Vibrational Analysis of the Spectra of 1,2,5-Oxadiazole, 1,2,5-Thiadiazole and 1,2,5-Selenadiazole

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Equilibrium geometries and harmonic force fields have been calculated for 1,2,5-oxadiazole, 1,2,5-thiadiazole and 1,2,5-selenadiazole at the SCF and MP2 levels of theory using the 6-31G** basis set (Binning–Curtiss for the selenium atom). Scaled quantum-mechanical (SOM) force fields have been calculated for the three molecules and some of their isotopomers using the experimental frequencies available from the literature. The IR absorption intensities were calculated using the computed dipole derivative tensors. The assignment of the experimental to the calculated frequencies was done first according to symmetry then mainly according to frequency order. The calculated vibrational spectra for the studied molecules by the scaled MP2 force fields are only slightly better than those calculated by the scaled SCF force fields. A good correlation was found between the scale factors obtained for both molecules and those obtained for 1,3,4-oxadiazole and 1,3,4-thiadiazole.

In recent years, *ab initio* methods have provided an efficient tool for the study of vibrational spectra of small organic molecules. In spite of computational progress, force-field calculations have been reported only for a limited number of unsubstituted five- or six-membered rings. *Ab initio* force field calculations have been reported for five-membered rings containing one heteroatom, furan, pyrrole and thiophene,[1] two nitrogen atoms, imidazole[2] and pyrazole,[3] and three nitrogen atoms, 1,2,3-triazole,[4] and six-membered rings containing one or more nitrogen atoms.[5] While no *ab initio* force field calculations have been reported for five-membered rings with two or more different heteroatoms. Consequently, no prediction for the behavior of *ab initio* force fields is known for such molecules. On the other hand, it is now increasingly important for *ab initio* force fields to be calculated after the inclusion of electron correlation. The simplest method to include electron correlation is based on second-order perturbation theory, often called the MP2[6] method. It is of interest then to compare the scaled force fields calculated at the SCF and MP2 levels of theory.

In the present paper we report force-field calculations for three 1,2,5-diazoles containing a third heteroatom, 1,2,5-oxadiazole (**OD**), 1,2,5-thiadiazole (**TD**) and 1,2,5-selenadiazole (**SD**). The force fields were calculated at the SCF and MP2 levels of theory using the 6-31G** basis set, except for the selenium atom, for which the Binning–Curtiss basis set was used. For simplicity the basis set for **SD** will be referred to as the 6-31G** basis set. The force fields were calculated at the optimized geometries assum-

ing C_{2v} symmetry. The calculated force fields and dipole derivative tensors were used to calculate the harmonic frequencies and IR absorption intensities for the parent molecules and some of their isotopomers. The experimental frequencies were assigned to the calculated frequencies first according to symmetry, then mainly according to frequency order. The calculated results lead to an analysis of the vibrational spectra of the studied molecules. Differences between the vibrational spectra calculated at the SCF and MP2 levels of theory will be discussed.

The vibrational spectra for **OD** have been reported by various authors.[7–10] The assignment of the fundamental vibrations was identical except for a few bands in the 900–800 cm^{-1} region. In 1976 Christensen *et al.*[11] reported the IR and Raman spectra of its -3,4-d$_2$ (d$_2$) and -3-d$_1$ (d$_1$) isotopomers. In addition, the assignment of the fundamental frequencies for the d$_0$ isotopomer was revised. This assignment has also been confirmed by Stiefvater[12] using double-resonance modulation (DRM) microwave spectroscopy for vibrationally excited **OD**.

For **TD** several authors[13–15] reported an incomplete assignment of the fundamental vibrations for the d$_0$, d$_2$ and d$_1$ isotopomers. In 1966 Soptrajanov *et al.*[16] reported a complete vibrational assignment of the fundamental vibrations for the d$_0$ and d$_2$ isotopomers, depending on the measured IR spectrum for the d$_0$ and d$_2$ isotopomers and the measured Raman spectra for the d$_0$ isotopomer. At the same time, Benedetti *et al.*[17,18] reported the IR and Raman spectra for **TD**-d$_0$. The experimental data reported in Refs. 16 and 17 are similar, which confirms the

Table 1. Equilibrium geometry for 1,2,5-oxadiazole.[a]

Coordinate	MINDO/3[b]	SCF/ STO-3G[b]	SCF/ 3-21G[b]	SCF/ 4-31G[c]	SCF/ 6-31G**[c]	MP2/ 6-31G**[c]	MW[d]
R(N–O)	1.340	1.385	1.427	1.396	1.333	1.372	1.3729 (6)
R(C = N)	1.304	1.313	1.279	1.280	1.275	1.328	1.3032 (13)
R(C–C)	1.456	1.440	1.444	1.437	1.429	1.403	1.4211 (9)
R(C–H)	1.105	1.081	1.063	1.062	1.069	1.075	1.0763 (5)
∠(N–O–N)	113.6	110.4	108.8	109.8	111.6	112.2	111.15 (8)
∠(O–N=C)	105.7	105.9	105.5	105.8	106.5	104.7	105.53 (5)
∠(N=C–C)	107.5	108.7	110.1	109.3	107.7	109.2	108.89 (3)
∠(N=C–H)	125.0	122.4	122.3	122.1	122.0	120.3	120.95 (3)
∠(C–C–H)	127.0	130.2	127.6	128.6	130.4	130.4	130.16 (3)
μ	2.79	2.97	4.55	4.78	3.81	3.30	3.38 (4)
E	–	–257.23340	–259.06708	–260.12469	–260.55114	–261.35185	

[a] Bond length in 10^{-10} m and angles in °. μ is the dipole moment in Debye. E is the energy in a.u. Uncertainity in parentheses.
[b] Ref. 31. [c] This work. [d] Microwave spectroscopy, Ref. 33–35.

vibrational assignment for the d_0 isotopomer. For **SD** the IR and Raman spectra were reported by Benedetti *et al.*[19]

Normal coordinate analysis using empirical force fields was also reported for **OD**, **TD** and **SD**.[20-22]

Calculational details

All *ab initio* calculations were performed using the CAD-PAC[23] program. The calculations were done assuming C_{2v} symmetry. First, optimized geometries were calculated at the SCF and MP2 levels of theory using the 6-31G** basis set for **OD**, **TD** and **SD** except for the selenium atom, for which the Binning–Curtiss (14s,11p,5d)/ [6s,4p,1d] basis set[24] was used. Next the cartesian-coordinate force fields and dipole derivative tensors were calculated at the same level at the corresponding optimized geometries. The calculated cartesian-coordinate force fields were transferred to internal coordinate force fields[25,26] using the internal coordinate definition described by Fogarasi and Pulay.[26] Vibrational frequencies were calculated by the program of Schnachtschneider[27] using the standard Wilson GF formalism.[28] The scaling of the internal coordinate force fields to from SQM force fields utilized the procedure described by Pulay and co-workers[25,29]

$$F_{ij}^{\text{scaled}} = (C_i C_j)^{1/2} F_{ij}^{\text{theor}} \qquad (1)$$

where C_i and C_j are scale factors to internal coordinates q_i and q_j, respectively. A least-square procedure was used to optimize the scale factors to minimize the difference between the experimental and calculated frequencies as indicated by the calculated r.m.s. deviation. Dipole strengths were calculated as described elsewhere.[30] To avoid interactions taking place in the vapor or liquid spectra, the calculated IR absorption intensities are compared mainly with the solution IR absorption intensities whenever available. In our preliminary calculations the SCF/4-31G basis set was used, and its results will be referred to whenever appropriate.

Results

Optimized geometries for **OD**, **TD** and **SD** at the SCF and MP2 levels of theory using the 6-31G** basis set are given in Tables 1–3. For comparison, SCF/STO-3G and SCF/3-21G optimized geometries for **TD** were also calculated and are shown in Table 2 to complement those reported for **OD**.[31] The optimized geometries using other basis sets[31] and by semi-empirical methods[31,32] and experimental geometries[33-40] for the studied molecule are given in Tables 1–3.

Cartesian-coordinate force fields were transferred to internal-coordinate force fields using a non-redundant set of internal coordinates defined in Table 4. The atom numbering employed for the three molecules is given in Fig. 1.

In the scaling step, eight scale factors were used in which similar internal coordinates where grouped, and each is assigned a unique scale factor as shown later in Table 11. Before the assignment of the experimental to the calculated frequencies, the experimental data were thoroughly examined to check the correctness of the
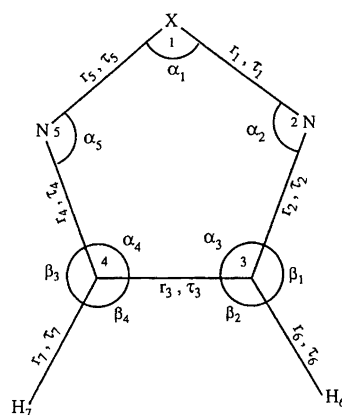

Fig. 1. Atom numbering and internal coordinates for 1,2,5-oxadiazole (X=O), 1,2,5-thiadiazole (X=S) and 1,2,5-selenadiazole (X=Se).

Table 2. Equilibrium geometry for 1,2,5-thiadiazole.[a]

Coordinate	CNDO/2[b]	SCF/ STO-3G[c]	SCF/ 3-21G[c]	SCF/ 4-31G[c]	SCF/ 6-31G**[c]	MP/ 6-31G**[c]	MW[d]	ED[e]
R(S–N)	1.60	1.771	1.762	1.774	1.639	1.644	1.6296 (1)	1.632 (5)
R(C = N)	1.34	1.295	1.279	1.276	1.284	1.342	1.3270 (1)	1.329 (8)
R(C–C)	1.41	1.472	1.463	1.458	1.439	1.407	1.4167 (5)	1.413 (10)
R(C–H)	1.08	1.086	1.067	1.067	1.074	1.079	1.0805 (3)	1.080 (10)
∠(N–S–N)	102	94.7	92.4	91.7	97.0	99.5	99.44 (0)	99.4 (2)
∠(S–N=C)	105	106.7	108.8	108.9	108.2	106.0	106.51 (1)	106.5 (4)
∠(N=C–C)	114	115.9	115.0	115.3	113.3	114.3	113.77 (1)	113.8
∠(N=C–H)	123	120.6	121.1	120.6	121.1	119.2	119.96 (2)	–
∠(C–C–H)	123	123.5	123.9	124.1	125.6	126.5	126.27 (1)	–
μ	–	2.63	2.48	2.48	2.04	1.39	1.565 (15)	–
E	–	−575.68548	−580.24695	−582.49688	−583.27492	−584.02739		

[a] See corresponding footnote in Table 1. [b] Ref. 32. [c] This work. [d] Microwave spectroscopy, Refs. 36 and 37. [e] Electron diffraction, Refs. 38 and 39.

assigned experimental frequencies. Since the d_0 and d_2 isotopomers have C_{2v} symmetry, their 15 fundamental vibrations are classified as: $6A_1 + 2A_2 + 5B_1 + 2B_2$. For the d_1 isotopomers they are classified as: $11A' + 4A''$. The selection rules for these modes are given elsewhere.[41] In the assignment of the experimental to the calculated frequencies, bands were assigned first according to symmetry and then mainly according to frequency order regardless of the calculated potential energy distribution (PED) or absorption intensities. This is mainly due to the relatively large separation between most successive bands with the same symmetry.

For OD and its d_2 and d_1 isotopomers the experimental data used in the calculations are those reported by Christensen et al.,[9,11] except for the out-of-plane modes, which are those reported by Stroyer-Hansen.[22] The assignment of the experimental to the calculated frequencies first according to symmetry and then according to frequency order was straightforward, with the exception of a few bands which are close in frequency. These are the 1036 and 1005 cm^{-1} bands for the d_0 isotopomer, the 939 and 914 cm^{-1} bands for the d_2 isotopomer and the 1004, 942 and 909 cm^{-1} bands for the d_1 isotopomer. The calculated IR absorption intensities with the SCF/6-31G** and

MP2/6-31G** force fields favors the frequency order assignment for the d_0 and d_2 isotopomer bands. However, for the d_1 isotopomer, the calculated IR absorption intensities would not favor a particular assignment. The bands for the d_0 and d_2 isotopomers were then assigned according to frequency order, and the three bands for the d_1 isotopomer were first left unassigned. The calculated frequencies for these bands using the MP2/6-31G** force field were 994, 958 and 898 cm^{-1} and using the SCF/6-31G** force field were 998, 954 and 900 cm^{-1}. Since the calculated frequencies for these three bands by both force fields are very close to each other and close to the experimental frequencies, these bands were then included in our final calculations according to the frequency-order assignment.

For the two bands at 888 and 820 cm^{-1} of the d_0 isotopomer, there is a controversy about the assignment of one band as an A_2 mode and the other band as a B_1 mode.[7-12] Since our calculations, with both force fields, could not resolve their assignment, these two bands were then left unassigned.

The experimental data used for the force-field calculations for TD and its d_2 isotopomer are from Ref. 17, except for the out-of-plane modes from Ref. 22. The sym-

Table 3. Equilibrium geometry for 1,2,5-selenadiazole.[a]

Coordinate	SCF/ 6-31G**[b]	MP2/ 6-31G**[b]	MW[c]
R(Se–N)	1.814	1.797	1.80 (2)
R(C=N)	1.268	1.335	
R(C–C)	1.465	1.417	
R(C–H)	1.076	1.081	
∠(N–Se–N)	90.76	94.5	94.5 (20)
∠(Se–N=C)	108.5	105.5	
∠(N=C–C)	116.2	117.3	
∠(N=C–H)	120.7	118.4	
∠(C–C–H)	123.1	124.3	
μ	1.81	0.96	1.11 (3)
E	−2583.12028	−2584.13158	

[a] See corresponding footnote in Table 1. [b] This work. [c] Microwave spectroscopy, Ref. 40.

Table 4. Internal coordinates.[a]

No.	Mode[b]1	Description[c]
q_1, q_5	r_1, r_5	N–X stretch
q_2, q_4	r_2, r_4	C=N stretch
q_3	r_3	C–C stretch
q_6, q_7	r_6, r_7	C–H stretch
q_8	$\alpha_1 + a(\alpha_2 + \alpha_5) + b(\alpha_3 + \alpha_4)$	Ring deformation
q_9	$(a-b)(\alpha_2 - \alpha_5) + (1-a)(\alpha_3 - \alpha_4)$	Ring deformation
q_{10}, q_{11}	$\beta_1 - \beta_2$, $\beta_3 - \beta_4$	CH rocking
q_{12}, q_{13}	τ_6, τ_7	CH wagging
q_{14}	$b(\tau_1 - \tau_5) + a(\tau_2 + \tau_4) + \tau_3$	Ring torsion
q_{15}	$(a-b)(\tau_4 - \tau_2) + (1-a)(\tau_5 - \tau_1)$	Ring torsion

[a] See Fig. 1 for defination of r, α, β and τ coordinates. [b] $a = \cos 144°$ and $b = \cos 72°$. Values of normalization constants are not given. [c] X=O for 1,2,5-oxadizole, X=S for 1,2,5-thiadiazole and X=Se for 1,2,5-selenadiazole.

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Table 5. Calculated vibrational frequencies and dipole strengths for 1,2,5-oxadiazole-d_0.[a]

Sym.	No.	Exptl.[b] Freq.	Int.	SCF Freq.	D	MP2 Freq.	D	Description[c]
A_1	1	3157	19	3164	0	3164	1	CH str.
	2	1418	72	1439	38	1411	63	CN str.
	3	1316	44	1304	11	1316	14	CN str.+CC str.
	4	1036	6	1026	12	1044	1	CC str.+CH rock.
	5	1005	48	992	52	989	25	Ring def.+NO str.
	6	872	94	841	293	858	89	NO str.
A_2	7	(888)	—	897	0	867	0	CH wag.
	8	641	—	637	0	627	0	Ring torsion
B_1	9	3144	13 (sh)	3151	1	3150	1	CH str.
	10	1541	2	1539	1	1550	1	CN str.
	11	1175	24	1166	8	1173	22	CH rock.
	12	953	70	954	119	963	67	Ring def.
	13	(820)	—	902	9	851	0	NO str.
B_2	14	838	112	836	168	856	177	CH wag.
	15	631	9	626	5	646	8	Ring torsion
R.m.s.				13		11		

[a] Frequencies in cm^{-1}, D is the dipole strnegth in 10^{-40} esu^2 cm^2. [b] Experimental data are from Refs. 9 and 11, except for the out-of-plane modes, which are from Ref. 22. Bands in paranthesis are not included in the fit. Sh: shoulder. [c] Potential energy distribution calculated by MP2/6-31G** force field. Only values greater than 20% are considered.

metry of the experimental fundamental vibrations for the d_0 isotopomer has been confirmed by different authors,[16-18,42] but no Raman data are available for the d_2 isotopomer. As a check for the correctness of the symmetry assignment of the fundamental vibrations for the d_2 isotopomer, the calculations were first performed while allowing the scale factors to vary with respect to the d_0 frequencies only. The calculated scale factors were then used to calculate the frequencies for the d_2 isotopomer. No significant change took place in the calculated frequencies or PED. The d_2 isotopomer bands were then included in the calculations.

For **SD** the only experimental data are those reported by Benedetti *et al.*,[19] and are for the d_0 isotopomer only.

In the assignment of the experimental to the calculated frequencies, it was found that the B_1 band at 1385 cm^{-1} and the A_2 band at 672 cm^{-1} are too far from their corresponding unscaled MP2 calculated frequencies, 1488 and 607 cm^{-1}, respectively, and contributed about half the r.m.s. deviation with either force field. These two bands were then left unassigned. The assignment of the other 13 fundamental vibrations was straightforward according to the frequency order under the C_{2v} symmetry constraint.

In all 43, 30 and 13 fundamental vibrations for **OD, TD** and **SD**, respectively, were used in the refinement of the scale factors. The calculated frequencies and IR absorption intensities using the MP2/6-31G** and SCF/6-

Table 6. Calculated vibrational frequencies and dipole strengths for 1,2,5-oxadiazole-d_2.[a]

Sym.	No.	Exptl.[b] Freq.	Int.[d]	SCF Freq.	D	MP2 Freq.	D	Description[c]
A_1	1	2356	—	2357	0	2359	0	CD str.
	2	1401	m	1414	21	1394	44	CN str.
	3	1222	m	1223	6	1223	15	CC str.+CN str.
	4	1004	vs	997	57	993	23	Ring def.
	5	895	s	870	201	898	55	NO str.
	6	744	vs	729	102	736	43	CD rock.
A_2	7	757	—	780	0	705	0	Ring torsion+CD wag.
	8	552	—	539	0	566	0	CD wag.+ring torsion
B_1	9	2359	w	2336	3	2335	0	CD str.
	10	1516	w	1503	0	1516	0	CN str.
	11	939	m	978	17	960	13	Ring def.
	12	914	s	904	97	906	56	CD rock.+ring def.
	13	808	w	834	6	812	3	NO str.+CD rock.
B_2	14	640	s	639	91	653	53	CD wag.
	15	631	w	624	1	644	54	Ring torsion
R.m.s.				18		17		

[a-c] See corresponding footnote in Table 5. [d] vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

Table 7. Calculated vibrational frequencies and dipole strengths for 1,2,5-oxadiazole-d$_1$.[a]

| Sym. | No. | Exptl.[b] | | SCF | | MP2 | | Description[c] |
		Freq.	Int.[d]	Freq.	D	Freq.	D	
A'	1	3151	m	3157	0	3157	1	CH str.
	2	2352	vw	2347	2	2347	0	CD str.
	3	1528	vw	1522	1	1534	1	CN str.
	4	1408	s	1425	29	1402	52	CN str.
	5	1280	m	1275	10	1282	16	CN str.+CC str.
	6	1101	m	1097	5	1104	13	CH rock+CC str.
	7	1004	vs	998	57	993	23	Ring def.
	8	942	s	954	85	957	51	Ring def.
	9	909	vs	901	44	900	51	NO str.
	10	831	m (sh)	865	181	851	18	NO str.
	11	779	s	771	113	775	40	CD rock+NO str.
A''	12	868	m (sh)	875	51	862	83	CH wag.
	13	712	s	720	66	686	41	CD wag.+ring torsion
	14	631	m	626	5	646	9	Ring torsion
	15	579	w	567	10	588	12	CD wag.+ring torsion
R.m.s.				12		11		

[a-c] See corresponding footnote in Table 5. [d] See corresponding footnote in Table 6.

31G** force fields for OD-d$_0$, d$_2$ and d$_1$, TD-d$_0$ and d$_2$ and SD-d$_0$ are given in Tables 5–10, respectively. The final scale factors are given in Table 11 and the corresponding scaled force fields are given in Table 12.

Discussion

The harmonic vibrational frequencies predicated at the SCF level are usually overestimated by about 10–20%. This is due to neglect of the electron correlation, neglect of anharmonicity and incompleteness of the basis set.[43] The harmonic vibrational frequencies predicated at the MP2 level are usually overestimated by only about 5%. This improvement over the SCF calculated frequencies is due to the inclusion of the electron correlation, although higher excitations in the correlated wavefunction are also neglected. The advantage of including the electron correlation in the MP2 force field calculation is at the expense of the CPU time, which is about five times that for the SCF force field calculation. Similar to the SCF force fields, there is a recent trend to scale the force fields calculated at the MP2 level.[44] It may be of interest then to compare the force fields calculated at both levels of theory.

Compared to the geometries determined experimentally by microwave spectroscopy, the geometries predicted by the 6-31G** basis set, both SCF and MP2, are in better agreement with the experimental geometries than those predicated by the other basis sets and semi-empirical

Table 8. Calculated vibrational frequencies and dipole strengths for 1,2,5-thiadiazole-d$_0$.[a]

| Sym. | No. | Exptl.[b] | | SCF | | MP2 | | Description[c] |
		Freq.	Int.[d]	Freq.	D	Freq.	D	
A$_1$	1	3106	w	3122	9	3122	3	CH str.
	2	1350	s	1380	74	1357	39	CH rock.+CC str.
	3	1251	—	1232	1	1258	2	CN str.
	4	1041	m	1021	26	1035	18	CC str.+CH rock.
	5	806	s	792	211	819	64	SN str.
	6	688	w	683	0	692	15	Ring def.+SN str.
A$_2$	7	908	—	927	0	887	0	CH wag.
	8	612	sh	596	0	616	0	Ring torsion
B$_1$	9	3108	—	3107	5	3107	0	CH str.
	10	1461	w	1465	0	1457	0	CN str.+CH rock.
	11	1227	s	1215	11	1227	34	CH rock.+CN str.
	12	895	s	904	200	890	66	Ring def.
	13	780	s	791	88	769	96	SN str.
B$_2$	14	838	vs	833	120	852	147	CH wag.
	15	520	s	504	239	533	195	Ring torsion
R.m.s.				15		10		

[a-c] See corresponding footnote in Table 5. [b] Experimental data are from Ref. 16 except for the out-of-plane modes are from Ref. 22. [d] See corresponding footnote in Table 6.

Table 9. Calculated vibrational frequencies and dipole strengths for 1,2,5-thiadiazole-d$_2$.[a]

Sym.	No.	Exptl.[b] Freq.	Int.[d]	SCF Freq.	D	MP2 Freq.	D	Description[c]
A$_1$	1	2318	m	2318	12	2319	5	CD str.
	2	1294	vs	1319	74	1303	38	CN str.+CC str.
	3	1183	vs	1165	6	1168	8	CN str.+CC str.
	4	849	vs	829	152	860	57	SN str.+CC str.
	5	753	vs	741	74	758	16	CD rock.+SN str.
	6	681	w	678	0	687	16	Ring def.
A$_2$	7	781	—	810	0	744	0	Ring torsion+CD wag.
	8	519	—	498	0	534	0	CD wag.+CD torsion
B$_1$	9	2320	—	2299	7	2298	1	CD str.
	10	1417	m	1425	3	1414	3	CN str.
	11	968	w	974	30	962	1	CD rock.
	12	869	vs	866	141	865	69	Ring def.
	13	751	—	757	103	743	103	SN str.
B$_2$	14	650	s	643	24	658	38	CD wag.
	15	506	s	491	267	520	237	Ring torsion
R.m.s.				16		14		

[a,c] See corresponding footnote in Table 5. [b] See corresponding footnote in Table 8. [d] See corresponding footnote in Table 6. Liquid-phase IR absorption intensity.

methods. The MP2/6-31G** optimized geometries are better than the SCF/6-31G** optimized geometries except for the C–C bond and N–O–N and C–C–H angles for **OD** and the N = C–C and N = C–H angles for **TD**. The SCF geometries have poor prediction of the N–S bond and N–S–N and N–Se–N angles owing to the inadequate treatment of the S and Se atoms, but when the electron correlation was included the agreement with the experimental geometries for these coordinates is excellent, although the uncertainty for the N–Se–N angle is high. The SCF/6-31G** optimized geometries for **OD** and **TD** predict the C = N and C–H bonds to be too short and the C–C bond too long, while the MP2/6-31G*** optimized geometries predict the C = N bond to

be too long, the C–C bond to be too short and the C–H bond almost exactly correct. Also the SCF/6-31G** overestimated the O–N = C, S–N = C and N = C–H angles and underestimated the N = C–C angle, while the situation is the opposite when electron correlation is included. The other SCF basis sets generally behave like the 6-31G** basis set, except for the N = C–C angle.

The average r.m.s. deviations for **OD**; three isotopomers, are 13 and 15 cm^{-1}, for **TD**, two isotopomers, they are 12 and 15 cm^{-1} and for **SD**, one isotopomer, they are 8 and 25 cm^{-1}, using the MP2/6-31G** and SCF/6-31G** force fields, respectively. Such values are justified taking into consideration that the anharmonicity and solvent perturbations are not included in the calcu-

Table 10. Calculated vibrational frequencies and dipole strengths for 1,2,5-selenadiazole-d$_0$.[a]

Sym.	No.	Exptl.[b] Freq.	Int.[d]	SCF Freq.	D	MP2 Freq.	D	Description[c]
A$_1$	1	3067	m	3055	40	3054	0	CH str.
	2	1360	s	1397	46	1344	229	CH rock.+CN str.
	3	1290	w	1245	0	1292	4	CN str.+CH rock.
	4	1008	m	1005	75	1015	56	CC str.+CH rock.
	5	728	s	713	373	728	305	SeN str.+ring def.
	6	489	vw	500	7	492	11	Ring def.+SeN str.
A$_2$	7	868	—	906	0	875	0	CH wag.+ ring torsion
	8	(672)	—	532	0	574	0	Ring torsion+CH wag.
B$_1$	9	3028	sh	3040	19	3040	55	CH str.
	10	(1385)	sh	1457	3	1501	0	CN str.+CH rock.
	11	1234	s	1228	84	1242	2	CH rock.+CN str.
	12	880	s	881	330	879	190	Ring def.
	13	589	s	590	173	587	60	SeN str.
B$_2$	14	833	s	804	211	827	324	CH wag.
	15	438	s	395	853	434	578	Ring torsion
R.m.s.				25		8		

[a,c] See corresponding footnote in Table 5. [b] Experimental data are from Ref. 19. [d] See corresponding footnote in Table 6.

lations. The average r.m.s. deviations using the MP2/6-31G** force fields are only slightly better than those with the SCF/6-31G** force fields using the same experimental assignment. We conclude that scaling can diminish the difference between the force fields calculated at the MP2 and SCF levels of theory. The average r.m.s. deviations using the SCF/4-31G force fields for OD and TD are about twice those with the SCF/6-31G** force fields. This indicates the necessity of using a large basis set for the studied molecules. The large r.m.s. deviation with the SCF/6-31G** force field for SD indicates that the 6-31G** basis set used at the SCF level is not large enough to produce a good prediction of the experimental frequencies.

The calculated IR absorption intensities with both force fields are generally in good correlation with the experimental IR absorption intensities, i.e. strong and weak bands are correctly predicted. For OD-d_0 (Table 5) where numerical values of the experimental IR absorption intensities are available, the agreement is excellent, especially with the MP2/6-31G** calculated IR absorption intensities. It is worth noting that the calculated IR absorption intensities for the ring deformation mode with the MP2/6-31G** force fields are sometimes wrongly predicted, e.g. the bands at 1004 cm^{-1} for OD-d_2, 1004 cm^{-1} for OD-d_1 and 688 cm^{-1} for TD-d_0.

For OD, d_0 isotopomer, two bands at 888 and 820 cm^{-1} were excluded from the calculations. The calculated frequencies with the SCF/6-31G** force field (Table 5) could not resolve the assignment of these two bands, since both bands are calculated at about 900 cm^{-1}. The calculated frequencies with the MP2/6-31G** force field favor the assignment of the 888 cm^{-1} band as an A_2 band and the 820 cm^{-1} band as a B_1 band. Notice also that the difference between the calculated and experimental frequencies for these two bands using the MP2/6-31G** force field is about twice the average r.m.s. deviation for this isotopomer.

For TD the calculated frequencies fit reasonably well with the experimental frequencies, especially for the d_2 isotopomer, the symmetry assignment of whose bands was not certain. The calculated IR absorption intensities for the d_2 isotopomer could not be correlated with the experimental intensities, since the experimental intensities

are for the liquid phase, where bands are usually broad and overlap.

For SD the B_1 band at 1385 cm^{-1} and the A_2 band at 672 cm^{-1} were not included in the calculations. The first band is calculated to be around 1480 cm^{-1} by both force fields. A weak depolarized band observed around 1501 cm^{-1} in the Raman spectrum of SD[21] assigned by those authors as a combination band may correspond to this B_1 band. The other A_2 band is calculated at 532 cm^{-1} by the SCF/6-31G** force field and at 574 cm^{-1} by the MP2/6-31G** force field. No band could be found in this region, probably since this band, with A_2 symmetry, is IR- and Raman-inactive.

Although the scale factors (SFs) optimized for the studied molecules (Table 11) are not well correlated, comparing these SFs with those optimized for similar molecules,[45] 1,3,4-oxadiazole (OD3) and 1,3,4-thiadiazole (TD3), we find that the correlation between the SFs for the five molecules is excellent except for the C = N stretch coordinate and the out-of-plane SFs for SD, in addition to the O–N, S–N and Se–N bonds. The poor correlation between the O–N, S–N and Se–N bonds SFs is due to the difference in the nature of these bonds. The correlation between SCF SFs is worse than that with the MP2 SFs, a reflection of the worse optimized geometries compared to the MP2 optimized geometries. The poorer correlation between the SFs for OD, TD and SD is a reflection of the worse optimized geometries predicted for these molecules compared to those obtained for OD3 and TD3, where there is a better correlation between their SFs.

The predicted C = N bond is too short and the C–C bond is too long for OD and TD by the SCF geometry, while the reverse is the case with the MP2 geometry, such that the SCF SFs for the C = N bond are smaller and the SCF SFs for the C–C bond are bigger than the corresponding MP2 SFs. This in fact is as expected, since a shorter predicted bond distance would result in bigger force constants and a smaller SF to bring the calculated frequencies close to the experimental frequencies, noting that the MP2 SFs are expected to be generally bigger than the SCF SFs, since the MP2 frequencies are less overestimated than the SCF frequencies. Note also that the divergence of the SCF and MP2 SFs is similar. Also,

Table 11. Scale factors for 1,2,5-oxadiazole (OD), 1,3,4-oxadiazole (OD3), 1,2,5-thiadiazole (TD), 1,3,4-thiadiazole (TD3) and 1,2,5-selenadiazole (SD).

Coordinate	MP2					SCF				
	OD	OD3	TD	TD3	SD	OD	OD3	TD	TD3	SD
q_1, q_5	0.806	–	0.943	–	0.913	0.627	–	0.867	–	0.797
q_2, q_4	1.066	0.975	0.991	0.969	1.052	0.703	0.714	0.665	0.689	0.590
q_3	0.856	–	0.825	–	0.838	0.877	–	0.867	–	0.921
q_6, q_7	0.876	0.876	0.879	0.867	0.857	0.834	0.831	0.835	0.826	0.819
q_8, q_9	0.968	0.986	0.971	0.935	0.975	0.804	0.799	0.834	0.835	0.837
q_{10}, q_{11}	0.908	0.942	0.932	0.908	0.934	0.770	0.813	0.778	0.759	0.831
q_{12}, q_{13}	1.001	1.007	0.973	0.987	0.903	0.732	0.696	0.732	0.704	0.657
q_{14}, q_{15}	0.948	0.969	1.001	0.955	0.888	0.804	0.789	0.827	0.832	0.724

Table 12. Scale force fields.[a]

		MP2			SCF		
i	j	OD	TD	SD	OD	TD	SD
1	1	3.837	4.044	3.081	4.026	4.095	3.048
1	2	0.356	0.375	0.364	0.532	0.609	0.334
1	3	-0.176	-0.192	-0.193	-0.353	-0.416	-0.260
1	4	0.252	0.346	0.310	0.409	0.516	0.300
1	5	0.582	0.045	0.027	0.328	-0.245	-0.094
1	6	-0.035	-0.013	-0.013	-0.035	-0.024	-0.025
1	7	-0.064	-0.057	-0.055	-0.044	-0.046	-0.044
1	8	-0.067	-0.123	-0.113	-0.077	-0.095	-0.162
1	9	-0.600	-0.642	-0.567	-0.629	-0.590	-0.498
1	10	-0.003	-0.007	0.009	-0.001	-0.005	0.000
1	11	-0.022	0.002	-0.001	-0.035	-0.007	-0.006
2	2	8.544	7.460	8.002	8.325	7.364	7.157
2	3	0.808	0.773	0.894	0.719	0.802	0.689
2	4	-0.339	-0.179	-0.250	-0.339	-0.312	-0.171
2	5	0.252	0.346	0.310	0.409	0.516	0.300
2	6	0.064	0.143	0.178	0.095	0.179	0.194
2	7	0.005	0.009	0.010	0.011	0.016	0.017
2	8	-0.646	-0.699	-0.691	-0.494	-0.500	-0.419
2	9	0.351	0.167	0.136	0.281	0.134	0.090
2	10	0.188	0.265	0.284	0.155	0.214	0.222
2	11	0.026	-0.007	-0.008	0.013	-0.013	-0.015
3	3	5.897	5.515	5.182	5.825	5.488	5.049
3	6	0.025	0.031	0.033	0.037	0.045	0.050
3	8	0.527	0.501	0.411	0.529	0.521	0.382
3	9	0.000	0.000	0.000	0.000	0.000	0.000
3	10	-0.090	-0.095	-0.105	-0.071	-0.081	-0.099
4	8	-0.646	-0.699	-0.691	-0.494	-0.500	-0.419
4	9	-0.351	-0.167	-0.136	-0.281	-0.134	-0.090
5	8	-0.067	-0.123	-0.113	-0.077	-0.095	-0.162
5	9	0.600	0.642	0.567	0.629	0.590	0.498
6	6	5.435	5.304	5.084	5.439	5.309	5.088
6	7	0.003	0.005	0.005	0.007	0.010	0.012
6	8	-0.040	-0.040	-0.047	-0.036	-0.039	-0.044
6	9	-0.098	-0.099	-0.104	-0.088	-0.097	-0.099
6	10	0.014	-0.006	-0.009	0.009	-0.008	-0.010
6	11	-0.002	-0.003	-0.002	-0.005	-0.007	-0.008
7	8	-0.040	-0.040	-0.047	-0.036	-0.039	-0.044
7	9	0.098	0.099	0.104	0.088	0.097	0.099
8	8	2.163	1.967	1.812	2.032	1.891	1.803
8	9	0.000	0.000	0.000	0.000	0.000	0.000
8	10	-0.092	-0.081	-0.080	-0.080	-0.071	-0.074
8	11	-0.092	-0.081	-0.080	-0.080	-0.071	-0.074
9	9	1.840	1.589	1.511	1.771	1.564	1.462
9	10	-0.015	-0.001	0.005	-0.015	0.000	0.008
9	11	0.015	0.001	-0.005	0.015	0.000	-0.008
10	10	0.431	0.484	0.497	0.418	0.462	0.498
10	11	-0.005	-0.004	-0.004	-0.004	-0.004	-0.001
12	12	0.253	0.283	0.283	0.239	0.273	0.271
12	13	0.008	0.008	0.009	0.007	0.009	0.007
12	14	-0.005	-0.042	-0.061	-0.033	-0.073	-0.091
12	15	-0.064	-0.077	-0.079	-0.065	-0.073	-0.077
13	14	-0.005	-0.042	-0.061	-0.033	-0.073	-0.091
13	15	0.064	0.077	0.079	0.065	0.073	0.077
14	14	0.284	0.270	0.240	0.334	0.309	0.267
14	15	0.000	0.000	0.000	0.000	0.000	0.000
15	15	0.363	0.427	0.364	0.320	0.363	0.288

[a] Force constants in mdyn Å^{-1}.

the C–H bond distances are predicted to be too short by the SCF geometry and almost exactly right by the MP2 geometry; this is reflected in a smaller SCF SFs corresponding to the C–H bond than the MP2 SFs.

Conclusion

The vibrational spectra were calculated for **OD**, **TD** and **SD** using the 6-31G** basis set at the SCF and MP2 levels of theory. Compared to the experimental geometries, the geometries predicted by the 6-31G** basis set, at both SCF and MP2 levels, were significantly better than the geometries predicted by other basis sets or semi-empirical methods. The calculated frequencies and IR absorption intensities obtained by the scaled MP2 force fields are only slightly better than those calculated by the scaled SCF force fields. The calculated frequencies, by both force fields, confirmed the experimental assignment for **OD** and **TD** and indicated some possible misassignments for **SD**. The poorer correlation between the SFs obtained for **OD**, **TD** and **SD** than those SFs obtained for **OD3** and **TD3** indicates that good predicted geometries are required to obtain a good correlation between the SFs.

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