

Research Article

Anharmonic Spectroscopic Investigation of Tellurophene and Its Perdeuterated Isotopomer: Application of Second-Order Perturbation Theory

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Vibrational spectra of tellurophene and of its perdeuterated isotopomer were computed using the DFT-B3LYP functional with the LANL2DZ(d,p) basis set. The frequencies of fundamental and overtone transitions were obtained in vacuum under the harmonic approximation and anharmonic second-order perturbation theory (PT2). On the whole the anharmonic corrections reduce the harmonic wavenumber values, in many cases better reproducing the observed fundamental frequencies. The largest anharmonic effects are found for the C–H and C–D stretching vibrations, characterized by relatively high anharmonic coupling constants (up to ca. 120 cm^{-1}). For the C–H/C–D stretches, the harmonic H \rightarrow D isotopic frequency red-shifts overestimate the observed data by $47\text{--}63\text{ cm}^{-1}$ (5.9–8.1%), whereas the PT2 computations exhibit significantly better performances, predicting the experimental data within $1\text{--}19\text{ cm}^{-1}$ (0.1–2.4%).

1. Introduction

Tellurophene is a five-membered heterocycle ($\text{C}_4\text{H}_4\text{Te}$, Figure 1) homologue of the furan molecule. Tellurophene-based compounds have received great attention for the development and fabrication of promising polymeric conductors [1, 2] and nonlinear optical materials [3–8]. The experimental structure of $\text{C}_4\text{H}_4\text{Te}$ is available from microwave measurements [9], whereas the infrared and Raman spectra of $\text{C}_4\text{H}_4\text{Te}$ and of its perdeuterated isotopomer ($\text{C}_4\text{D}_4\text{Te}$) were recorded in various phases [10–14]. On the theoretical side, the vibrational spectra of $\text{C}_4\text{H}_4\text{Te}$ were previously calculated in vacuum under the harmonic approximation by using Hartree-Fock [7] and Density Functional Theory (DFT) computations [15]. However, as well-known in the literature, the harmonic treatment often overestimates experimental wavenumbers of fundamentals and overtones, in particular, of the highest-energy spectral regions [16]. To partially circumvent this deficiency, harmonic frequencies can be corrected through scaling procedures [17, 18] or direct anharmonic calculations [19–21]. Anharmonic terms are usually

calculated by means of variational [19] or perturbative [20, 21] treatments. As established in the literature [22], the perturbative methods are less accurate than the variational ones. Nevertheless, many recent results attest satisfactory performances of the perturbative methodologies, especially for the prediction of anharmonic contributions to fundamentals and overtones of cyclic compounds [22–30].

In this work we investigate the effects of the anharmonic corrections on the vibrational wavenumbers of fundamental and overtone transitions of $\text{C}_4\text{H}_4\text{Te}$ and $\text{C}_4\text{D}_4\text{Te}$. The anharmonic terms were predicted in the gas phase using the second-order perturbation theory (PT2) as described in detail by Barone [20]. The calculations were performed using the hybrid three-parameters B3LYP DFT method [31, 32] with the LANL2DZ(d,p) basis set [33, 34]. Anharmonic PT2-DFT spectra have been previously reported for the congeners furan [22, 25], thiophene [22], and more recently selenophene [30]. To the best of our knowledge, anharmonic theoretical wavenumbers of fundamental and overtone transitions of tellurophene and its perdeuterated isotopomer have been computed here for the first time.

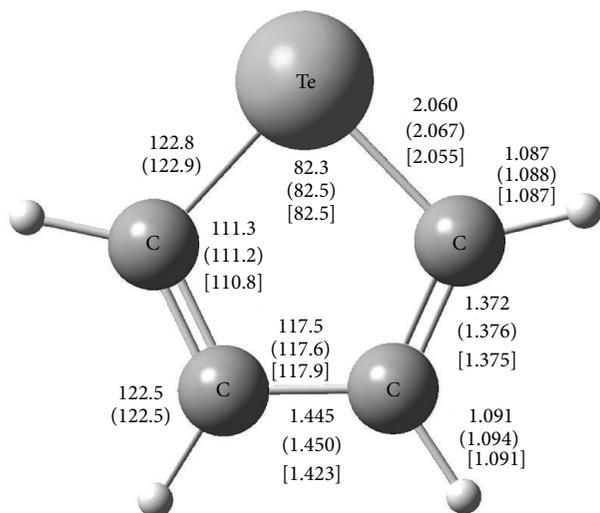


FIGURE 1: B3LYP/LANL2DZ(d,p) geometrical parameters (r_e structure) of tellurophene. The data reported in the round brackets refer to the B3LYP/LANL2DZ(d,p) vibrationally averaged geometry (r_z structure). The data reported in the square brackets refer to the experimental geometry [9].

2. Computational Details

The current computations were exclusively performed with the GAUSSIAN 09 package [35]. The structure of C₄H₄Te were fully optimized under the C_{2v} point group symmetry using the B3LYP functional with the LANL2DZ(d,p) basis set. The vibrational wavenumbers of C₄H₄Te and C₄D₄Te were determined at the B3LYP/LANL2DZ(d,p) level under the harmonic approximation through analytical computations. Anharmonic terms were calculated numerically using the PT2 procedure implemented in the GAUSSIAN 09 program (option: Freq (VibRot, Anharmonic)) [20]. There are many reports in the literature confirming that the PT2 treatment in combination with DFT methods provides satisfactory performances, especially for computing anharmonic vibrational frequencies of cyclic structures [22–30]. In particular, the PT2 method and the B3LYP functional have been employed with success to obtain the vibrational spectra of the homologues furan [22, 25], thiophene [22], and more recently selenophene [30]. The used PT2 scheme computes the third and fourth energy derivatives with respect to the normal coordinates through a numerical differentiation procedure described in detail in [20]. The potential energy surface (V) can be expanded including anharmonic contributions up to the quartic term as

$$\frac{V}{hc} = \frac{1}{2} \sum_i \omega_i q_i^2 + \frac{1}{6} \sum_{ijk} \Phi_{ijk} q_i q_j q_k + \frac{1}{24} \sum_{ijkl} \Phi_{ijkl} q_i q_j q_k q_l, \quad (1)$$

where ω_i are the harmonic wavenumbers, q_i are the dimensionless normal coordinates, Φ_{ijk} and Φ_{ijkl} , are respectively,

the third- and fourth-order force constants. The Φ_{ijk} and Φ_{ijkl} values are obtained through a finite difference scheme using quadratic normal coordinate force constants (Φ_{ij}) calculated analytically and performing displacements along each normal coordinate (δq_i):

$$\Phi_{ijk} = \frac{1}{3} \left[\frac{\Phi_{jk}(+\delta q_i) - \Phi_{jk}(-\delta q_i)}{2\delta q_i} + \frac{\Phi_{ki}(+\delta q_j) - \Phi_{ki}(-\delta q_j)}{2\delta q_j} + \frac{\Phi_{ij}(+\delta q_k) - \Phi_{ij}(-\delta q_k)}{2\delta q_k} \right],$$

$$\Phi_{ijkk} = \frac{\Phi_{ij}(+\delta q_k) + \Phi_{ij}(-\delta q_k) - 2\Phi_{ij}(0)}{\delta q_k^2},$$

$$\Phi_{iikk} = \frac{1}{2} \left[\frac{\Phi_{ii}(+\delta q_k) + \Phi_{ii}(-\delta q_k) - 2\Phi_{ii}(0)}{\delta q_k^2} + \frac{\Phi_{kk}(+\delta q_i) + \Phi_{kk}(-\delta q_i) - 2\Phi_{kk}(0)}{\delta q_i^2} \right]. \quad (2)$$

As commonly adopted in the literature [24–26, 29, 30], step size displacements of 0.025 Å along the normal coordinates were used in the present work. The fundamental frequencies (ν_i) were determined from the ω_i , diagonal (χ_{ii}) and off-diagonal (χ_{ij}) anharmonic constants [20]:

$$\nu_i = \omega_i + 2\chi_{ii} + \frac{1}{2} \sum_{j \neq i} \chi_{ij}. \quad (3)$$

3. Result and Discussion

Figure 1 displays the bond lengths and angles of C₄H₄Te calculated at the B3LYP/LANL2DZ(d,p) level. In addition, the figure reports the available experimental data obtained by microwave measurements [9]. The B3LYP/LANL2DZ(d,p) geometry is in good agreement with the observed one, especially for the bond lengths C–Te (within 0.005 Å), C=C (within 0.003 Å), and C–H (the calculated and experimental values are identical), as well as for the bond angles (within 0.2–0.5°). Figure 1 also presents the vibrationally averaged geometries (r_z structure) calculated by the vibration-rotation interaction constant values [20]. In line with previous studies on cyclic compounds [29, 30], the vibrational averaging corrections lengthen the bond lengths of C₄H₄Te by 0.001–0.003 Å, whereas the bond angles vary within 0.2° (C–Te–C).

The experimental infrared and Raman spectra of C₄H₄Te and C₄D₄Te were obtained in vapour, liquid, CCl₄ solution, and solid phase [10–14]. Theoretically, some calculations on the C₄H₄Te isotopomer were previously performed using the harmonic treatment [7, 15]. In Tables 1 and 2 we present the B3LYP/LANL2DZ(d,p) harmonic (ω) and anharmonic wavenumbers (ν), infrared intensities (I_{IR}) and Raman activities (A_{Raman}) of C₄H₄Te and C₄D₄Te, together with the available observed data for comparison [12]. The assignments of the vibrations were performed using normal modes as

TABLE 1: Vibrational harmonic, ω , and anharmonic, ν , wavenumbers (cm^{-1}), infrared intensities, I_{IR} (km/mol), and Raman activities A_{Raman} ($\text{\AA}^4/\text{amu}$) of $\text{C}_4\text{H}_4\text{Te}$.

	Description ^a	I_{IR}	Calc. ^b		Exp. ^c		
			A_{Raman}	ω		ν	
A ₁	1	$\nu\text{C-H}$	3	317	3237	3089	3084 (3106)
	2	$\nu\text{C-H}$	12	259	3191	3052	3045 (3064)
	3	$\nu\text{C=C} + \nu\text{C-C} + \delta\text{C-H}$	25	54	1465	1430	1432
	4	$\nu\text{ring} + \delta\text{C-H}$	12	3	1341	1311	1316
	5	$\delta\text{C-H}$	2	5	1103	1083	1079
	6	Ring breathing + $\delta\text{C-H}$	1	22	1010	986	984
	7	δring	18	22	702	692	687
	8	$\delta\text{C-Te-C}$	0	9	385	380	380
A ₂	9	$\gamma\text{C-H}$	0	1	911	894	912
	10	$\gamma\text{C-H}$	0	0	684	663	690
	11	τring	0	0	512	503	507
	12	$\nu\text{C-H}$	3	2	3234	3085	3084
	13	$\nu\text{C-H}$	4	118	3176	3037	3030 (3047)
	14	$\nu\text{C=C} + \delta\text{C-H}$	3	0	1548	1516	1516
B ₁	15	$\delta\text{C-H}$	31	3	1255	1220	1246
	16	$\delta\text{C-H}$	0	4	1099	1077	1079
	17	δring	3	0	805	794	797
	18	$\nu\text{C-Te}$	2	8	557	547	552
	19	$\gamma\text{C-H}$	0	0	876	859	884
B ₂	20	$\gamma\text{C-H}$	132	0	683	667	674
	21	τring	5	0	358	355	354
		rms deviation ^d			66	11	
	rms deviation ^e			144	6		
	rms deviation ^f			21	12		

^a ν : stretching; δ : in-plane bending; τ : torsion; γ : out-of-plane bending.

^bCalculations were carried out in vacuum at the B3LYP/LANL2DZ(d,p) level.

^cLiquid phase [12]. The values in parentheses refer to the gas phase [11].

^dAll vibrational modes.

^e $\nu\text{C-H}$ modes.

^fAll vibrational modes excluding $\nu\text{C-H}$ modes.

displacements in redundant internal coordinates (in the GAUSSIAN 09, the option: Freq = IntModes) and also through the graphical program Chemcraft [36]. The title compounds belong to the C_{2v} symmetry point group with the 21 normal modes categorized as $8A_1 + 3A_2 + 7B_1 + 3B_2$. All the modes with the exception of the A_2 vibrations are infrared active. It is worth noting that, the current assignments of the transitions reasonably agree with those previously determined by experimental [12] and computational [7, 15] studies. The complete sets of experimental fundamentals of both the investigated isotopomers are available from measurements in liquid phase [12], whereas three C-H stretching transitions (modes numbers 1, 2, and 13) of $\text{C}_4\text{H}_4\text{Te}$ were also detected in gas [11].

The harmonic frequencies systematically overestimate the experimental data with the notable exception of the modes numbers 9, 10, and 19 for $\text{C}_4\text{H}_4\text{Te}$ and of the modes numbers 10 and 19 for $\text{C}_4\text{D}_4\text{Te}$. In the present study, we determined the root mean square (rms) deviation between the experimental and calculated wavenumbers which is defined as follows:

$$\text{rms} = \left[\frac{1}{n} \sum_i^n (\nu_i^{\text{exp.}} - \nu_i^{\text{calc.}})^2 \right]^{1/2}, \quad (4)$$

where ν_i is a vibrational frequency value. The rms deviations are included in Tables 1 and 2 for all the modes, the C-H/C-D stretching vibrations ($\nu\text{C-H}/\nu\text{C-D}$), and all the modes except for the $\nu\text{C-H}$ and $\nu\text{C-D}$ vibrations. When considering all the vibrational transitions, the rms deviations between the harmonic and observed data are 66 cm^{-1} for $\text{C}_4\text{H}_4\text{Te}$ and 43 cm^{-1} for $\text{C}_4\text{D}_4\text{Te}$. These rms deviations are noticeably reduced if we exclude the $\nu\text{C-H}$ and $\nu\text{C-D}$ modes, becoming 21 cm^{-1} and 18 cm^{-1} , respectively. On the whole, the modification of the basis set for the C and H atoms [$\text{LANL2DZ(d,p)} \rightarrow 6\text{-311G(d,p)}$] does not produce significant effects on the harmonic wavenumber values of $\text{C}_4\text{H}_4\text{Te}$ (the data are available on request from the author), giving a rms deviation of 63 cm^{-1} with respect to the experimental data. Specifically, the performances of the 6-311G(d,p) in comparison to the LANL2DZ(d,p) basis set are slightly improved for the C-H stretches (rms deviation of 135 versus 144 cm^{-1}), but worsened for the remaining modes (rms deviation of 23 versus 21 cm^{-1}). Therefore, for the anharmonic computations the use of the smaller LANL2DZ(d,p) basis set for all the atoms can be considered a reasonable choice. Although the experimental wavenumber values of the 21 fundamentals were obtained in liquid phase [12] and the present

TABLE 2: Vibrational harmonic, ω , and anharmonic, ν , frequencies (cm^{-1}), infrared intensities, I_{IR} (km/mol), and Raman activities A_{Raman} ($\text{\AA}^4/\text{amu}$) of $\text{C}_4\text{D}_4\text{Te}$.

	Description ^a	I_{IR}	Calc. ^b		ω	ν	Exp. ^c
			A_{Raman}	ν			
A ₁	1	$\nu\text{C-D}$	2	143	2400	2294	2308
	2	$\nu\text{C-D}$	3	104	2355	2270	2262
	3	$\nu\text{C=C} + \nu\text{C-C} + \delta\text{C-D}$	31	57	1443	1409	1405
	4	$\nu\text{ring} + \delta\text{C-D}$	11	7	1208	1169	1180
	5	$\delta\text{C-D}$	2	23	839	828	824
	6	Ring breathing + $\delta\text{C-D}$	0	10	782	770	768
	7	δring	14	12	640	632	630
	8	$\delta\text{C-Te-C}$	0	9	374	371	370
A ₂	9	$\gamma\text{C-D}$	0	1	753	742	741
	10	$\gamma\text{C-D}$	0	0	533	520	548
	11	τring	0	0	438	432	437
	12	$\nu\text{C-D}$	1	4	2395	2313	2308
	13	$\nu\text{C-D}$	1	55	2339	2249	2240
	14	$\nu\text{C=C} + \delta\text{C-D}$	7	0	1493	1458	1455
B ₁	15	$\delta\text{C-D}$	12	2	1002	986	995
	16	$\delta\text{C-D}$	2	4	853	840	811
	17	δring	1	0	706	697	704
	18	$\nu\text{C-Te}$	3	7	524	517	522
	19	$\gamma\text{C-D}$	0	0	683	673	696
B ₂	20	$\gamma\text{C-D}$	77	0	506	497	502
	21	τring	3	0	329	325	326
		rms deviation ^d			43	12	
	rms deviation ^e			91	10		
	rms deviation ^f			18	12		

^a ν : stretching; δ : in-plane bending; τ : torsion; γ : out-of-plane bending.

^bCalculations were carried out in vacuum at the B3LYP/LANL2DZ(d,p) level.

^cLiquid phase [12].

^dAll vibrational modes.

^e $\nu\text{C-H}$ modes.

^fAll vibrational modes excluding $\nu\text{C-H}$ modes.

calculations were performed in vacuum, the introduction of the PT2 anharmonic corrections generally improves the agreement between the observed and computed data; for all the vibrational transitions the rms deviations are 11 cm^{-1} for $\text{C}_4\text{H}_4\text{Te}$ and 12 cm^{-1} for $\text{C}_4\text{D}_4\text{Te}$. As should be expected, the calculated harmonic wavenumbers overestimate the anharmonic figures, the zero-point energy (ZPE) correction, a physicochemical property of fundamental importance for an accurate determination of thermochemical and kinetic parameters, being influenced by the anharmonic corrections. Indeed, when passing from the harmonic to the PT2 anharmonic treatment, the ZPE for $\text{C}_4\text{H}_4\text{Te}$ ($\text{C}_4\text{D}_4\text{Te}$) decreases from 40.22 (32.30) to 39.72 (31.44) kcal/mol.

As can be appreciated from the data reported in Tables 1 and 2, the largest anharmonic contributions are found for the $\nu\text{C-H}$ and $\nu\text{C-D}$ transitions (modes. numbers 1, 2, 12, and 13), decreasing the harmonic frequency values of $\text{C}_4\text{H}_4\text{Te}$ by $140\text{--}150\text{ cm}^{-1}$ (ca. 4%) and of $\text{C}_4\text{D}_4\text{Te}$ $80\text{--}110\text{ cm}^{-1}$ (ca. 3-4%), in agreement with previous PT2 computations on other cyclic compounds [22-30]. As a consequence, the agreement between the experimental and calculated wavenumbers for the $\nu\text{C-H}$ and $\nu\text{C-D}$ stretches is significantly improved by

the anharmonic treatment (within $1\text{--}14\text{ cm}^{-1}$, 0.03-0.61%). Note that when we consider the gas phase experimental $\nu\text{C-H}$ fundamentals of $\text{C}_4\text{H}_4\text{Te}$ (modes numbers 1, 2, and 13, Table 1), the experimental/calculation deviations are slightly augmented (up to 17 cm^{-1}). To elucidate the origin of the above large anharmonic effects, as a case test, we analysed the contributions of the anharmonic constant values ($\chi_{i,j}$) for the $\nu\text{C-H}$ modes numbers 1 and 2 of $\text{C}_4\text{H}_4\text{Te}$ (Figure 2). The most significant $\chi_{i,j}$ corrections are produced by the diagonal term ($\chi_{i,i}$) as well as by the coupling with the remaining C-H stretching modes. In the specific case of the modes numbers 1 and 2, the largest anharmonic coupling are $\chi_{1,12}$ and $\chi_{2,13}$, which are predicted to be ca. -120 cm^{-1} and recover about 80% of the total anharmonic corrections ($\omega - \nu$, (3)). Other nonnegligible anharmonic contributions, although less substantial than $\chi_{1,12}$ and $\chi_{2,13}$, are given by the $\chi_{1,1}$, $\chi_{2,2}$ (ca. -30 cm^{-1} for both the couplings), and $\chi_{1,2}$ (-12 cm^{-1}) terms.

For the $\nu\text{C-H}/\nu\text{C-D}$ modes, we evaluated the H \rightarrow D isotopic wavenumber downward shifts ($\Delta\nu_{\text{H/D}} = \nu\text{C-H} - \nu\text{C-D}$) obtained by the harmonic and anharmonic calculations. The deviations of the calculated $\Delta\nu_{\text{H/D}}$ data from the observed values are reported in Figure 3, together with the percentage

TABLE 3: Wavenumbers of first overtones (cm^{-1}) of tellurophene isotopomers.

Symm.	Mode no. ^a	$\text{C}_4\text{H}_4\text{Te}$			$\text{C}_4\text{D}_4\text{Te}$		
		Calc. ^b		Exp. ^c	Calc. ^b		Exp. ^c
		ω	ν	ν	ω	ν	ν
A_1	1	6474	6144		4801	4575	
	2	6382	6047		4711	4516	
	3	2931	2848	2851	2886	2810	
	4	2683	2617	2627	2415	2343	
	5	2205	2167	2160	1678	1652	
	6	2019	1968	1966	1563	1541	
	7	1404	1382		1279	1263	1254
	8	769	759	758	748	740	
A_2	9	1823	1788	1822	1505	1485	
	10	1369	1322	1385	1067	1039	
	11	1024	1009	1014	877	864	872
	12	6469	6083		4789	4598	
	13	6351	6013		4679	4478	
B_1	14	3096	3019	3015	2986	2921	2916
	15	2510	2451		2004	1969	
	16	2199	2154		1706	1680	
	17	1611	1588		1412	1393	
	18	1114	1093	1111	1049	1031	1049
B_2	19	1753	1717	1768	1367	1347	1383
	20	1367	1331		1013	993	
	21	716	709		657	650	

^aSee Tables 1 and 2 for the mode description.

^bCalculations were carried out in vacuum at the B3LYP/LANL2DZ(d,p) level.

^cLiquid phase, [12].

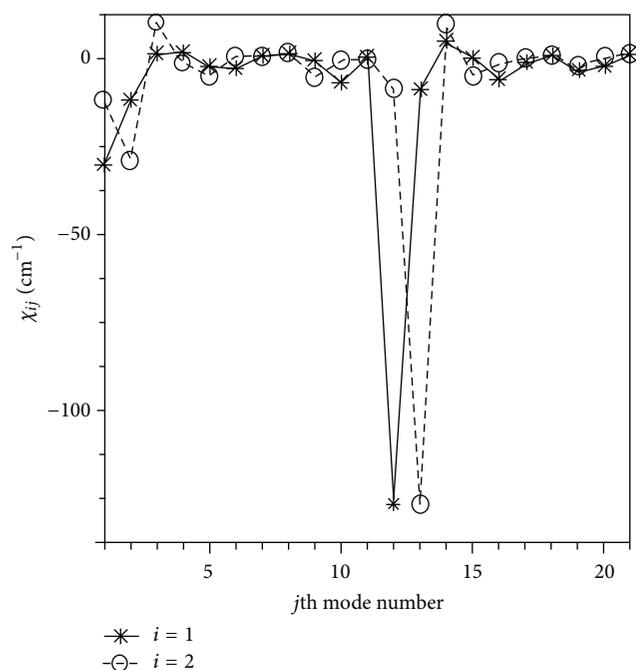


FIGURE 2: B3LYP/LANL2DZ(d,p) anharmonic vibrational constants for the C–H stretching modes numbers 1 and 2 with the vibrational modes $j = 1$ –21 of $\text{C}_4\text{H}_4\text{Te}$. For the mode numbering, see Table 1.

errors. The harmonic approximation overestimates the experimental shifts by 47 – 63 cm^{-1} (5.9–8.1%), whereas the anharmonic computations, with the exception of mode number 1, underestimate the isotopic shifts showing smaller errors (1 – 19 cm^{-1} , 0.1–2.4%). The results are particularly excellent for the mode number 2.

Table 3 collects the frequencies of the overtone bands of title compounds obtained using the harmonic and anharmonic approaches, together with the available experimental data which are only limited to eleven ($\text{C}_4\text{H}_4\text{Te}$) and five ($\text{C}_4\text{D}_4\text{Te}$) vibrational modes. Confirming the above results of the fundamentals, the greatest anharmonic corrections for the overtones occur for the $\nu\text{C-H}$ ($\nu\text{C-D}$) transitions, which reduce the harmonic values by ca. 5–6% (4–5%).

In Figures 4 and 5 we plot the infrared and Raman spectra obtained by the anharmonic calculations using pure Lorentzian band-shapes with a full width at half maximum of 10 cm^{-1} . The C–H and C–D stretching transitions are placed in the highest-wavenumber regions of the vibrations spectra. The lowest-energy region of the infrared spectra of $\text{C}_4\text{H}_4\text{Te}$ and $\text{C}_4\text{D}_4\text{Te}$ is mainly characterized by an isolated and strong absorption located at 667 cm^{-1} ($I_{\text{IR}} = 132 \text{ km/mol}$) and 497 cm^{-1} ($I_{\text{IR}} = 77 \text{ km/mol}$), respectively, to be compared with the experimental values of 674 cm^{-1} (–1%) and 502 cm^{-1} (–1%), respectively. The vibrational analysis ascribes this

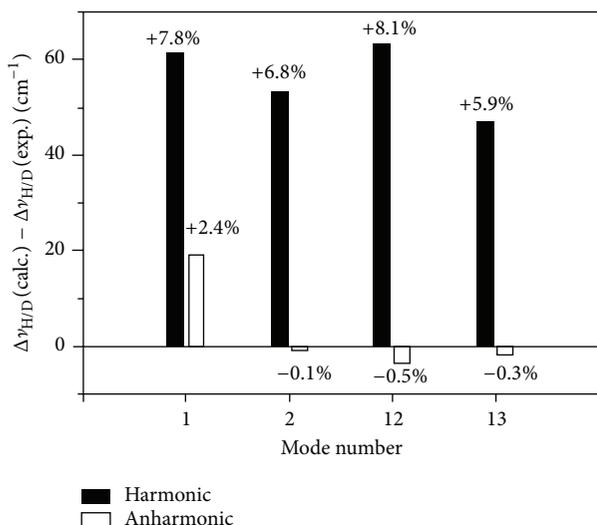


FIGURE 3: Deviation of the B3LYP/LANL2DZ(d,p) H→D isotopic wavenumber shifts ($\Delta\nu_{\text{H/D}}$) for the C–H and C–D stretching modes from experiment [12]. The reported values refer to the percentage deviations.

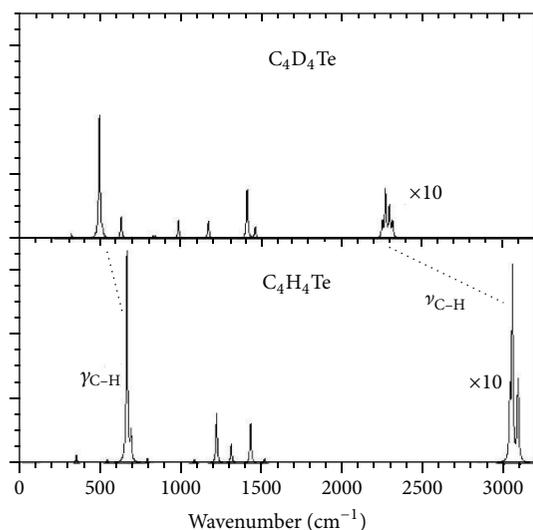


FIGURE 4: Anharmonic infrared spectra of $\text{C}_4\text{H}_4\text{Te}$ (bottom) and $\text{C}_4\text{D}_4\text{Te}$ (top). Lorentz line-shapes with half-width of 10 cm^{-1} are used. B3LYP/LANL2DZ(d,p) results.

transition (mode number 20) to a pure out-of-plane C–H (and C–D) bending deformation, $\gamma_{\text{C-H}}$ ($\gamma_{\text{C-D}}$). A graphical representation of the atomic displacement vectors involved in this vibration is depicted in Figure 6(a).

The most active transitions in the Raman spectra of $\text{C}_4\text{H}_4\text{Te}$ and $\text{C}_4\text{D}_4\text{Te}$ involve the C–H and C–D stretches (Tables 1 and 2). From the present calculations, an almost isolated and relatively intense peak ($A_{\text{Raman}} \sim 50 \text{ \AA}^4/\text{amu}$) located near 1400 cm^{-1} appears in the Raman spectra of both tellurophene and its perdeuterated isotopomer. This transition (mode number 3) also visible in the infrared spectra is assigned to the C=C + C–C bonds stretchings with

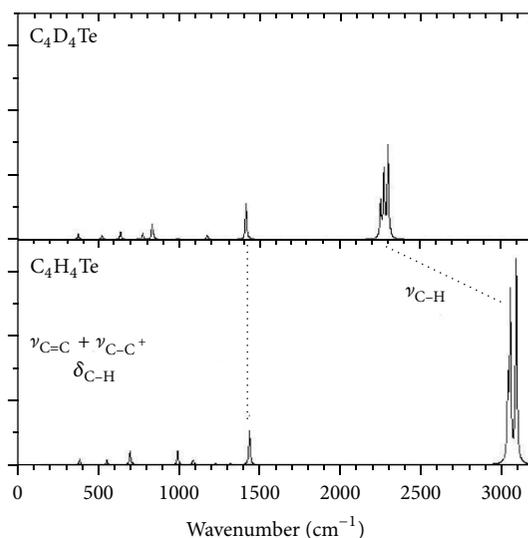


FIGURE 5: Anharmonic Raman spectra of $\text{C}_4\text{H}_4\text{Te}$ (bottom) and $\text{C}_4\text{D}_4\text{Te}$ (top). Lorentz line-shapes with half-width of 10 cm^{-1} are used. B3LYP/LANL2DZ(d,p) results.

the nonnegligible contribution from the in-plane C–H (C–D) bending motion (Figure 6(b)). The present harmonic computations place this band at 1465 cm^{-1} ($\text{C}_4\text{H}_4\text{Te}$) and 1443 cm^{-1} ($\text{C}_4\text{D}_4\text{Te}$), overestimating the observed wavenumbers of 1432 cm^{-1} (+2.3%) and 1405 cm^{-1} (+2.7%), respectively. Note that the corresponding PT2 anharmonic frequencies here calculated at 1430 cm^{-1} ($\text{C}_4\text{H}_4\text{Te}$) and 1409 cm^{-1} ($\text{C}_4\text{D}_4\text{Te}$), give a noticeably better agreement with experiment (within 0.1–0.3%).

4. Conclusions

In this work we computed harmonic and PT2 anharmonic vibrational frequencies of fundamentals and overtone bands of $\text{C}_4\text{H}_4\text{Te}$ and $\text{C}_4\text{D}_4\text{Te}$. The computations were performed in vacuum at the B3LYP/LANL2DZ(d,p) level of theory. The infrared and Raman spectral profiles were simulated using Lorentzian band-shapes and the most informative transitions were discussed. In general, the calculated harmonic frequencies deviate from the observed ones, with rms deviations of 66 and 43 cm^{-1} for $\text{C}_4\text{H}_4\text{Te}$ and $\text{C}_4\text{D}_4\text{Te}$, respectively. The introduction of the PT2 anharmonic contributions in several cases significantly reduces the calculation/experiment discrepancy, giving rms deviations of 11 cm^{-1} ($\text{C}_4\text{H}_4\text{Te}$) and 12 cm^{-1} ($\text{C}_4\text{D}_4\text{Te}$). A vibrational analysis reveals that the anharmonic corrections are especially conspicuous for the $\nu_{\text{C-H}}$ and $\nu_{\text{C-D}}$ transitions, decreasing the harmonic wavenumber values, respectively, by $140\text{--}150\text{ cm}^{-1}$ (ca. 4%) and $80\text{--}110\text{ cm}^{-1}$ (ca. 3–4%), and noticeably improving the agreement with the experimental data. As a consequence, in comparison to the harmonic approximation, the observed H→D isotopic frequency red-shifts for the C–H and C–D stretches are better reproduced by the PT2 scheme with deviation up to $1\text{--}19\text{ cm}^{-1}$ (0.1–2.4%). Important anharmonic effects (ca. 35 cm^{-1} , 2.3%) are also found for the mode

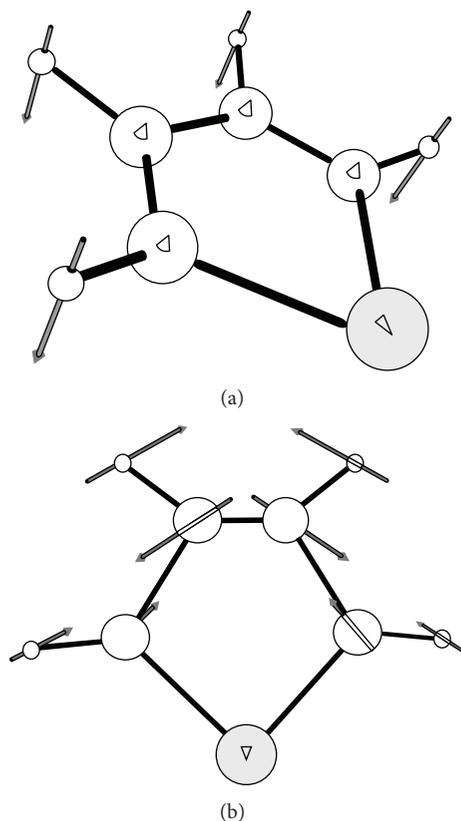


FIGURE 6: Atom vector displacements for the normal modes of C_4H_4Te : (a) $\nu C-H$ (mode number 20); (b) $\nu C=C + \nu C-C + \delta C-H$ (mode number 3). B3LYP/LANL2DZ(d,p) results.

number 3 ($\nu C=C + \nu C-C + \delta C-H$, $\nu C=C + \nu C-C + \delta C-D$), characterized by a relatively intense peak in the Raman spectra. In line with the recent literature, the present results on tellurophene isotopomers confirm that the anharmonic PT2-DFT approach can be employed to accurately predict the infrared and Raman spectra of heterocyclic compounds.

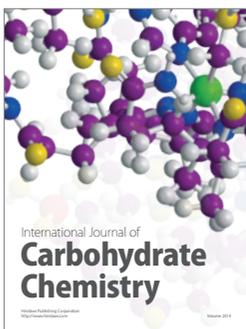
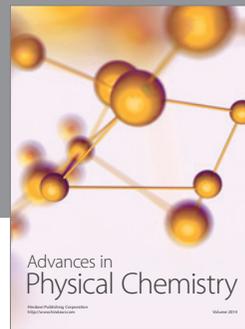
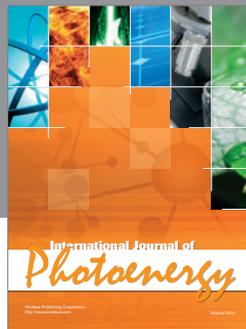
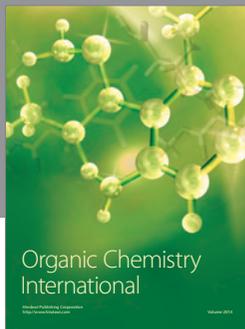
Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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