Structure Dependent Energy Transport: Relaxation-Assisted 2DIR Measurements and Theoretical Studies

Valeriy M. Kasyanenko,[#] Sarah L. Tesar,[#] Grigory I. Rubtsov,[&] Alexander L. Burin,[#] Igor V. Rubtsov[#]

[#] Department of Chemistry, Tulane University, New Orleans, LA 70118
[&] Institute for Nuclear Research of the Russian Academy of Sciences, Moscow 117312, Russian Federation
E-mail: irubtsov@tulane.edu

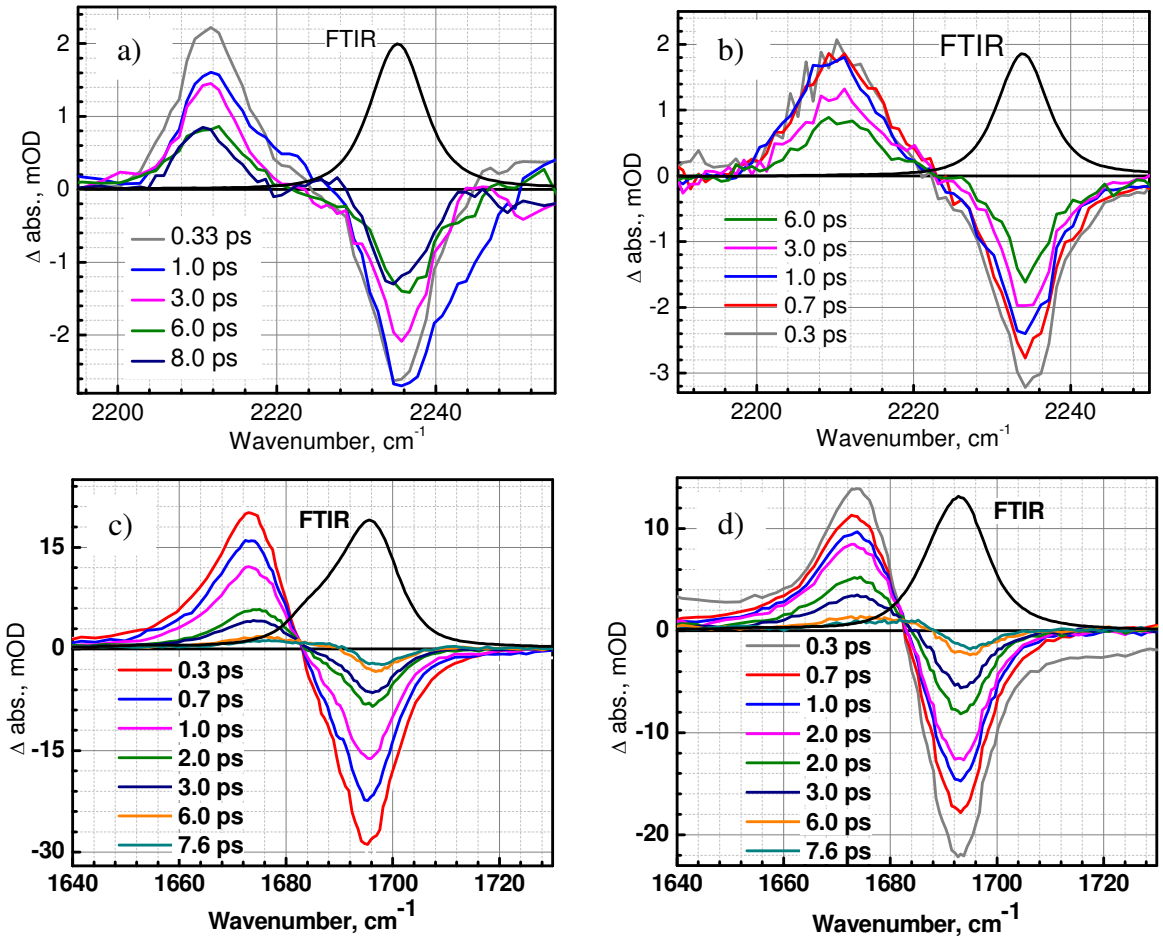


Figure S1. Diagonal pump-probe spectra for meta and para-AcPhCN measured at different delay times (see inset) along with the linear absorption spectrum for a) meta CN, b) para CN, c) meta CO, and d) para CO modes.

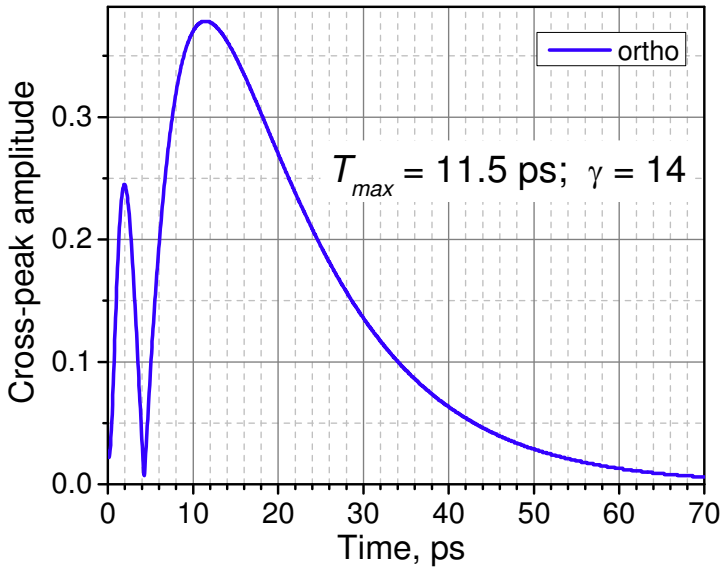


Figure S2. Modeled CN/CO cross-peak amplitudes as a function of the waiting time, *T*, for o-AcPhCN. In this calculation the mode #1 was taken into account. The following values were used for the modeling Γ = 10 cm^{-1}, σ = 23 cm^{-1}.

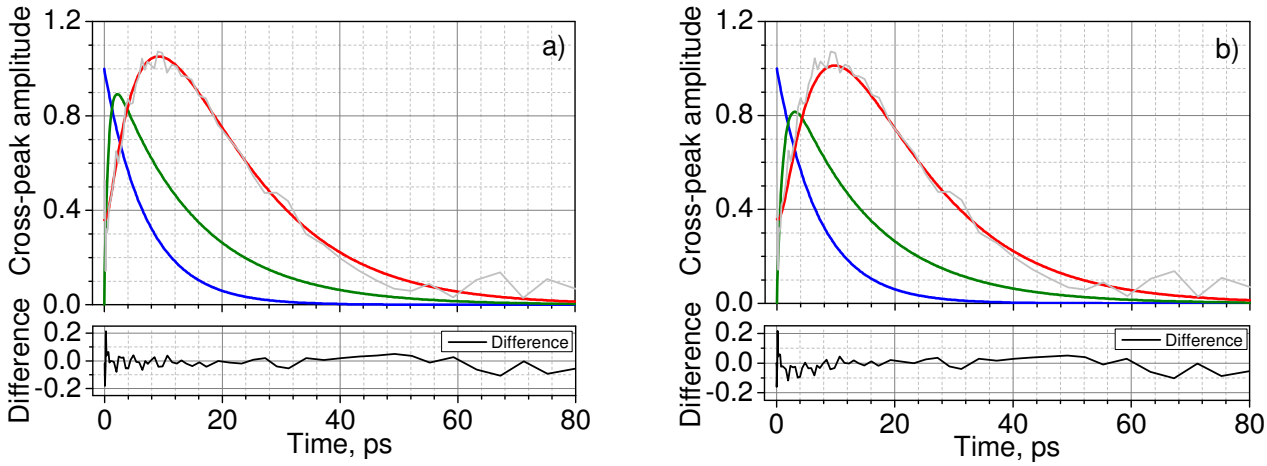
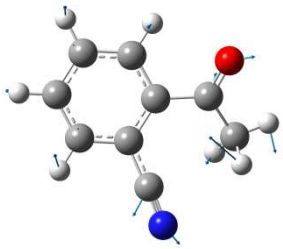
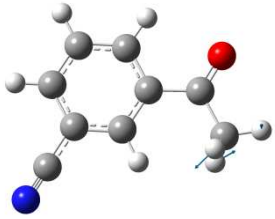
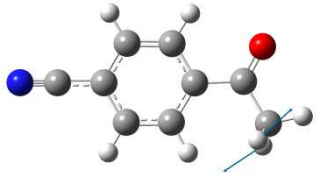
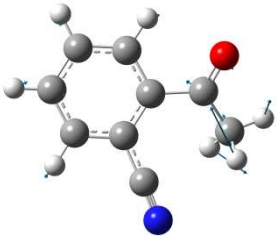
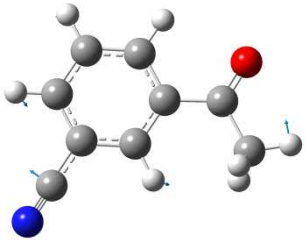
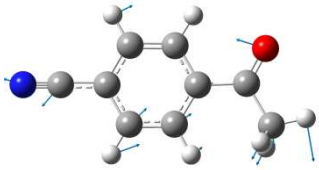
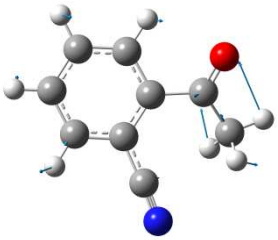
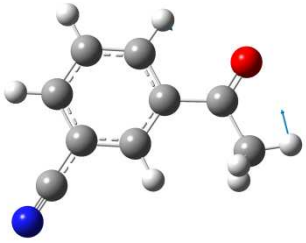
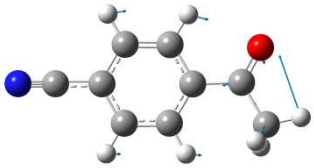
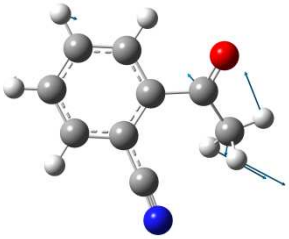
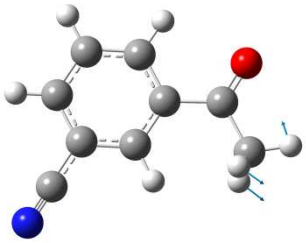
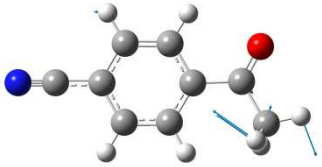
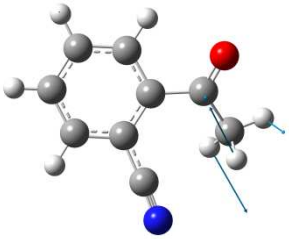
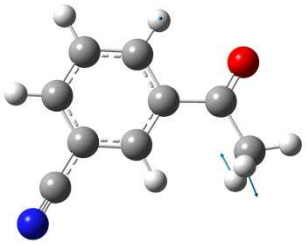
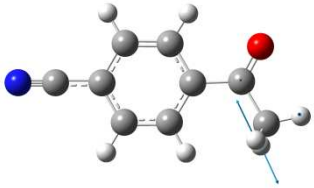


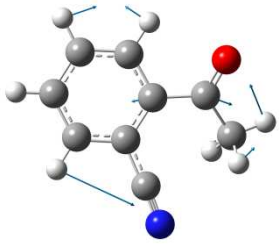
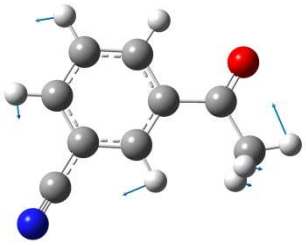
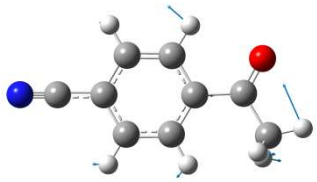
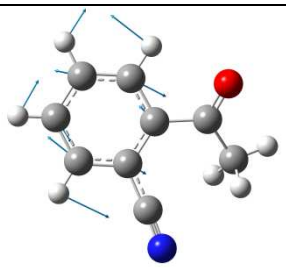
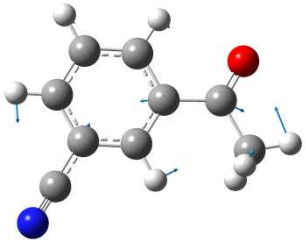
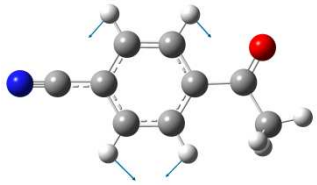
Figure S3. Two convolution fits (red) for the same data set (m-AcPhCN, grey) are presented to illustrate the selection of the error bars for the obtained parameters (Fig. 6). Panel a) shows the best fit results to the data using the two-exponential function with a rise time of 0.7 ps and a decay time of 14 ps. Panel b) shows the best fit when the rise time of the two-exponential function was fixed at 1.1 ps while the decay time was varied and found to be at 14 ps as well. The difference between the experiment and fit (black line) shows a clear wavy tendency in panel b).

Table S1. Anharmonic vibrational frequencies and anharmonicity constants, $\Delta_{CO/j}$, for o-, m-, and p-AcPhCN.

Mode number, *j*	o-AcPhCN		m-AcPhCN		p-AcPhCN	
	ω_{anharm}, cm^{-1}	$\Delta_{CO/j}$, cm^{-1}	ω_{anharm}, cm^{-1}	$\Delta_{CO/j}$, cm^{-1}	ω_{anharm}, cm^{-1}	$\Delta_{CO/j}$, cm^{-1}
1	29.50	0.648	44.4	0.273	52.4	0.117
2	107.4	-0.101	120.5	-0.083	76.9	-0.122
3	147.4	0.463	126.7	-0.113	131.1	-0.056
4	172.4	-0.173	147.2	-2.33	158.4	-2.455
5	158.3	-0.344	165.0	-0.167	205.8	-0.285
6	235.3	0.23	232.5	-0.263	227.6	-0.548
7	332.6	0.318	365.0	-0.333	328.8	-0.224
8	384.4	-0.165	385.2	-0.205	400.8	-0.317
9	394.1	0.052	418.1	-0.529	399.1	-0.299
10	450.2	-1.517	421.3	0.336	435.7	0.048
11	495.6	-0.518	478.9	-1.064	538.1	-2.214
12	565.0	-0.265	541.8	-0.965	545.9	-0.655
13	590.3	-1.68	568.7	-1.18	571.4	-0.447
14	598.2	-1.35	608.0	-3.006	597.5	-1.248
15	614.0	-0.419	628.0	-0.791	642.4	-1.452
16	690.7	-0.295	693.4	-0.362	649.8	-0.087
17	744.9	-0.195	695.9	-0.09	732.0	-0.204
18	770.8	-0.151	812.8	0.046	782.6	-0.486
19	799.2	-0.07	859.8	0.543	834.4	-0.075
20	890.3	0.035	906.9	-0.068	853.6	-0.047
21	953.6	-4.147	942.1	-4.252	942.6	-4.668
22	971.2	0.184	944.9	0.045	965.3	-0.089
23	999.8	0.068	998.9	-0.167	990.2	-0.01
24	1020.6	-2.1	999.4	-0.058	1017.7	-0.197
25	1041.9	-0.503	1026.2	-2.319	1026.5	-2.374
26	1069.4	-0.808	1084.5	-1.183	1069.3	-1.441
27	1115.7	0.39	1091.7	-0.349	1119.8	-0.299
28	1177.8	-0.079	1179.7	-0.097	1185.3	-0.21
29	1191.0	-0.204	1184.9	-1.087	1198.3	-0.118
30	1228.2	-0.819	1253.2	-1.579	1238.4	-0.912
31	1267.5	-0.659	1291.9	0.105	1295.4	-0.653
32	1299.3	-0.504	1315.7	-0.393	1308.8	-0.658
33	1361.7	-0.601	1357.0	-0.502	1356.8	-0.532
34	1421.5	-0.684	1413.2	-1.017	1407.0	-1.827
35	1437.0	0.279	1440.8	-0.958	1443.8	-1.005
36	1445.5	-0.465	1440.4	-0.537	1442.2	-0.546
37	1475.8	0.633	1479.9	-0.169	1495.6	-0.359
38	1539.8	-0.597	1554.7	-1.04	1558.6	-1.309
39	1591.8	-1.016	1601.6	-0.368	1605.1	-0.611
40 (C=O)	1714.3	-19.52	1721.6	-19.20	1719.6	-19.09
41 (C≡N)	2296.1	-0.047	2300.5	0.069	2300.8	-0.036
42	2948.7	-1.691	2955.7	-1.251	2955.9	-1.056
43	2966.2	-1.417	2953.5	-1.377	2952.6	-1.376
44	2998.5	-0.389	3004.0	-0.38	3003.2	-0.41
45	3054.1	-0.055	3031.3	-0.008	3038.5	0.246
46	3033.9	-0.026	3069.9	0.216	3058.6	0.656
47	3096.5	-0.087	3052.9	0.239	3087.8	0.388
48	3069.8	-0.567	3078.8	-0.127	3077.7	0.332

Table S2. Normal mode displacement vectors for the selected modes for the three isomers of AcPhCN. The mode numbers are indicated in the table.

ortho	meta	para
 #10	 #4	 #4
 #13	 #13	 #11
 #14	 #14	 #15
 #21	 #21	 #21
 #24	 #25	 #25

 #30	 #26	 #26
 #39	 #30	 #34