Research Article

Infrared and Raman Spectra of C_4H_4Se and C_4D_4Se Isotopomers: A DFT-PT2 Anharmonic Study

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IR and Raman spectra of selenophene and of its perdeuterated isotopomer have been obtained in gas phase through density-functional theory (DFT) computations. Vibrational wavenumbers have been calculated using harmonic and anharmonic second-order perturbation theory (PT2) procedures with the B3LYP method and the 6-311G** basis set. Anharmonic overtones have been determined by means of the PT2 method. The introduction of anharmonic terms decreases the harmonic wavenumbers, giving a significantly better agreement with the experimental data. The most significant anharmonic effects occur for the C-H and C-D stretching modes, the observed H/D isotopic wavenumber redshifts being satisfactorily reproduced by the PT2 computations within $6\text{--}20\text{ cm}^{-1}$ (1–3%). In the spectral region between 500 cm^{-1} and 1500 cm^{-1} , the IR spectra are dominated by the out-of-plane C-H (C-D) bending transition, whereas the Raman spectra are mainly characterized by a strong peak mainly attributed to the C=C + C-C bonds stretching vibration with the contribution of the in-plane C-H (C-D) bending deformation. The current results confirm that the PT2 approach combined with the B3LYP/6-311G** level of calculation is a satisfactory choice for predicting vibrational spectra of cyclic molecules.

1. Introduction

Calculated harmonic vibrational wavenumbers of organic compounds typically deviate from experimental fundamental data, especially overestimating observed wavenumbers of high-energy X-H (X = C, O, N) stretches [1]. Two principal procedures can be employed in practice to correct the shortcomings of the harmonic approximation: (1) scaling methods [2, 3] and (2) anharmonic computations [4–7]. Scaling factors are usually derived for a certain level of theory and basis set by fitting computed harmonic frequencies to experimental data for restricted subsets of molecules. Scaling corrections often work adequately, even if there are specific cases for which scaling factor transferability could originate questionable results [8, 9]. A much more rigorous treatment is furnished by anharmonic computations that are commonly performed through perturbative [4–6] or variational [7] methods. Anharmonic perturbative approaches are generally proven to be less accurate than variational schemes [10], although they are particularly reliable for predicting fundamental wavenumbers of semirigid cyclic compounds [10–17].

In this contribution we report some interesting results on the performances of the anharmonic second-order perturbation theory (PT2) [6] as implemented in the GAUSSIAN 09 program [18] to predict vibrational wavenumbers. We have chosen to study selenophene (C_4H_4Se) and its perdeuterated isotopomer (C_4D_4Se), for which experimental vibrational spectra with complete assignments of all the transitions are available from the literature [19–23]. Theoretically, the vibrational spectra of selenophene were previously computed at ab initio and density-functional theory (DFT) methods under the harmonic approximation [24–27]. In the present study we have used the hybrid functional B3LYP [28, 29] with the fairly flexible 6-311G** basis set [1]. Anharmonic PT2 B3LYP/6-311G** calculations have been recently performed with success on naphthalene, reproducing accurately the experimental wavenumbers [16]. Overtone wavenumbers of C_4H_4Se and C_4D_4Se have been here predicted for the first time. We also will discuss briefly the most intense vibrational transitions of the IR and Raman spectra. Selenophene which is homologue of the furan molecule has long been the subject of many experimental and theoretical studies as promising

TABLE 1: Structural parameters of C_4H_4Se and C_4D_4Se ^a.

Parameter ^b	B3LYP/6-311G**		exp. ^c
	r_e	r_z	
Se-C ₁	1.876	1.883	1.863
C ₁ =C ₂	1.360	1.365	1.370
C ₂ -C ₃	1.432	1.438	1.423
C ₁ -H	1.079	1.080	1.078
C ₂ -H	1.083	1.086	1.081
C ₁ -Se-C ₄	87.0	87.1	87.7
Se-C ₁ =C ₂	111.5	111.4	111.2
C ₁ =C ₂ -C ₃	115.0	115.1	114.9
Se-C ₁ -H	120.6	120.6	124.4
C ₁ -C ₂ -H	122.3	122.3	122.5
A	0.25234 (0.20745)	0.25044 (0.20609)	
B	0.11171 (0.10174)	0.11113 (0.10123)	
C	0.07743 (0.06826)	0.07694 (0.06786)	
μ	0.378		0.4

^aAll values refer to C_4H_4Se except for the perdeuterated isotopomer (values in parentheses).

^bBond lengths in Å, bond angles in degrees, rotational constants in cm^{-1} , and dipole moments in D.

^cMicrowave measurements [35].

building block of π -conjugated polymers for nonlinear optical applications [27, 30–34].

2. Computational Details

All calculations were carried out with the GAUSSIAN 09 package. Geometry of selenophene was fully optimized under the C_{2v} point group symmetry using the B3LYP functional with the 6-311G** basis set. The harmonic frequencies of selenophene and its perdeuterated isotopomer were obtained using an analytical procedure. The anharmonic corrections to wavenumbers were computed through the PT2 treatment. The PT2 procedure in combination with DFT methods is proven to be adequate to predict anharmonic vibrational wavenumbers of cyclic compounds [10–17], including the homologues furan [10, 13] and thiophene [10]. Under the PT2 approximation, third and semidiagonal fourth energy derivatives with respect to normal coordinates were determined using a numerical differentiation scheme implemented in GAUSSIAN 09. Specifically, we used a step-size displacement of 0.025 Å along the normal coordinate as usually adopted in the literature [12–14]. Fundamental frequencies (ν_i) were obtained from harmonic (ω_i), diagonal (χ_{ii}), and off-diagonal (χ_{ij}) anharmonic constant values as [6]:

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

Besides the PT2 approach, as commonly adopted in the literature, we corrected the computed harmonic wavenumbers by using a scaling factor previously determined by Irikura et al. [36] through a least-mean-squared fitting procedure between 3310 experimental and calculated wavenumbers. In the specific case of the B3LYP/6-311G** level,

FIGURE 1: Atom numbering for selenophene.

the scaling factor is 0.9669. The assignments of the vibrational transitions were obtained on the basis of normal modes, as displacements in redundant internal coordinates (in GAUSSIAN 09, option Freq = IntModes) and also through the visualization software Chemcraft [37].

3. Result and Discussion

3.1. Geometry, Rotational Constants, and Dipole Moment.

The computed bond lengths, angles, and dipole moment (μ) of selenophene (Figure 1) are listed in Table 1, together with the gas phase experimental data for comparison [35]. The B3LYP/6-311G** geometry agree reasonably well with experiment, with a root mean square (rms) deviation $\{\text{rms} = [(1/n) \sum_i^n (x_i^{\text{exp}} - x_i^{\text{calc}})^2]^{1/2}\}$ where x_i is a geometrical parameter value for the bond lengths of 0.008 Å and for bond angles of 1.7°. In Table 1 the vibrationally averaged geometries (r_z structure) determined using vibration-rotation interaction constant computations [6] are also reported. As can be appreciated from the data in the table, the inclusion of vibrational averaging corrections increases the bond lengths by 0.001–0.007 Å, whereas the bond angles deviate within 0.1°. Table 1 also includes rotational constants (A, B, and C) for C_4H_4Se and C_4D_4Se . The results show that the vibrational averaging corrections little affect the rotational constants which are much more dependent on the H/D isotopic effects, with the values of C_4D_4Se being decreased by ca. 20% with respect to those of C_4H_4Se .

The dipole moment is directed along the C_2 symmetry axis and is here calculated at 0.378 D, in good agreement with the experimental datum of 0.4 D [35] and previous theoretical estimates [25, 30].

3.2. Vibrational Spectra of C_4H_4Se and C_4D_4Se . Experimentally IR and Raman spectra of selenophene were previously investigated by Cataliotti and coworkers [19–23]. Some of theoretical studies restricted to C_4H_4Se were previously carried out under the harmonic approximation [24–27]. To the best of our knowledge anharmonic vibrational wavenumbers of fundamentals and overtones of selenophene and of its perdeuterated isotopomer are lacking to date. Tables 2 and 3 collect the B3LYP/6-311G** harmonic and anharmonic wavenumbers (ω and ν), IR intensities (I_{IR}), and Raman activities (A_{Raman}) of C_4H_4Se and C_4D_4Se . These tables

TABLE 2: 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 $\text{C}_4\text{H}_4\text{Se}$.

	Description ^a	I_{IR}	A_{Raman}	B3LYP6-311G**			exp. ^b
				ω	ω^c	ν	ν
A_1	1 $\nu\text{C-H}$	1.9	253.1	3244	3137	3119	3100
	2 $\nu\text{C-H}$	7.8	180.4	3194	3088	3072	3063
	3 $\nu\text{C=C} + \nu\text{C-C} + \delta\text{C-H}$	18.3	38.0	1463	1415	1424	1419
	4 $\nu\text{ring} + \delta\text{C-H}$	2.4	4.1	1373	1328	1347	1341
	5 $\delta\text{C-H}$	2.9	6.3	1103	1066	1090	1080
	6 Ring breathing + $\delta\text{C-H}$	2.4	11.8	1033	999	1016	1010
	7 δring	21.5	16.2	765	740	753	758
	8 $\delta\text{C-Se-C}$	0.2	7.2	460	445	454	456
A_2	9 $\gamma\text{C-H}$	0.0	1.0	923	892	911	905
	10 $\gamma\text{C-H}$	0.0	1.5	685	662	681	685
	11 τring	0.0	0.0	552	534	547	541
B_1	12 $\nu\text{C-H}$	1.1	1.3	3242	3135	3116	3100
	13 $\nu\text{C-H}$	4.6	106.9	3180	3075	3058	3054
	14 $\nu\text{C=C} + \delta\text{C-H}$	0.2	0.0	1565	1513	1530	1515
	15 $\delta\text{C-H}$	22.1	0.8	1268	1226	1241	1243
	16 $\delta\text{C-H}$	1.2	5.7	1105	1068	1091	1080
	17 δring	1.2	0.2	839	811	829	820
	18 $\nu\text{C-Se}$	0.8	5.3	621	600	609	623
B_2	19 $\gamma\text{C-H}$	0.0	0.1	885	856	875	870
	20 $\gamma\text{C-H}$	131.5	0.5	707	684	703	700
	21 τring	2.4	1.8	401	388	397	394
rms deviation ^d				63	18	9	
rms deviation ^e				23	14	8	
rms deviation ^f				136	30	13	

^a ν : stretching; δ : in-plane bending, γ : out-of-plane bending, τ : torsion.^b Reference [21].^c Scaled harmonic wavenumbers. The scaling factor of 0.9669 was taken from Irikura et al. [36].^d All the vibrational modes.^e All the vibrational modes excluding the $\nu\text{C-H}$ modes.^f $\nu\text{C-H}$ modes.

also include the available experimental data [21–23] for comparison. Selenophene belongs to the C_{2v} symmetry point group with 21 normal modes classified as $8A_1 + 3A_2 + 7B_1 + 3B_2$, with all except for the A_2 modes being IR active. The present assignments of the vibrational modes are in good agreement with both experimental [21–23] and previous theoretical investigations [24–27].

In Figures 2 and 3 we plot the percentage deviations $((\omega_i^{\text{calc.}} - \omega_i^{\text{exp.}})/(\omega_i^{\text{exp.}})) \times 100$ of the B3LYP/6-311G** harmonic and anharmonic vibrational wavenumber values from the experimental data of $\text{C}_4\text{H}_4\text{Se}$ and $\text{C}_4\text{D}_4\text{Se}$, respectively. Not surprisingly, the harmonic wavenumbers of $\text{C}_4\text{H}_4\text{Se}$ and $\text{C}_4\text{D}_4\text{Se}$ systematically overestimate the experimental values: in fact the percentage deviations from the observed data are within 4.6% and 6.5%, respectively, whereas the rms deviations for all the modes are calculated to be 63 and 38 cm^{-1} , respectively. When excluding the C–H stretches ($\nu\text{C-H}$), these rms deviations are reduced to 23 cm^{-1} and 22 cm^{-1} , respectively. For $\text{C}_4\text{H}_4\text{Se}$, when the harmonic wavenumbers are corrected by the scaling factor of 0.9669, the rms deviation

for all the modes decreases to 18 cm^{-1} , whereas the percentage deviations from the experimental data are within 3.7%. As can be appreciated from Figures 2 and 3, in comparison to both the harmonic and scaled harmonic values, the anharmonic wavenumbers are in better agreement with experiment (with the exceptions of mode no. 10 for $\text{C}_4\text{H}_4\text{Se}$ and modes no. 11 and 18 for $\text{C}_4\text{D}_4\text{Se}$, which are better reproduced by the harmonic computations), with a percentage error within 2.2% for $\text{C}_4\text{H}_4\text{Se}$ and 5.3% for $\text{C}_4\text{D}_4\text{Se}$. In line with previous results found for other cyclic compounds [10–17], the most significant anharmonic corrections occur for the $\nu\text{C-H}$ vibrations, which reduce the harmonic wavenumber values by 122–126 cm^{-1} (ca. –4%), improving noticeably the agreement with the experimental data (within 4–19 cm^{-1} , 0.1–0.6%). It is worth noting that, for a certain i th C–H (or C–D) stretching mode, the largest vibrational anharmonic constants ($\chi_{i,j}$) involve the remaining C–H (or C–D) stretches as well as the diagonal term. In Figure 4 we report the calculated $\chi_{i,j}$ ($i = 1, j = 1\text{--}21$) values for mode no. 1, taken as an example. The results show that the most significant contribution originates

TABLE 3: 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 $\text{C}_4\text{D}_4\text{Se}$.

	Description ^a	I_{IR}	B3LYP6-311G**			exp. ^b
			A_{Raman}	ω	ν	ν
A_1	1 $\nu\text{C-D}$	1.4	115.3	2409	2334	2335
	2 $\nu\text{C-D}$	1.7	68.6	2360	2283	2280
	3 $\nu\text{C=C} + \nu\text{C-C} + \delta\text{C-D}$	21.4	40.4	1436	1403	1398
	4 $\nu\text{ring} + \delta\text{C-D}$	4.9	6.8	1239	1215	1210
	5 Ring breathing + $\delta\text{C-D}$	1.0	19.7	863	849	847
	6 $\delta\text{C-D}$	1.0	4.9	788	781	774
	7 δring	16.4	7.6	691	682	683
	8 $\delta\text{C-Se-C}$	0.3	6.6	446	441	444
A_2	9 $\nu\text{C-D}$	0.0	0.8	766	757	748
	10 $\nu\text{C-D}$	0.0	0.0	532	527	528
	11 τring	0.0	0.0	473	469	475
B_1	12 $\nu\text{C-D}$	0.3	0.1	2402	2335	2335
	13 $\nu\text{C-D}$	1.8	54.1	2344	2264	2267
	14 $\nu\text{C=C} + \delta\text{C-D}$	2.1	0.0	1506	1475	1460
	15 $\delta\text{C-D} + \nu\text{C-Se}$	8.9	0.4	1018	994	1001
	16 $\delta\text{ring} + \delta\text{C-D}$	3.3	4.3	858	849	806
	17 $\delta\text{C-D}$	0.1	0.1	733	726	718
	18 $\nu\text{C-Se}$	1.4	4.8	588	578	592
B_2	19 $\nu\text{C-D}$	0.2	0.2	694	687	690
	20 $\nu\text{C-D}$	74.9	0.1	525	522	520
	21 τring	0.5	1.1	366	363	362
rms deviation ^c				38	11	
rms deviation ^d				22	12	
rms deviation ^e				75	2	

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

^b References [22, 23].

^c All the vibrational modes.

^d All the vibrational modes excluding the $\nu\text{C-H}$ modes.

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

from the coupling with the mode no. 15, with the $\chi_{1,15}$ value being calculated to be -108 cm^{-1} for $\text{C}_4\text{H}_4\text{Se}$ and -47 cm^{-1} for $\text{C}_4\text{D}_4\text{Se}$. Through (1), these anharmonic terms determine ca. 90% ($\text{C}_4\text{H}_4\text{Se}$) and 60% ($\text{C}_4\text{D}_4\text{Se}$) of the total anharmonic corrections. Thus, on going from the harmonic to the anharmonic data of $\text{C}_4\text{H}_4\text{Se}$, the rms deviation from the observed values for all the modes is decreased by ca. one order of magnitude (from 63 to 9 cm^{-1}). Note that for the perdeuterated isotopomer the rms deviations are much more closer to each other, being 38 cm^{-1} for the harmonic and 11 cm^{-1} for the anharmonic values.

The high-energy IR and Raman spectral regions for $\text{C}_4\text{H}_4\text{Se}$ ($\text{C}_4\text{D}_4\text{Se}$) are exclusively characterized by the $\nu\text{C-H}$ ($\nu\text{C-D}$) peaks, predicted in the 3058–3119 cm^{-1} (2264–2335 cm^{-1}) wavenumber range by the anharmonic computations, in good agreement with experiment [21–23]. Figures 5 and 6 display the anharmonic B3LYP/6-311G** vibrational spectra in the 1500–500 cm^{-1} wavenumber range for $\text{C}_4\text{H}_4\text{Se}$ and $\text{C}_4\text{D}_4\text{Se}$, respectively. The spectral profiles were constructed with pure Lorentzian band shapes with a full width

at half maximum of 10 cm^{-1} . In these figures we also show graphical representations of the atomic displacement vectors of the most interesting vibrations. As can be appreciated from Figure 5, the IR spectrum of $\text{C}_4\text{H}_4\text{Se}$ is dominated by an absorption ($I_{\text{IR}} = 131.5\text{ km/mol}$) located at 703 cm^{-1} (707 and 684 cm^{-1} under the harmonic and scaled harmonic approximation, resp.). This mode is attributed to a pure out-of-plane C–H bending deformation. It is worth noting that the anharmonic calculations are in satisfactory agreement with experiment, which gives a very strong peak at 700 cm^{-1} (0.4%). The corresponding absorption in the calculated spectrum of the perdeuterated isotopomer (Figure 6) is placed at 522 cm^{-1} ($I_{\text{IR}} = 74.9\text{ km/mol}$), which well reproduces the observed datum of 520 cm^{-1} .

In the Raman spectra of selenophene and its perdeuterated isotopomer the A_1 symmetry $\nu\text{C-H}$ and $\nu\text{C-D}$ vibrations (modes no. 1 and 2) are characterized by the highest A_{Raman} values (Tables 2 and 3). As can be seen from Figures 5 and 6, for wavenumbers $<1500\text{ cm}^{-1}$, the strongest Raman peak is placed at 1424 cm^{-1} ($A_{\text{Raman}} = 38.0\text{ \AA}^4/\text{amu}$) for

TABLE 4: B3LYP/6-311G** first overtone wavenumbers (cm^{-1}) of selenophene isotopomers.

Symm.	Mode number ^a	$\text{C}_4\text{H}_4\text{Se}$		$\text{C}_4\text{D}_4\text{Se}$	
		Harmonic	Anharmonic	Harmonic	Anharmonic
A_1	1	6488	6185	4818	4646
	2	6388	6092	4720	4544
	3	2927	2840	2873	2799
	4	2746	2690	2477	2434
	5	2206	2185	1725	1696
	6	2066	2029	1576	1563
	7	1529	1503	1382	1364
	8	919	907	892	883
A_2	9	1847	1821	1531	1515
	10	1369	1363	1064	1055
	11	1104	1095	946	938
B_1	12	6484	6178	4804	4645
	13	6360	6060	4689	4503
	14	3130	3044	3011	2943
	15	2535	2484	2036	1986
	16	2209	2183	1717	1697
	17	1678	1658	1465	1454
	18	1243	1214	1176	1150
B_2	19	1771	1750	1388	1374
	20	1413	1407	1050	1045
	21	802	794	733	726

^aSee Tables 2 and 3 for the mode description. FIGURE 2: Percentage deviation relative to experiment [21] of the B3LYP/6-311G** wavenumbers of $\text{C}_4\text{H}_4\text{Se}$. FIGURE 3: Percentage deviation relative to experiment [22, 23] of the B3LYP/6-311G** wavenumbers of $\text{C}_4\text{D}_4\text{Se}$.

$\text{C}_4\text{H}_4\text{Se}$ and at 1403 cm^{-1} ($A_{\text{Raman}} = 40.4\text{ \AA}^4/\text{amu}$) for $\text{C}_4\text{D}_4\text{Se}$. This vibrational transition (mode no. 3) is mainly assigned to the $\text{C}=\text{C} + \text{C}-\text{C}$ bonds stretching with the

nonnegligible contribution from the in-plane $\text{C}-\text{H}$ ($\text{C}-\text{D}$) bending motions. The abovecalculated wavenumbers can be compared with the experimental values of 1419 cm^{-1} (+0.4%) and 1398 cm^{-1} (+0.4%), respectively.

FIGURE 4: Anharmonic vibrational constants for the C-H stretching mode no. 1 with the vibrational modes ($\chi_{1,j}$, $j = 1-21$) of C_4H_4Se and C_4D_4Se . B3LYP/6-311G** results. For the mode numbering see Tables 2 and 3.

FIGURE 5: B3LYP/6-311G** anharmonic IR (bottom) and Raman (top) spectra of C_4H_4Se in the 500–1500 cm^{-1} wavenumber range. Lorentz line shapes with half-width of 10 cm^{-1} were used.

In Figure 7 we compare the computed (harmonic and anharmonic) and experimental H/D isotopic wavenumber shifts for all the $\nu C-H$ vibrations (modes 1, 2, 12, and 13). Following the experimental results, upon deuteration the $\nu C-H$ wavenumbers are downward shifted by 765–787 cm^{-1} . Under the harmonic approximation the $\nu C-H-\nu C-D$ wavenumber

FIGURE 6: B3LYP/6-311G** anharmonic IR (bottom) and Raman (top) spectra of C_4D_4Se in the 500–1500 cm^{-1} wavenumber range. Lorentz line shapes with half-width of 10 cm^{-1} were used.

shifts are calculated to be in the 834–840 cm^{-1} wavenumber range, overestimating the observed shifts by 50–75 cm^{-1} (6–10%). The introduction of the anharmonic corrections noticeably improves the accordance with experiment within 6–20 cm^{-1} (1–3%). For the remaining vibrations the magnitudes of the anharmonic corrections for the H/D isotopic shifts are little relevant.

Table 4 lists the wavenumber values for the overtone transitions of C_4H_4Se and C_4D_4Se here calculated under the harmonic and anharmonic treatments. Similarly to the results of the fundamental wavenumbers, the largest anharmonic effects are found for the $\nu C-H$ ($\nu C-D$) vibrations, with the harmonic data being decreased by 5% (3–4%).

4. Conclusions

The gas-phase equilibrium structure and harmonic and anharmonic IR and Raman spectra of selenophene and of its perdeuterated isotopomer have been determined and analyzed at the B3LYP/6-311G** level of theory. The overtone transitions have been here computed under the harmonic and anharmonic procedures. On the whole the harmonic wavenumbers overestimate the experimental data of the fundamental transitions with an rms deviation of 63 cm^{-1} for C_4H_4Se and 38 cm^{-1} for C_4D_4Se . The corresponding rms deviations for the anharmonic calculations are reduced to 9 and 11 cm^{-1} , respectively. In particular, the C-H and C-D stretches are strongly affected by the anharmonic corrections, which reproduce the experimental H/D isotopic frequency shifts within 6–20 cm^{-1} (1–3%). The present results suggest that the anharmonic PT2 scheme in combination with the B3LYP functional and the 6-311G** basis set can be

FIGURE 7: H/D isotopic wavenumber shifts for the C–H stretching modes between C_4H_4Se and C_4D_4Se . Comparison between experimental [21–23], harmonic, and anharmonic B3LYP/6-311G** data.

considered a promising method to calculate the vibrational spectra of cyclic compounds for which observed data are incomplete or not yet available in the literature.

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