

**Supporting Information for**  
**Modifying Vibrational Energy Flow in Aromatic Molecules: Effects of Ortho Substitution**

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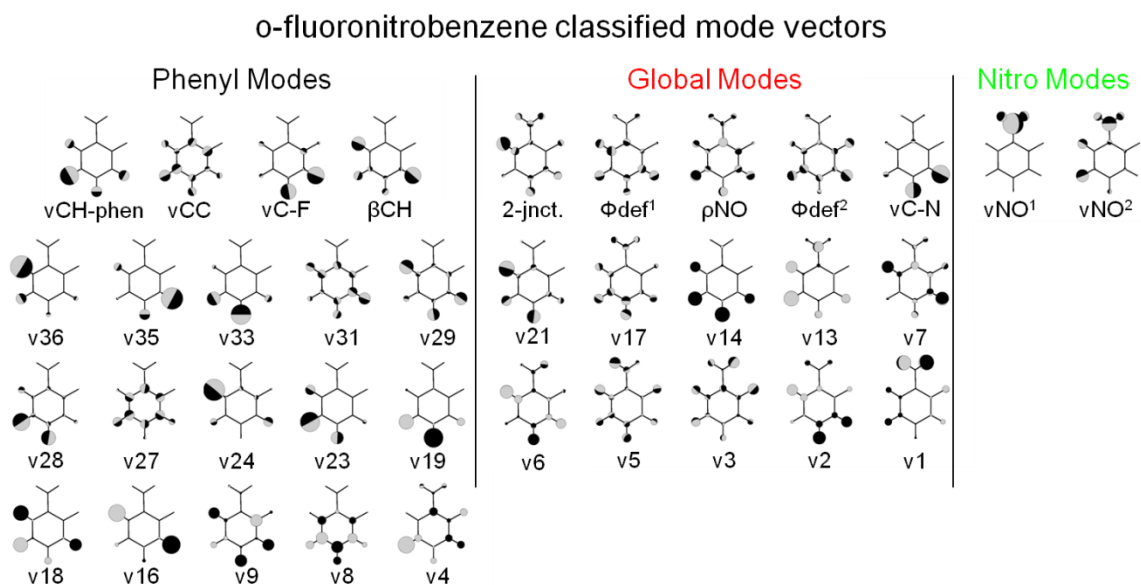
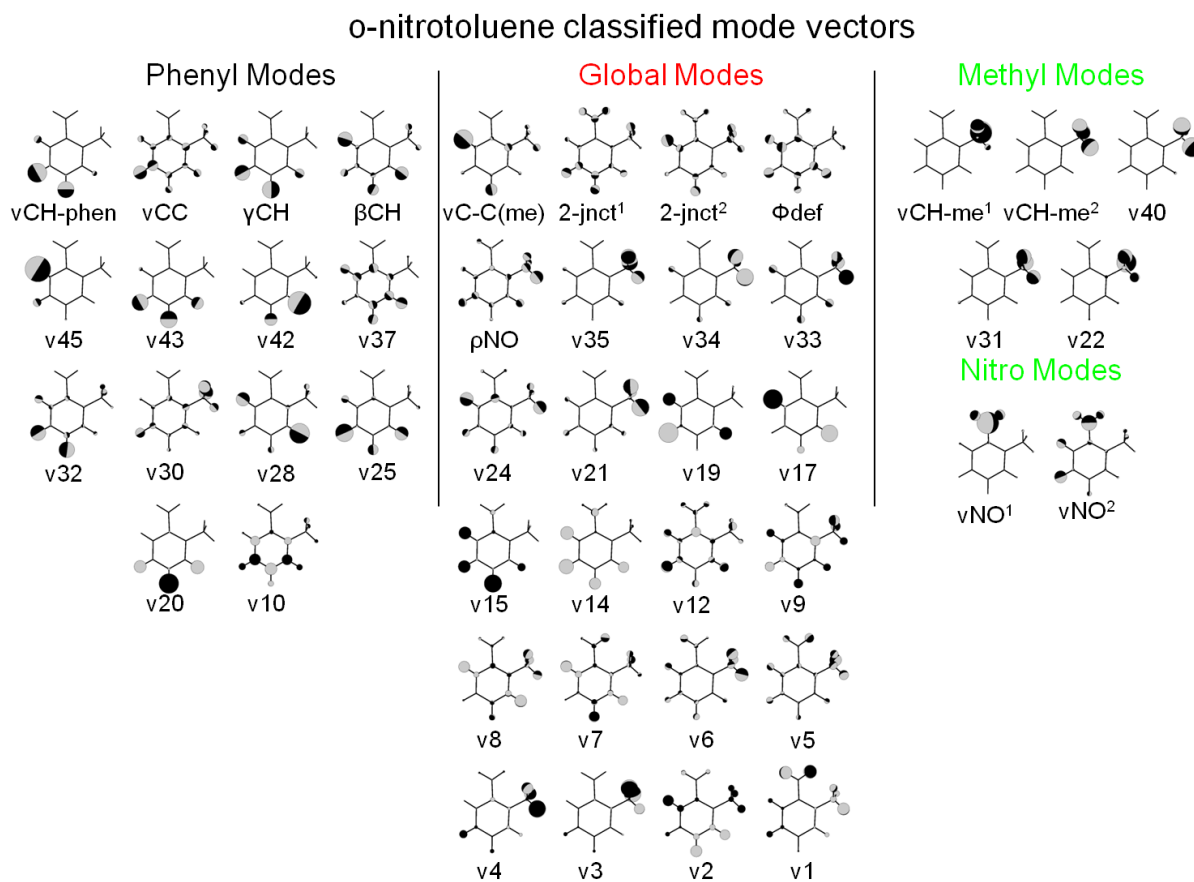
**Normal Modes and Mode Classification**

We computed the normal modes using MP2 perturbation theory with 6-31G as the basis, using the Gaussian 09 computational package, and compared the results with previous assignments<sup>S1-S4</sup>. The results are shown in table S1, where the Raman-active transitions are assigned and the transitions too weak to observe via transient anti-Stokes spectroscopy are numbered. The computed Raman intensities were all normalized and are included in table S1. Figure S1 shows each of the normal modes, which were divided into three sets, substituent modes, phenyl modes or global modes. The mode classifications were made based on their Potential Energy Distributions (PED) computed using the VEDA-4 software package.<sup>S5</sup> The software carries out Vibrational Energy Distribution Analysis (VEDA) to determine PED's for the computed normal mode vectors. A wonderful review of this method can be found online.<sup>S6</sup> As a summary, the VEDA method transforms the Cartesian normal mode vectors into a new basis of internal 2,3 and 4 body coordinates. The contribution of each internal coordinate basis to the total potential energy of each mode is decomposed to give their PED distribution. Modes with 80% or more of their potential energy contributed by phenyl or substituent localized were

coordinates classified as phenyl or substituent. If there was less than 80% in either phenyl or substituent localized coordinates or if there was 80% or more in global coordinates the mode was classified as global.

#### Literature cited

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- (S4) Arjunan, V.; Govindaraja, S. T.; Sakiladevi, S.; Kalaivani, M.; Mohan, S., Spectroscopic, Electronic Structure and Natural Bond Orbital Analysis of O-Fluoronitrobenzene and P-Fluoronitrobenzene: A Comparative Study. *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy* **2011**, 84 (1), 196-209.
- (S5) Jamroz, M. H., Vibrational Energy Distribution Analysis VEDA 4, *Warsaw* **2004-2010**
- (S6) Jamroz, M. H., Vibrational energy distribution analysis (VEDA): Scopes and limitations, *Spectrochim Acta A* **2013**, 114, 220-230.



**Figure S1.** Classified normal modes of o-nitrotoluene and o-fluoronitrobenzene computed using MP2 perturbation theory with the 6-31G basis set. Relative sphere sizes indicate relative displacement while the grey and white filling represents the displacement direction.

o-nitrotoluene vibrational assignments

mode	MP2	Raman int.	experimental	PED(%)	classification	mode	MP2	Raman int.	experimental	PED(%)	classification
v45	3180	0.69		phenyl(100)	phenyl	v22	1050	0.01		phenyl(7) subs(93)	subs
vCH-phen (v44)	3162	1	3100	phenyl(100)	phenyl	v21	1012	0.02		phenyl(33) subs(62)	global
v43	3149	0.6		phenyl(100)	phenyl	v20	870	0		global(10) phenyl(90)	phenyl
v42	3135	0.43		phenyl(100)	phenyl	v19	867	0.01		global(38) phenyl(62)	global
vCH-me <sup>1</sup> (v41)	3121	0.44		subs(100)	subs	2-jnct <sup>1</sup> (v18)	842	0.02	881	global(22) phenyl(28) subs(50)	global
v40	3118	0.32		subs(100)	subs	v17	816	0.03		phenyl(14) global(86)	global
vCH-me <sup>2</sup> (v39)	3030	0.81	2950	subs(100)	subs	2-jnct <sup>2</sup> (v16)	784	0.1	811	global(21) subs(23) phenyl(56)	global
vNO <sup>1</sup> (v38)	1737	0.37	1532	subs(100)	subs	v15	752	0		subs(28) phenyl(31) global(41)	global
v37	1639	0.14		subs(5) phenyl(95)	phenyl	v14	704	0.02		phenyl(21) global(26) subs(53)	global
vCC (v36)	1610	0.22	1610	subs(1) phenyl(99)	phenyl	Φdef (v13)	665	0.03	689	global(8) subs(22) phenyl(68)	global
v35	1511	0.08		phenyl(23) subs(73)	global	v12	572	0.04	570	subs(2) phenyl(42) global(56)	global
v34	1504	0.07		global(1) phenyl(29) subs(66)	global	pNO (v11)	536	0.04	570	subs(5) global(33) phenyl(62)	global
v33	1501	0.08		global(5) subs(47) phenyl(48)	global	v10	468	0		global(3) subs(4) phenyl(93)	phenyl
v32	1462	0.02		subs(4) global(7) phenyl(89)	phenyl	v9	446	0.01		subs(3) phenyl(32) global(65)	global
v31	1435	0.12		global(2) phenyl(13) subs(84)	subs	v8	411	0		subs(10) phenyl(39) global(51)	global
v30	1429	0.04		global(2) subs(11) phenyl(87)	phenyl	v7	375	0.01		global(13) subs(27) phenyl(60)	global
vNO <sup>2</sup> (v29)	1379	0.65	1362	phenyl(5) global(14) subs(81)	subs	v6	346	0.01		global(17) phenyl(38) subs(45)	global
v28	1295	0.02		global(5) subs(11) phenyl(85)	phenyl	v5	245	0		global(4) phenyl(9) subs(87)	global
vC-C(me) (v27)	1224	0.08	1225	subs(1) global(38) phenyl(61)	global	v4	219	0.02		subs(8) phenyl(35) global(57)	global
γCH (v26)	1187	0.04	1178	phenyl(100)	phenyl	v3	198	0.01		subs(4) phenyl(10) global(86)	global
v25	1166	0.04		subs(9) global(10) phenyl(81)	phenyl	v2	131	0.03		subs(6) phenyl(15) global(79)	global
v24	1098	0.02		subs(11) global(17) phenyl(62)	global	v1	63	0.02		subs(2) phenyl(4) global(94)	global
βCH (v23)	1063	0.12	1065	global(3) subs(7) phenyl(90)	phenyl						

o-fluoro-nitrobenzene vibrational assignments

mode	MP2	Raman int.	experimental	PED(%)	classification
v36	3149	1		phenyl(100)	phenyl
v35	3144	0.64		phenyl(100)	phenyl
vCH-phen (v34)	3135	0.63	3100	phenyl(100)	phenyl
v33	3122	0.41		phenyl(100)	phenyl
vNO <sup>1</sup> (v32)	1733	0.45	1545	subs(100)	subs
v31	1621	0.11		subs(1) phenyl(99)	phenyl
vCC (v30)	1614	0.21	1614	global(3) phenyl(97)	phenyl
v29	1497	0.06		global(4) phenyl(96)	phenyl
v28	1457	0.02		global(4) phenyl(96)	phenyl
v27	1422	0.03		subs(1) global(2) phenyl(97)	phenyl
vNO <sup>2</sup> (v26)	1362	0.54	1366	global(4) phenyl (5) subs(81)	subs
vC-F (v25)	1270	0.07	1270	phenyl(100)	phenyl
v24	1247	0.04		subs(2) global(4) phenyl(94)	phenyl
v23	1170	0.04		subs(2) global(3) phenyl(95)	phenyl
vC-N (v22)	1145	0.05	1150	subs(7) global(16) phenyl(77)	global
v21	1090	0.01		subs(7) global(15) phenyl(78)	global
βCH (v20)	1033	0.12	1054	global(1) phenyl(99)	phenyl
v19	866	0		phenyl(100)	phenyl
v18	862	0.01		global(1) phenyl(99)	phenyl
v17	840	0.01		global(13) subs(31) phenyl(56)	global
v16	800	0.04		subs(5) phenyl(95)	phenyl
2-jnct. (v15)	790	0.11	839	global(9) subs(30) phenyl(61)	global
v14	744	0		global(22) phenyl(78)	global
v13	700	0.02		phenyl(28) global(72)	global
Φdef (v12)	650	0.02	686	global(11) subs(27) phenyl(62)	global
pNO (v11)	571	0.03	600	subs(2) global(43) ring(55)	global
βCCC (v10)	529	0.03	565	subs(6) global(15) phenyl(79)	global
v9	487	0.01		subs(5) global(9) phenyl(86)	phenyl
v8	454	0		global(4) phenyl(96)	phenyl
v7	423	0.01		subs(5) global(19) phenyl(76)	global
v6	371	0.01		subs(8) global(25) phenyl(67)	global
v5	338	0.01		subs(6) global(33) phenyl(62)	global
v4	233	0.03		subs(2) global(11) phenyl(87)	phenyl
v3	213	0		subs(5) phenyl(16) global(79)	global
v2	129	0.04		subs(4) phenyl(16) global(80)	global
v1	59	0.02		phenyl(5) global(95)	global

**Table S1** Vibrational frequencies and mode classifications of o-nitrotoluene and o-fluoronitrobenzene. The named modes are those that are visible in the experiment while others are only numbered. The included computed Raman intensities are normalized.