

Supporting Information for

Unidirectional Vibrational Energy Flow in Nitrobenzene

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Normal Modes and Mode Classification

To monitor vibrational energy in nitrobenzene, rather than analyzing the behavior of individual modes it was more intuitive to classify them as having global-, phenyl- or substituent-localized motion and track the energy in these types of modes. Examples of these classifications are shown in figure S1. We classified the normal modes by comparing the relative amounts of atomic displacement involved in each. It should be noted that normal modes can also be classified using the potential energy distribution percentage (PED%) which describes each mode as a linear combination of internal, rather than cartesian, coordinates.^{S1,S2} In the PED method one can quantify how much an internal coordinate, for example the O-N-O angle in nitrobenzene, contributes to the total potential energy of a given normal mode. However, we found our simplified classification method to be sufficient. We computed the normal modes using MP2 perturbation theory with 6-31G as the basis using the Gaussian 09 computational package and compared these with previous work aimed at assigning them.^{S3,S4} These results are shown in

table S1 where the Raman-visible modes are assigned and the invisible modes are numbered. Figure S2 illustrates each of the normal modes. Modes with displacement primarily restricted to the substituent (substituent mode), the phenyl ring (phenyl mode) or delocalized throughout the molecule (global mode) are also appropriately indicated.

References

- (S1) Bienko, D. C.; Michalska, D.; Roszak, S.; Wojciechowski, W.; Nowak, M. J.; Lapinski, L., *J Phys Chem A* **1997**, *101* (42), 7834-7841.
- (S2) Nowak, M. J.; Lapinski, L.; Bienko, D. C.; Michalska, D., *Spectrochim Acta A* **1997**, *53* (6), 855-865.
- (S3) Nyquist, R. A., *Appl Spectrosc* **1990**, *44* (4), 594-599.
- (S4) El'kin, P.; Pulin, V.; Kosterina, E., *J Appl Spectrosc* **2005**, *72* (4), 483-487.

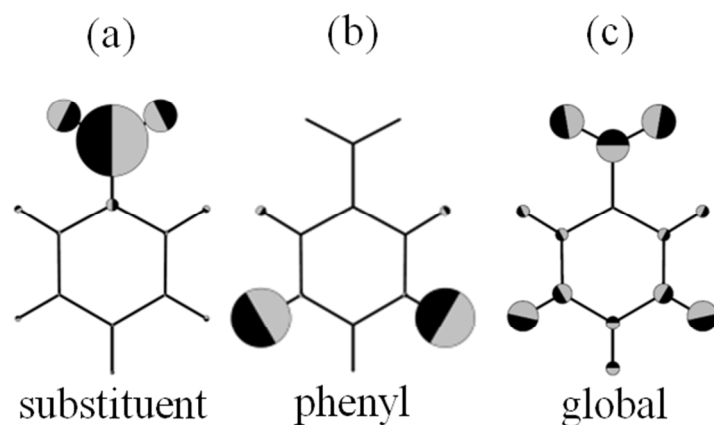


Figure S1. Classification of normal modes. (a) Modes with displacement exclusively on the substituent are substituent modes. (b) Modes with displacement exclusively on the ring are phenyl modes. (c) Modes with displacement on both substituent and ring are global modes.

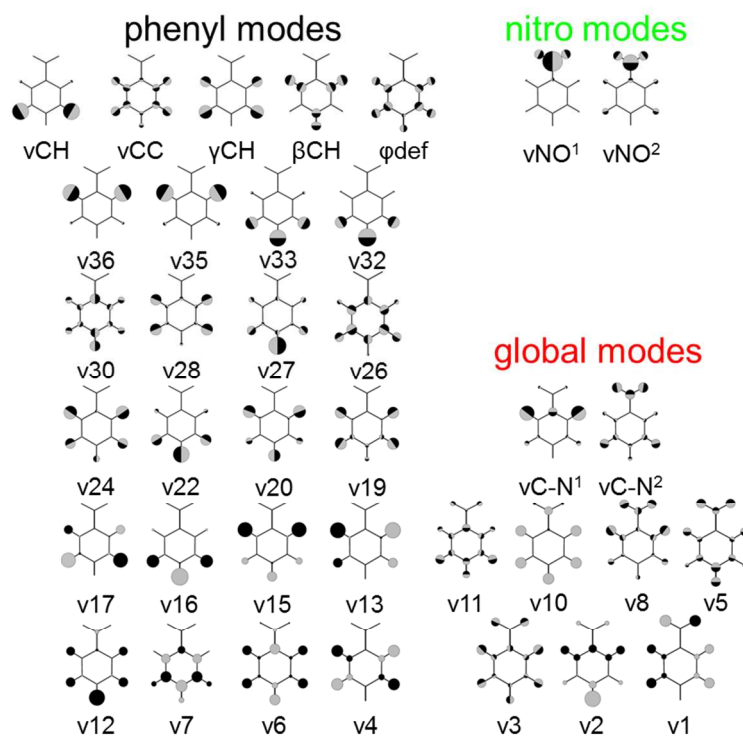


Figure S2. Normal modes of nitrobenzene computed using MP2 perturbation theory, and their division into three categories, phenyl modes, nitro modes and global modes.

mode	classification	MP2	experimental
v36	phenyl	3091.83	
v35	phenyl	3091.56	
vCH-phen (v34)	phenyl	3065.83	3074
v33	phenyl	3057.55	
v32	phenyl	3046.40	
vNO ¹ (v31)	subs.	1693.83	1512
v30	phenyl	1582.07	
vCC (v29)	phenyl	1570.99	1590
v28	phenyl	1452.43	
v27	phenyl	1428.43	
v26	phenyl	1397.14	
vNO ² (v25)	subs.	1338.62	1335
v24	phenyl	1277.93	
γ CH (v23)	phenyl	1156.37	1154
v22	phenyl	1147.33	
vC-N ¹ (v21)	global	1087.28	1098
v20	phenyl	1061.59	
v19	phenyl	1002.52	
β CH (v18)	phenyl	966.64	1000
v17	phenyl	857.94	
v16	phenyl	852.12	
v15	phenyl	834.53	
vC-N ² (v14)	global	806.67	845
v13	phenyl	780.62	
v12	phenyl	717.83	
v11	global	656.14	
v10	global	651.36	
ϕ def (v9)	phenyl	589.42	605
v8	global	497.41	
v7	phenyl	470.21	
v6	phenyl	395.91	
v5	global	382.22	
v4	phenyl	375.05	
v3	global	250.62	
v2	global	159.75	
v1	global	31.04	

Table S1. Normal mode calculation results in cm⁻¹. Experimental frequency values are shown for modes visible in our experiment are assigned (and numbered). Those not seen in experiment are only numbered.