data of thiophene, the maximal differences being 0.027 Å for bond lengths and 1.13° for bond angles. Distortions yielded by the methyl substitution are also small, especially those related to interatomic distances, for which the highest distortion is 0.004 Å. Deviations are also negligible for the bond angles, except between the two C=C−C angles, which are calculated with a difference of 1.67°. Finally, the optimized structure agrees with the C_s symmetry, supporting

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TABLE 4: Symmetrized Pulay Coordinates Used in This Work for the Vibrational Analysis of 3-Methylthiophene

no.[a]	coordinated[b]	description
	A′ Species	
1	$r_{5\,8}$	$C_\alpha H$ stretching
2	$r_{3\,7}$	$C_\beta H$ stretching
3	$r_{2\,6}$	$C_\alpha H$ stretching
4	$6^{-1/2}(2r_{9\,12} - r_{9\,11} - r_{9\,10})$	CH_3 antisym stretching
5	$3^{-1/2}(r_{9\,12} + r_{9\,11} + r_{9\,10})$	CH_3 sym stretching
6	$r_{2\,3}$	C=C stretching
7	$r_{4\,5}$	C=C stretching
8	$6^{-1/2}(2\beta_{11\,9\,10} - \beta_{11\,9\,12} - \beta_{10\,9\,12})$	CH_3 antisym bending
9	$6^{-1/2}(\beta_{11\,9\,10} + \beta_{11\,9\,12} + \beta_{10\,9\,12} - \beta_{4\,9\,12} - \beta_{4\,9\,11} - \beta_{4\,9\,10})$	CH_3 sym bending
10	$r_{3\,4}$	C−C stretching
11	$2^{-1/2}(\beta_{4\,5\,8} - \beta_{1\,5\,8})$	$C_\alpha H$ in-plane bending
12	$2^{-1/2}(\beta_{4\,3\,7} - \beta_{2\,3\,7})$	$C_\beta H$ in-plane bending
13	$2^{-1/2}(\beta_{3\,2\,6} - \beta_{1\,2\,6})$	$C_\alpha H$ in-plane bending
14	$r_{4\,9}$	CX stretching
15	$6^{-1/2}(2\beta_{4\,9\,12} - \beta_{4\,9\,11} - \beta_{4\,9\,10})$	CH_3 rocking
16	$r_{1\,5}$	CS stretching
17	$r_{1\,2}$	CS stretching
18	$(2.5)^{-1/2}[\beta_{2\,1\,5} - 0.809017(\beta_{1\,5\,4} + \beta_{1\,2\,3}) + 0.309017(\beta_{5\,4\,3} + \beta_{2\,3\,4})]$	ring sym in-plane bending
19	$(9.045)^{-1/2}[1.118033(\beta_{1\,2\,3} - \beta_{1\,5\,4}) + 1.809017(\beta_{5\,4\,3} - \beta_{2\,3\,4})]$	ring antisym in-plane bending
20	$2^{-1/2}(\beta_{4\,5\,8} - \beta_{1\,5\,8})$	CX in-plane bending
	A″ Species	
21	$2^{-1/2}(r_{9\,11} - r_{9\,10})$	CH_3 antisym stretching
22	$2^{-1/2}(\beta_{11\,9\,12} - \beta_{10\,9\,12})$	CH_3 antisym bending
23	$6^{-1/2}(\beta_{4\,9\,11} - \beta_{4\,9\,10})$	CH_3 rocking
24	ϕ_8	CH out-of-plane bending
25	ϕ_7	CH out-of-plane bending
26	ϕ_6	CH out-of-plane bending
27	$(2.5)^{-1/2}[\tau_{3\,4} - 0.809017(\tau_{5\,4} + \tau_{2\,3}) + 0.309017(\tau_{1\,5} + \tau_{1\,2})]$	ring sym. out-of-plane bending
28	$(9.045)^{-1/2}[1.118033(\tau_{5\,4} - \tau_{2\,3}) + 1.809017(\tau_{1\,5} - \tau_{1\,2})]$	ring antisym out-of-plane bending
29	ϕ_9	CX out-of-plane bending
30	$\tau_{4\,9}$	CH_3 torsion

[a] Arbitrary numbering. [b] The atomic numbering is defined in Figure 1. r_{ij} is the stretching vibrations of the bond between atoms i and j. β_{ijk} is the in-plane vibration of the angle between atoms i, j, and k. ϕ_i is the out-of-plane vibration of the atom i. τ_{ij} is the torsion vibration respect to the bond between atoms i and j, which was defined as described in refs 36 and 37.

our previous conclusions from the vibrational analysis. As a consequence, all the atoms of the molecule are placed in the symmetry plane with the exception of two hydrogens from the methyl group, which are equivalent. In addition, the hydrogen atom of the methyl group which is coplanar to the thiophene ring is in the *cis* conformation with respect to the nearest double bond.

As previously mentioned, the 6-31G** Cartesian force field was transformed into a set of internal coordinates; they were defined according to the Pulay methodology[23] and are listed in Table 4. From this force field, we have obtained the SQM force field by applying the set of optimized scaling factors shown in Table 5. The complete force field is listed in Tables 6 and 7, whereas Table 8 shows the results concerning frequencies, intensities, and potential energy distribution, together with the experimental data discussed above.

In relation to the theoretical spectra, the 6-31G** SQM force field reproduces the experimental frequencies with a root mean square error of ± 8 cm^{-1}. In addition, the normal vibration description agrees with the proposed assignments in most of the cases. As expected, the assignments for the fundamental

TABLE 5: Scaling Factors Applied to the 6-31G Force Field of 3-Methylthiophene**

coordinates[a]	description[b]	factor[c]	coordinates[a]	description[b]	factor[c]
1, 2, 3	$\nu(CH)$	0.828 (1)	15	$r(CH_3)$	0.819 (4)
4, 21	$\nu_a(CH_3)$	0.827 (2)	23	$r(CH_3)$	0.772 (1)
5	$\nu_s(CH_3)$	0.845 (1)	16, 17	$\nu(CS)$	0.865 (8)
6, 7	$\nu(C=C)$	0.729 (1)	18, 19	$\delta(ring)$	0.954 (9)
8, 22	$\delta_a(CH_3)$	0.813 (15)	20	$\delta(CX)$	0.948 (3)
9	$\delta_s(CH_3)$	0.793 (3)	24, 25, 26	$\gamma(CH)$	0.696 (3)
10	$\nu(CC)$	0.808 (2)	27, 28	$\gamma(ring)$	0.965 (40)
11, 12, 13	$\delta(CH)$	0.808 (1)	29	$\gamma(CX)$	0.887 (22)
14	$\nu(CX)$	0.808 (5)	30	$\tau(CH_3)$	0.965 (40)

[a] The numbering corresponds to the coordinates defined in Table 4.
[b] See Table 1 for symbols: s = symmetric, a = antisymmetric.
[c] Dispersion on optimized scaling factors in parentheses.

vibrations having the highest frequencies (up to 1400 cm^{-1}) have been unambiguously confirmed, and all of them can be assigned to very local modes. On the contrary, the normal coordinates involved in the remaining frequencies are extensively coupled. Consequently the bands measured below 1400 cm^{-1} cannot be assigned to a single coordinate, with the exception of those related to the methyl bending vibrations, and only the PED matrix can give their correct descriptions. Nevertheless the assignments proposed in Table 1 in general correspond to the more significant vibration of each frequency. The assignments for the observed bands at 1385 and 1378 cm^{-1} were uncertain, and in our opinion, both the $\delta_s(CH_3)$ and $\nu(CC)$ vibrations had to be involved in these two frequencies. The theoretical spectrum predicts them with minimal deviations, and their descriptions show an extensive mixing involving the $\delta_s(CH_3)$, $\nu(CC)$, and $\delta(CH)$ coordinates. In addition, the C−C stretching mode has some significant contributions (more that 10% of PED) in four theoretical frequencies between 1400 and 800 cm^{-1}, thus making a simple assignment difficult for it. Similar behavior is observed for the $\nu(CX)$ normal mode, but its contribution is negligible for the frequency of 936 cm^{-1} (the experimental value is 931 cm^{-1}), to which it was initially assigned. On the basis of the PED, this frequency should be assigned to a $\delta(ring)$ vibration, while a definitive assignment for the $\nu(CX)$ vibration remains uncertain.

Concerning the out-of-plane (A″) vibrations, a very strong interaction has been predicted between the three $\gamma(CH)$ modes and both the $\gamma(ring)$ and $\gamma(CX)$ modes. Especially for the theoretical frequencies 874 and 842 cm^{-1}, and SQM force field has calculated significant contributions of the $\gamma(CH)/\gamma(ring)$ off-diagonal force constants. The proposed assignments coincide, for all of these frequencies, with the most contributing coordinate of the corresponding potential energy distribution.

As previously mentioned, the scaling factors shown in Table 5 were obtained by an iterative process fitting the theoretical frequencies to those observed for 3-MTP. During the refinement period we tried to maintain, as far as possible, the minimal number of different scaling factors, and the coordinates with the same description were multiplied by an identical factor; they are listed in the same rows of the Table 5. The only exception were the two methyl rocking coordinates, for which the factors 0.819 and 0.772, corresponding to the A′ and A″ $r(CH_3)$ vibrations, respectively, were obtained. On the other hand, we would like to emphasize that these scaling factors are very similar to those reported for a 6-31G SQM force field of phthalonitrile,[32] especially concerning the C−H ring vibrations. The involved scaling factors for phthalonitrile were 0.82, 0.80, and 0.67 for the stretching, in-plane bending and out-of-plane bending vibrations, respectively, and are close to those reported in the present paper, namely, 0.828, 0.808, and 0.696 for the same vibrations. The differences are also negligible for the

TABLE 6: Scaled 6-31G** In-Plane Force Field[a] for the 3-Methylthiophene Molecule (Force Constants in millidyne per angstrom)

no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	5.272 22																			
2	0.003 06	5.150 81																		
3	−0.001 33	0.008 06	5.294 04																	
4	0.007 32	−0.004 13	0.000 17	4.754 51																
5	0.003 71	0.004 19	0.000 97	0.040 87	4.947 51															
6	0.053 10	0.007 03	0.000 19	0.008 19	0.001 66	7.013 80														
7	−0.025 51	0.084 95	−0.023 50	−0.009 43	0.012 19	−0.273 23	7.106 46													
8	0.001 63	0.001 44	0.053 26	−0.131 77	0.007 30	−0.004 34	−0.005 70	0.553 60												
9	−0.004 05	−0.006 03	0.000 04	−0.000 08	0.105 45	−0.012 28	−0.004 88	0.002 26	0.535 70											
10	−0.013 16	0.064 10	−0.001 73	−0.005 04	0.001 10	0.537 93	0.521 11	0.003 32	−0.018 16	5.021 38										
11	0.001 62	0.004 83	−0.013 18	0.005 07	0.002 48	0.092 63	−0.013 33	0.001 07	−0.002 28	−0.006 29	0.425 17									
12	0.006 08	0.000 64	−0.002 90	−0.005 26	0.002 69	−0.002 60	−0.114 74	0.001 42	−0.001 74	0.103 54	0.011 18	0.446 37								
13	−0.002 63	−0.003 93	0.002 64	0.001 95	0.001 45	−0.011 86	0.086 01	−0.000 34	−0.001 08	−0.008 91	0.014 67	0.009 77	0.419 76							
14	0.003 37	0.011 74	0.003 81	−0.036 38	0.119 16	0.178 63	−0.015 41	−0.023 40	−0.274 77	0.180 60	−0.012 74	−0.008 38	0.003 46	4.311 93						
15	0.004 81	−0.003 84	0.002 61	0.093 16	−0.000 58	−0.015 74	−0.001 65	−0.013 06	−0.004 72	0.040 75	0.002 46	−0.002 85	0.005 78	0.016 92	0.648 86					
16	0.061 33	−0.040 06	−0.012 45	0.000 29	0.012 94	0.476 39	0.229 78	0.004 24	−0.020 94	−0.226 57	−0.134 49	−0.001 87	0.028 53	0.029 67	−0.015 83	3.894 99				
17	−0.006 91	−0.003 35	0.059 85	0.011 86	−0.013 60	0.225 78	0.505 34	0.000 74	0.014 72	−0.235 13	0.026 00	0.000 73	−0.131 84	−0.076 46	0.003 30	−0.222 22	3.951 07			
18	0.087 00	−0.049 19	0.083 49	0.003 03	−0.005 37	−0.291 00	−0.287 09	0.068 69	0.015 10	0.429 69	−0.046 27	0.001 83	−0.046 06	−0.101 77	0.017 97	0.102 47	1.107 73	1.859 02		
19	0.084 40	0.133 28	−0.075 22	0.004 22	−0.020 99	0.144 59	−0.152 29	0.001 32	0.032 50	−0.016 76	0.050 96	0.030 05	−0.052 16	−0.216 82	−0.024 24	−0.372 07	0.401 30	0.018 61	1.579 90	
20	0.015 59	−0.004 25	0.007 16	0.061 21	0.000 33	−0.172 11	−0.020 29	0.015 76	0.012 79	0.152 99	0.005 95	−0.013 54	0.013 09	−0.035 36	0.119 55	0.010 78	0.018 92	0.072 35	−0.026 28	0.739 49

[a] Scaling factors from Table 5. See Table 4 for numbering.
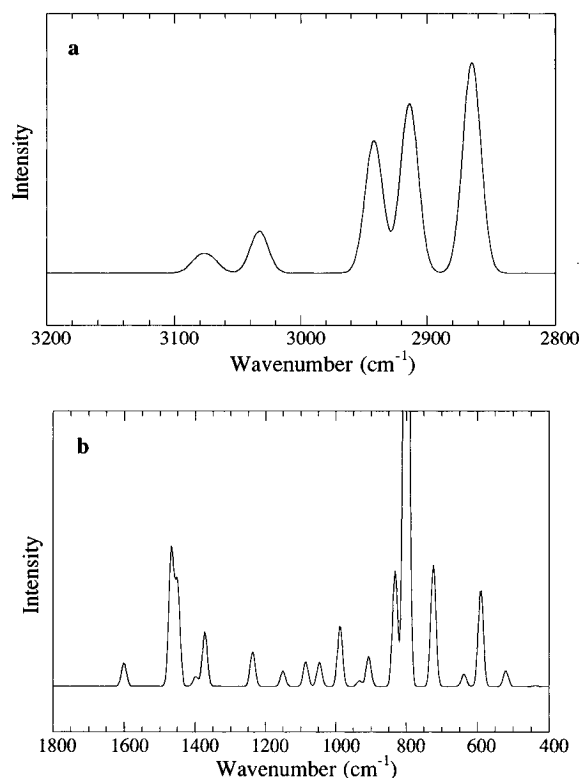
Figure 5. Infrared spectrum of 3-methylthiophene as predicted by the 6-31G** *ab initio* basis set: (a) 2800−3200 cm^{-1} region; (b) 400−1800 cm^{-1} region.

C—C stretching coordinates, in line with the SQM philosophy,[15] but the δ(ring) and γ(ring) vibrations are significantly different between phthalonitrile and 3-MTP as a consequence of the presence of the sulfur atom.

The complete list of scaled force constants obtained for 3-MTP are shown in Tables 6 and 7, and they can be compared with those reported for the thiophene molecule.[7,33−35] The force constants obtained here for the C—H coordinates do not appreciably differ from both scaled-MNDO[7] and experimental[33] force fields of thiophene, as can be seen in Table 9. Like the related vibrational frequencies, these force constants remain practically unchanged upon methyl substitution. On the contrary, this behavior is not observed for force constants involving the C—C and C—S bonds. In fact, the scaled-MNDO force constants reported for these coordinates[7] are significantly lower than the experimental ones,[33] and those obtained in the present work are lower than the semiempirical data. In our opinion this is the consequence of a more realistic prediction of the off-diagonal force constants, in addition to the effect of the methyl group; these force constants have a greater contribution in the 6-31G** SQM force field. The most extreme case is the ν(C=C) force constant, which reported values are 8.704 (thiophene, experimental[33]), 7.923 (thiophene, scaled-MNDO[7]), and 7.106 mdyn/Å (3-MTP, 6-31G**, present work).

The fit between calculated and experimental vibrational frequencies is not the only criterium for evaluating the value of a quantum-mechanical force field. Infrared absorption intensities and Raman activities and depolarization ratios can also be compared with the experimental ones. The whole set of 6-31G** calculated values for 3-MTP are included in Table 8. We have displayed in Figure 5 the predicted infrared spectra from these data, where all of the frequencies have been scaled by a factor of 0.9 in order to permit a better comparison with the experimental spectra shown in Figure 2. As can be observed, there is a good correlation between theoretical and

SQM Force Field and Vibrational Spectra of 3-MTP

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TABLE 7: Scaled 6-31G** Out-of-Plane Force Field[a] for the 3-Methylthiophene Molecule (Force Constants in millidynes per angstrom or Equivalent Units)

no.	21	22	23	24	25	26	27	28	29	30
21	4.675 841									
22	0.158 637	0.544 086								
23	0.118 577	0.014 498	0.592 823							
24	0.004 363	−0.002 221	0.020 431	0.236 744						
25	0.002 455	0.005 105	0.022 391	0.010 792	0.291 285					
26	−0.003 628	0.002 394	0.002 550	0.032 917	−0.002 692	0.250 965				
27	−0.020 839	−0.006 394	−0.050 632	−0.056 546	−0.125 034	0.064 252	0.482 906			
28	0.011 020	0.006 616	0.039 526	0.096 796	0.013 304	0.097 201	0.002 372	0.494 375		
29	−0.028 309	0.008 158	−0.074 506	0.001 088	0.005 107	−0.013 208	−0.128 693	−0.023 788	0.476 045	
30	0.019 914	−0.001 576	0.006 789	0.002 446	0.002 924	−0.004 027	−0.014 774	0.012 209	−0.021 175	0.034 825

[a] Scaling factors from Table 5. See Table 4 for numbering.

TABLE 8: Scaled 6-31G** Frequencies,[a] Infrared Intensities, and Raman Activities[b] Calculated for 3-Methylthiophene

vibra-tion	exptl freq	calcd freq	IR intens	Raman activity	ρ^c	PED[d] (greater 10%)
				A′ Species		
ν_1	3111	3113	2.59	126.5	0.24	$96\nu(C_\alpha H)$
ν_2	3104	3104	2.30	70.3	0.34	$100\nu(C_\alpha H)$
ν_3	3062	3064	8.09	89.5	0.42	$96\nu(C_\beta H)$
ν_4	2971	2973	25.44	67.8	0.74	$93\nu_a(CH_3)$
ν_5	2923	2924	40.55	151.8	0.02	$93\nu_s(CH_3)$
ν_6	1543	1556	2.54	1.78	0.56	$63\nu(C=C)$, $11\delta(C_\beta H)$
ν_7	1447	1464	14.67	34.79	0.44	$84\delta_a(CH_3)$
ν_8	1407	1401	6.12	28.76	0.23	$78\nu(C=C)$
ν_9	1385	1389	1.08	9.85	0.73	$44\delta_s(CH_3)$, $23\nu(CC)$, $12\delta(C_\alpha H)$
ν_{10}	1373	1373	5.91	5.52	0.36	$49\delta_s(CH_3)$, $11\nu(C-C)$, $20\delta(C_\alpha H)$
ν_{11}	1234	1247	3.74	0.85	0.17	$42\delta(C_\alpha H)$, $27\delta(C_\beta H)$
ν_{12}	1154	1150	1.67	6.39	0.61	$54\delta(C_\alpha H)$, $25\nu(CX)$
ν_{13}	1080	1075	2.65	8.33	0.69	$40\delta(C_\alpha H)$, $35\delta(C_\beta H)$, $16\nu(C=C)$
ν_{14}	993	990	6.57	4.99	0.25	$59r(CH_3)$, $16\nu(C=C)$
ν_{15}	931	935	3.26	4.79	0.18	$48\delta_a(ring)$, $22\nu(CC)$, $12\delta(C_\alpha H)$
ν_{16}	857	862	12.52	1.85	0.49	$69\nu(CS)$, $11\delta_s(ring)$
ν_{17}	830	829	21.04	10.59	0.14	$60\delta(CS)$, $15\nu(CC)$, $14\delta_s(ring)$
ν_{18}	659	671	1.37	4.74	0.74	$34\nu(CS)$, $32\delta_s(ring)$, $13\delta_a(ring)$
ν_{19}	542	544	1.74	10.69	0.32	$29\delta_s(ring)$, $23\nu(CX)$, $21\nu(CS)$, $13\delta_a(ring)$
ν_{20}	329	328	0.94	0.14	0.66	$88\delta(CX)$, $11r(CH_3)$
				A″ Species		
ν_{21}	2945	2941	32.56	93.69	0.75	$101\nu_a(CH_3)$
ν_{22}	1452	1447	4.84	18.42	0.75	$95\delta_a(CH_3)$
ν_{23}	1036	1036	2.62	1.04	0.75	$76r(CH_3)$
ν_{24}	874	874	0.62	0.66	0.75	$82\gamma(CH)$, $76\gamma(ring)$
ν_{25}	762	742	68.01	1.51	0.75	$88\gamma(CH)$, $68\gamma(ring)$
ν_{26}	685	679	13.19	3.38	0.75	$70\gamma(CH)$, $13\gamma(ring)$, $13\gamma(CX)$
ν_{27}	594	604	10.55	0.20	0.75	$54\gamma(CH)$, $34\gamma(CX)$
ν_{28}	464	463	0.10	2.53	0.75	$46\gamma(ring)$, $25\gamma(CH)$
ν_{29}	238	235	2.33	2.15	0.75	$42\gamma(CX)$, $37\gamma(ring)$, $18\gamma(CH)$
ν_{30}		134	0.05	0.18	0.75	$105\tau(CH_3)$

[a] All frequencies are cm^{-1}. [b] Infrared intensities (km/mol) and Raman activities (Å^4/amu) are nonscaled values. [c] Depolarization ratios. [d] See Table 4 for coordinate descriptions. Contributions from coordinates with the same character have been added to clarify the normal mode descriptions.

TABLE 9: Comparison between the 6-31G** SQM Diagonal Force Constants of 3-Methylthiophene and Force Constants Reported for Thiophene (in millidynes per angstrom or Equivalent Units)

		thiophene	
coordinates[a]	3-MTP 6-31G**	MNDO[b]	exptl[c]
1, 3	5.283	5.346	5.314
2	5.151	5.265	5.193
6, 7	7.060	7.923	8.704
10	5.021	5.437	6.574
11, 13	0.436	0.408	0.418
12	0.446	0.431	0.435
16, 17	3.923	4.177	4.794
18	1.859	2.150	
19	1.580	1.767	
24, 26	0.244	0.327	0.333
25	0.291	0.399	0.400
27	0.483	0.447	
28	0.494	0.418	

[a] The numbering corresponds to the coordinates defined in Table 4. [b] Data from ref 22. [c] Data from ref 28.

1800 cm^{-1} region the spectral pattern also agrees with the observed infrared spectrum, and we would like to emphasize that previous assignments proposed for vibrations ν_{18} and ν_{26} have been supported by the predicted infrared intensities and Raman activities. In addition, the calculated depolarization ratios for these two bands, 0.74 and 0.75, respectively, explain that the corresponding observed values were uncertain.

Conclusions

The infrared and Raman spectra of 3-methylthiophene have been recorded, and a general assignment of its fundamental vibrations has been proposed on the basis of the experimental results and prior works on thiophene. The spectra are fully compatible with a C_s symmetry for this molecule, a carbon and one hydrogen atom from the methyl group being in the ring plane. In addition, the band contours obtained for the stretching methyl vibrations from the gas phase infrared spectrum agreed with this structure. The quadratic force field using an *ab initio* method at the 6-31G** level was computed. This calculation required the previous optimization of the molecular geometry, and the results also supported the C_s symmetry. The initial force field was taken as the starting point of a refinement process by mean of a scaling factor set, which was optimized in the final step by taking into account our previous assignments. The SQM force field reproduced the experimental frequencies with an rms error of ±8 cm^{-1}. On the basis of the potential energy distribution obtained, some assignment questions were answered. Infrared intensities and Raman activities were evaluated from the dipole moment and polarizability derivatives, respectively, at the same level of calculation. The comparison with the experimental intensities are satisfactory.

experimental data, and most of the bands are correctly predicted. In addition, the calculated intensities compare well with those reported for thiophene.[34] A successful comparison was obtained in the 2800−3200 cm^{-1} region, where the intensities for the carbon−hydrogen stretching vibrations clearly discriminate between aromatic and aliphatic hydrogen atoms. In the 400−

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