Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

Jeppe Fock, Jakob Kryger Sørensen, Emanuel Lörtscher, Tom Vosch, Christian A. Martin, Heike Riel, Kristine Kilså, Thomas Bjørnholm, and Herre van der Zant

May 30, 2011

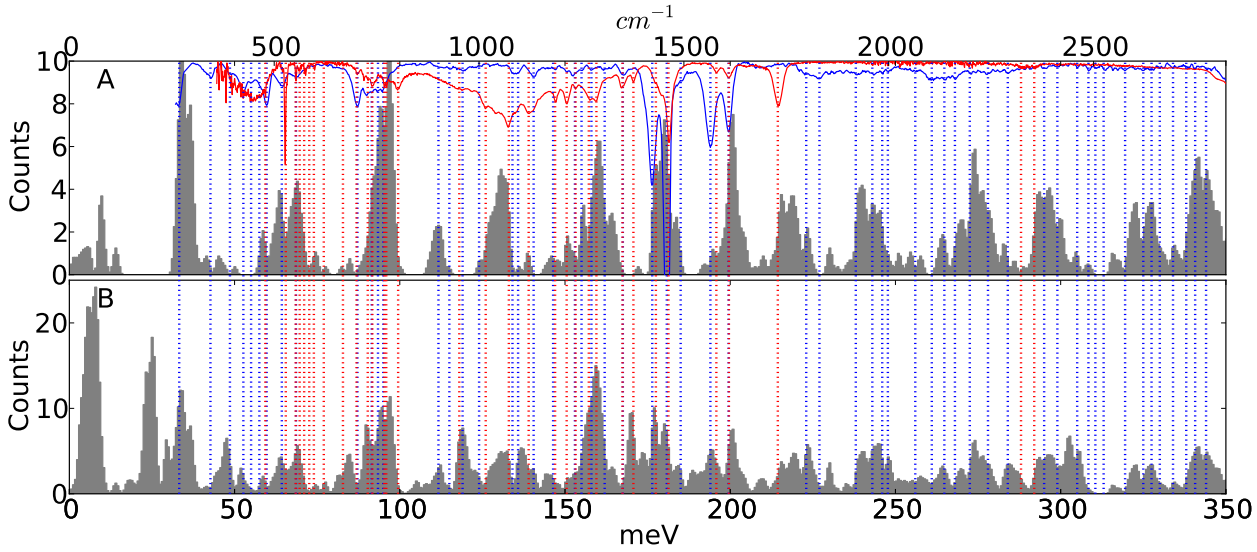

Figure S1 Histograms of peaks in $\frac{d^2I}{dV^2}$ at $V > 0$ from fluorene dumbbell junctions in the $10^{-4}G_0$ region. Only symmetric peaks/dips are included in the histograms. A) Histograms constructed from a single breaking trace B) Histograms constructed using peak positions from four different opening traces (including the histogram in "A"). Raman (blue) and IR (red) spectra are overlaid and peak positions are indicated with vertical dashed lines.

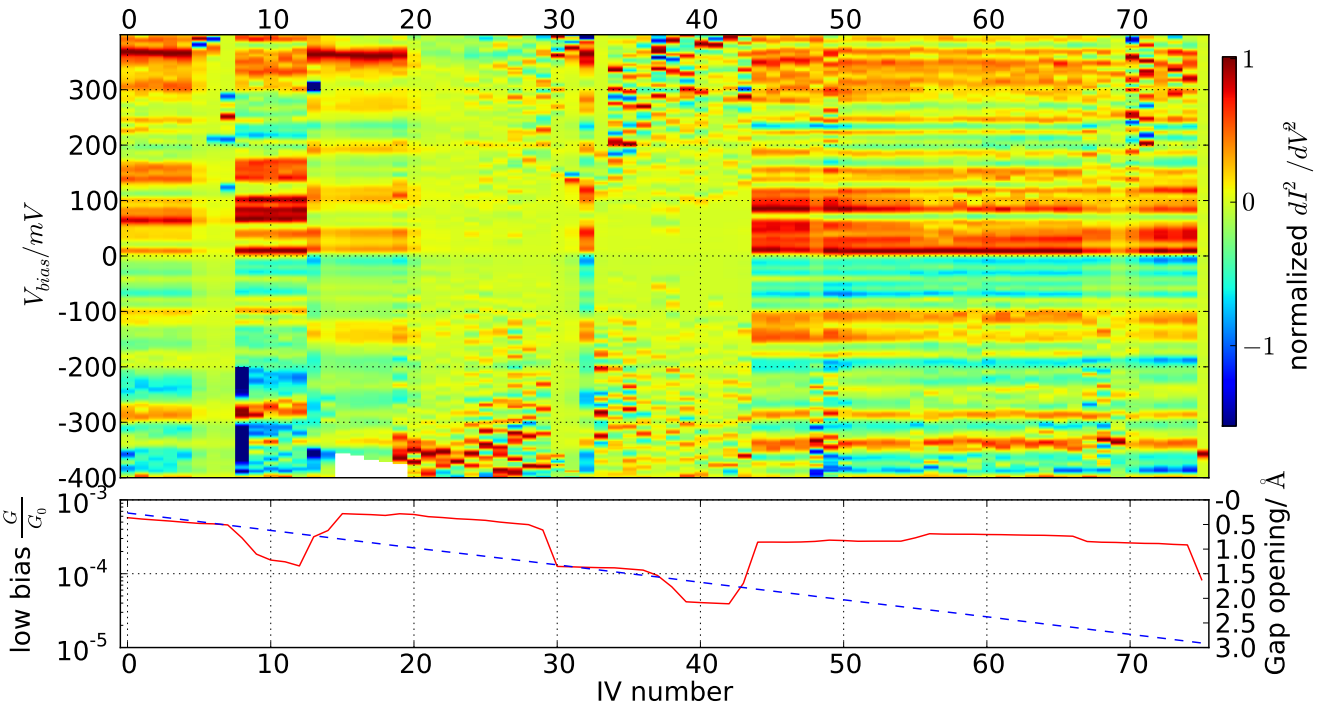

Figure S2 Evolution of an IETS opening trace. x-axis is the IV number. Top) $\frac{d^2I}{dV^2}$ is normalized to the maximum value for each $I(V)$, see colourbar for the scale. Bottom) Red curve (left y-axis) is low-bias conductance, blue curve (right y-axis) is the approximate value for the relative opening of the junction.

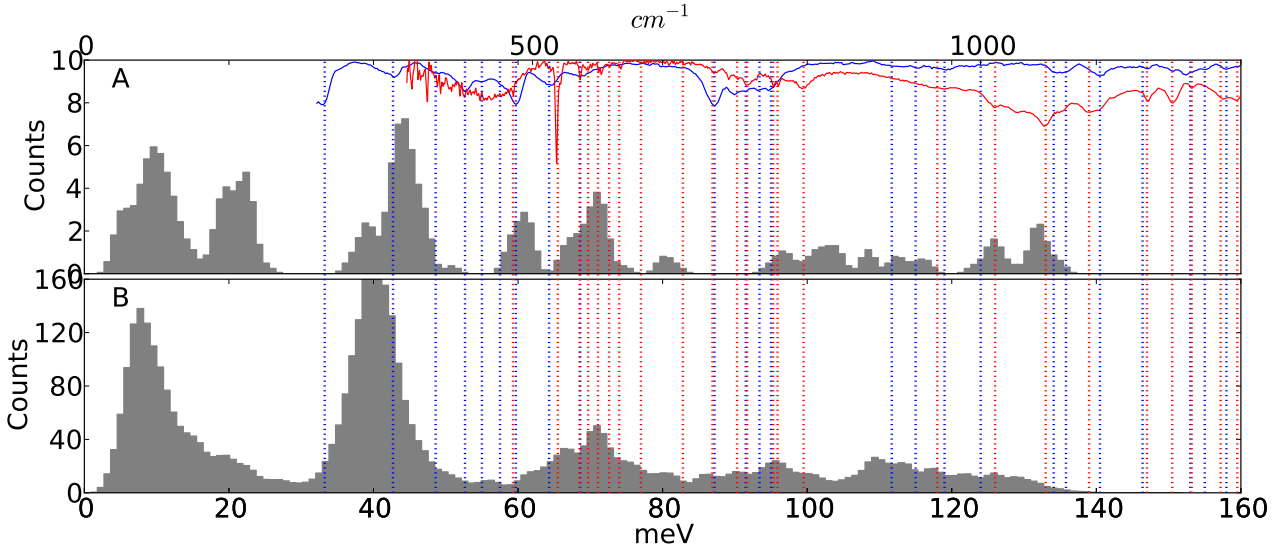

Figure S3 Histograms of peaks in $\frac{d^2I}{dV^2}$ at $V > 0$ from fluorene dumbbell junctions in the $10^{-2}G_0$ region. Only symmetric peaks/dips are included in the histograms. A) Histograms constructed using peak positions from Fig 6. B) Histograms constructed using peak positions from four different opening traces (including the histogram in "A"). Raman (blue) and IR (red) spectra are overlaid and peak positions are indicated with vertical dashed lines.

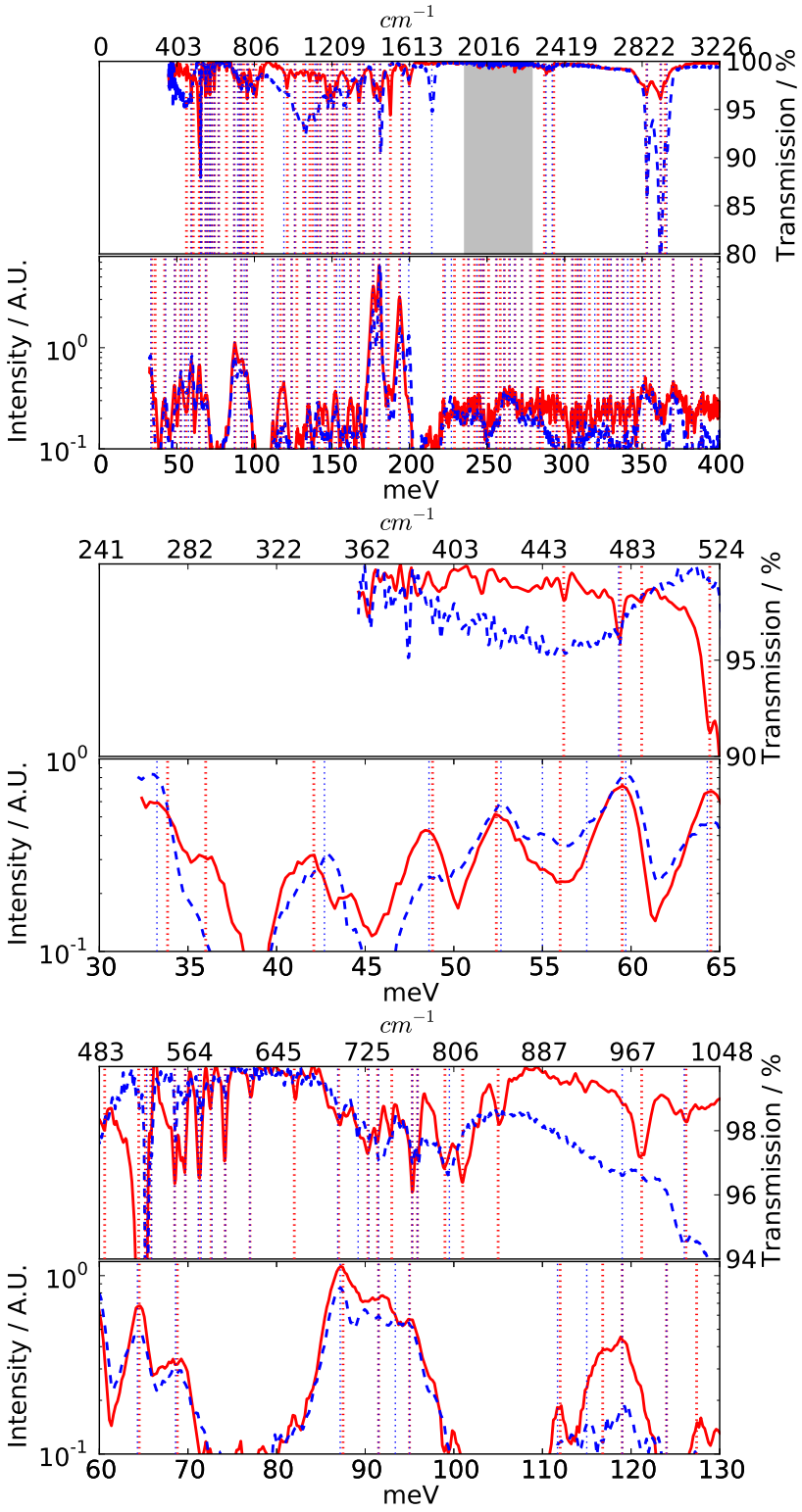

Figure S4 Top) IR and Raman for fluorene dumbbell (blue dashed line) and tadpole molecule (red solid line). The gray box indicates the self-absorbency of the diamond crystal used in the ATR-FTIR measurement. Left y-axis and bottom curves are Raman signals. Right y-axis and top curves are IR transmittance (baseline corrected). Bottom) and Centre) Zoom in of IR and Raman spectra

C60 table		**Fluorene dumbbell**		**Tadpole**		**C60**		**Toluene**	
Mode	Energy	Raman	IR	Raman	IR	Raman	IR	Raman	IR
-	-	-	-	-	-	-	-	**26.8**	-
Hg(1)	33.7	33.2	-	33.9	-	33.7	-	-	-
-	-	-	-	**36.0**	-	-	-	-	-
T3u(1)	42.5	42.7	-	42.1	-	-	-	42.7	42.8
Gu(1)	43.8	-	-	-	-	-	-	-	-
Hu(1)	50.0	48.6	-	48.8	-	-	-	-	-
Hg(2)	53.7	52.7	-	52.4	-	53.7	-	-	-
-	-	55.0	-	56.0	56.2	-	-	-	-
-	-	57.5	-	-	59.4	-	-	-	57.5
Gg(1)	60.1	59.7	59.3	59.5	60.6	-	-	57.7	-
Ag(1)	**61.5**	-	-	-	-	**61.5**	-	-	-
-	-	-	-	-	**64.4**	-	-	-	-
T1u(1)	65.2	64.3	65.3	64.5	65.2	-	65.2	64.6	64.6
Hu(2)	66.2	-	65.9	-	65.8	-	-	-	66.6
T3g(1)	68.6	68.6	68.5	68.8	68.5	-	-	-	-
Gg(2)	70.3	-	69.7	-	69.7	-	-	-	-
T1g(1)	70.4	-	-	-	-	-	-	-	-
T1u(2)	71.3	-	71.2	-	71.3	-	71.3	-	-
-	-	-	**71.5**	-	-	-	-	-	-
-	-	-	72.7	-	72.6	-	-	-	-
-	-	-	74.2	-	74.2	-	-	-	-
-	-	-	77.0	-	77.0	-	-	77.2	77.2
Hu(3)	**82.8**	-	-	-	**82.1**	-	-	-	-
Hg(3)	87.9	87.2	86.9	87.5	87.0	87.9	-	-	-
-	-	-	89.2	-	-	-	-	-	86.2
-	-	-	90.4	-	90.3	-	-	-	-
Gg(3)	91.3	91.5	91.5	91.5	91.4	-	-	90.5	90.4
Hu(4)	92.1	-	-	-	-	-	-	-	-
T3u(2)	93.4	93.4	-	-	93.0	-	-	-	-
T3g(2)	93.7	-	-	-	-	-	-	-	-
Gu(2)	94.7	95.0	-	95.0	-	-	-	-	-
-	-	-	95.3	-	95.3	-	-	-	-
Hg(4)	95.7	-	95.9	-	95.9	95.7	-	-	-
Gu(3)	96.2	-	-	-	-	-	-	97.5	97.3
T3g(3)	98.7	-	99.5	-	99.0	-	-	100.3	98.7
-	-	-	-	-	**101.0**	-	-	-	-
T1g(2)	**103.0**	-	-	-	-	-	-	**104.5**	-
-	-	-	-	-	105.0	-	-	-	104.4
-	-	111.7	-	112.0	-	-	-	111.1	111.0
-	-	115.0	-	116.8	-	-	-	-	115.2
-	-	-	-	-	-	-	-	-	**117.3**
Gu(4)	119.1	119.0	119.0	119.0	-	-	-	117.8	119.8
T3u(3)	**120.6**	-	-	-	**121.2**	-	-	-	-
Au	122.0	124.0	-	124.0	-	-	-	121.6	121.6
-	-	-	-	-	-	-	-	**123.2**	-
-	-	-	-	-	-	-	-	-	**124.2**
-	-	-	126.0	127.4	126.2	-	-	124.5	127.6
-	-	-	-	-	-	-	-	**127.7**	-

to be cont'd on next page

C60 table		**Fluorene dumbbell**		**Tadpole**		**C60**		**Toluene**	
Mode	Energy	Raman	IR	Raman	IR	Raman	IR	Raman	IR
-	-	-	-	-	131.7	-	-	-	129.1
Gg(4)	133.8	134.1	133.0	134.4	-	-	-	-	134.0
Hg(5)	136.3	135.8	-	135.4	135.7	136.3	-	-	137.0
-	-	-	139.0	-	137.5	-	-	-	-
-	-	-	**140.2**	-	-	-	-	-	-
-	-	140.5	-	141.5	140.5	-	-	143.2	143.2
-	-	-	142.3	-	142.6	-	-	-	-
T1u(3)	146.5	146.4	147.2	145.5	147.2	-	146.5	146.1	146.1
T3u(4)	149.4	-	150.5	-	149.9	-	-	149.8	149.9
Hu(5)	151.6	153.0	-	152.0	151.2	-	-	-	-
-	-	-	153.2	-	153.2	-	-	-	-
Hg(6)	155.2	155.0	-	157.0	-	155.2	-	154.2	154.9
-	-	-	157.2	-	-	-	-	-	156.2
T1g(3)	159.8	158.0	159.5	-	159.0	-	-	-	-
Gu(5)	162.3	162.0	-	162.0	161.5	-	-	-	-
Gg(5)	**162.4**	-	-	-	-	-	-	-	**162.5**
Hu(6)	**166.6**	-	-	-	-	-	-	**164.8**	-
T3g(4)	166.8	167.5	167.0	167.0	167.2	-	-	-	-
-	-	-	167.8	-	167.8	-	-	-	-
-	-	-	170.7	-	170.3	-	-	171.0	170.7
Gu(6)	176.3	176.4	-	-	-	-	-	-	175.4
Hg(7)	176.7	-	-	176.6	-	176.7	-	-	-
T1u(4)	177.2	-	177.5	-	177.0	-	177.2	178.0	-
-	-	-	-	-	-	-	-	-	**180.4**
Ag(2)	182.3	180.8	181.3	180.4	181.0	182.3	-	180.6	181.0
Gg(6)	183.7	185.0	-	-	-	-	-	184.9	185.0
-	-	-	-	186.3	-	-	-	-	188.0
-	-	-	-	-	**187.7**	-	-	-	-
T3u(5)	**189.1**	-	-	-	-	-	-	-	**189.7**
Hu(7)	194.3	194.0	-	193.6	-	-	-	-	194.0
Hg(8)	195.3	-	195.8	-	195.0	195.3	-	196.5	-
-	-	199.5	-	-	200.0	-	-	198.9	198.3
-	-	-	199.6	-	-	-	-	201.1	201.1
-	-	-	214.4	-	-	-	-	-	215.1
-	-	223.0	-	222.0	-	-	-	-	223.4
-	-	227.0	-	229.0	-	-	-	-	230.4
-	-	-	-	**235.0**	-	-	-	-	-
-	-	238.0	-	238.0	-	-	-	-	-
-	-	-	-	-	-	-	-	-	**240.8**
-	-	243.5	-	242.0	-	-	-	-	242.9
-	-	246.0	-	245.0	-	-	-	-	245.9
-	-	-	-	**247.0**	-	-	-	-	-
-	-	247.7	-	247.8	-	-	-	-	247.0
-	-	-	-	**251.0**	-	-	-	-	-
-	-	256.0	-	256.0	-	-	-	-	-
-	-	-	-	**258.5**	-	-	-	-	-
-	-	261.0	-	261.2	-	-	-	-	-
-	-	264.8	-	264.4	-	-	-	-	-

to be cont'd on next page

C60 table		**Fluorene dumbbell**		**Tadpole**		**C60**		**Toluene**	
Mode	Energy	Raman	IR	Raman	IR	Raman	IR	Raman	IR
-	-	268.0	-	268.0	-	-	-	-	268.3
-	-	272.5	-	272.5	-	-	-	-	-
-	-	278.0	-	278.0	-	-	-	-	280.6
-	-	-	-	**282.5**	-	-	-	-	-
-	-	284.0	-	284.0	287.0	-	-	-	-
-	-	-	288.0	285.8	-	-	-	-	-
-	-	-	292.0	292.5	-	-	-	-	-
-	-	295.0	-	295.0	293.0	-	-	-	-
-	-	-	-	**296.6**	-	-	-	-	-
-	-	299.0	-	300.0	-	-	-	-	299.2
-	-	305.0	-	305.0	-	-	-	-	-
-	-	-	-	**307.2**	-	-	-	-	-
-	-	308.4	-	309.0	-	-	-	-	-
-	-	310.5	-	310.5	-	-	-	-	-
-	-	313.0	-	316.0	-	-	-	-	-
-	-	319.5	-	321.6	-	-	-	-	320.7
-	-	-	-	-	-	-	-	-	**323.2**
-	-	325.0	-	325.5	-	-	-	-	-
-	-	327.5	-	328.0	-	-	-	-	326.3
-	-	330.0	-	329.6	-	-	-	-	-
-	-	334.0	-	334.0	-	-	-	-	-
-	-	338.0	-	337.4	-	-	-	339.2	339.2
-	-	**340.7**	-	-	-	-	-	-	-
-	-	344.0	-	343.0	-	-	-	-	-
-	-	-	-	**347.4**	-	-	-	-	-
-	-	350.8	-	351.6	353.0	-	-	350.5	-
-	-	-	353.2	-	-	-	-	-	354.8
-	-	356.0	-	356.0	-	-	-	355.8	356.2
-	-	361.0	-	361.0	362.0	-	-	362.0	362.4
-	-	-	362.0	-	-	-	-	-	363.3
-	-	-	366.0	-	365.0	-	-	-	366.0
-	-	370.0	-	370.0	-	-	-	369.8	369.6
-	-	-	-	-	-	-	-	**372.3**	-
-	-	-	-	-	-	-	-	**374.1**	-
-	-	-	-	-	-	-	-	-	**375.9**
-	-	-	-	-	-	-	-	**376.8**	-
-	-	-	-	-	-	-	-	-	**379.5**
-	-	-	-	-	-	-	-	-	**380.3**
-	-	-	-	-	-	-	-	-	**380.3**
-	-	382.0	-	382.0	-	-	-	378.9	383.1
-	-	388.0	-	388.0	-	-	-	-	385.6

Table S1 Energies in meV. IR and Raman peak positions for the fluorene dumbbell, tadpole molecule and toluene compared to modes for C_{60}. Unique peaks are highlighted in boldface. Due to noisy IR signal for the fluorene dumbbell molecule in the region between 70 and 125 meV not all peaks have necessarily been detected. Thus the IR peaks for the tadpole in this region may not be unique (see 4).

IETS	Raman	IR	Closets C_{60} mode
21.0	-	-	-
26.0	-	-	-
35.4	33.2	-	Hg(1) (33.7)
38.9	-	-	T3u(1) (42.5)
50.0	48.6	-	Hu(1) (50.0)
55.0	55.0	-	Hg(2) (53.7)
70.5	68.6	71.2	T1g(1) (70.4)
76.1	-	77.0	-
91.3	91.5	91.5	Gg(3) (91.3)
95.7	95.0	95.9	Hg(4) (95.7)
100.0	-	99.5	T3g(3) (98.7)
106.0	-	-	T1g(2) (103.0)
111.0	111.7	-	-
118.0	119.0	119.0	Gu(4) (119.1)
123.0	124.0	126.0	Au (122.0)
138.0	135.8	139.0	Hg(5) (136.3)
141.5	140.5	142.3	-
155.5	155.0	157.2	Hg(6) (155.2)
165.0	167.5	167.0	Hu(6) (166.6)
175.7	176.4	177.5	Gu(6) (176.3)
184.0	185.0	181.3	Gg(6) (183.7)
194.2	194.0	195.8	Hu(7) (194.3)
201.0	199.5	199.6	-
212.0	-	214.4	-
222.5	223.0	-	-
233.0	-	-	-
243.0	243.5	-	-
246.0	246.0	-	-
256.0	256.0	-	-
261.0	261.0	-	-
268.0	268.0	-	-
279.0	278.0	-	-
286.0	284.0	-	-
290.0	-	288.0	-
293.5	295.0	292.0	-
305.0	305.0	-	-
308.5	308.4	-	-
321.8	319.5	-	-
327.0	327.5	-	-
334.0	334.0	-	-
339.4	340.7	-	-
343.6	344.0	-	-
348.0	350.8	-	-

Table S2 Energies in meV. Column 1) Peak position of IETS histogram. 2) and 3) closest Raman and IR peak respectively. Column 4) The closest C_{60} mode (energy in parenthesis)

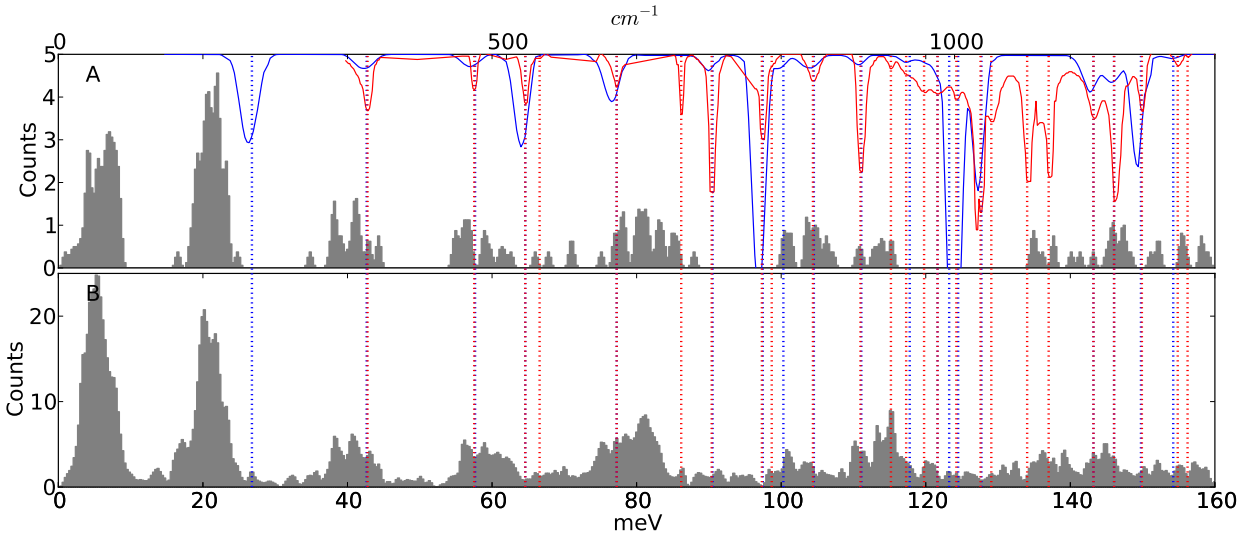

Figure S5 Histograms of peaks in $\frac{d^2I}{dV^2}$ at $V > 0$ from toluene junctions (reference). The junction conductances were approximately $10^{-4}G_0$. Only symmetric peaks/dips are included in the histograms. A) Histograms constructed using peak positions from a single opening trace. B) Histogram constructed using peak positions from 8 different opening traces (including the histogram in "A"). Raman (blue) and IR (red) spectra of toluene are overlaid and peak positions are indicated with vertical dashed lines.

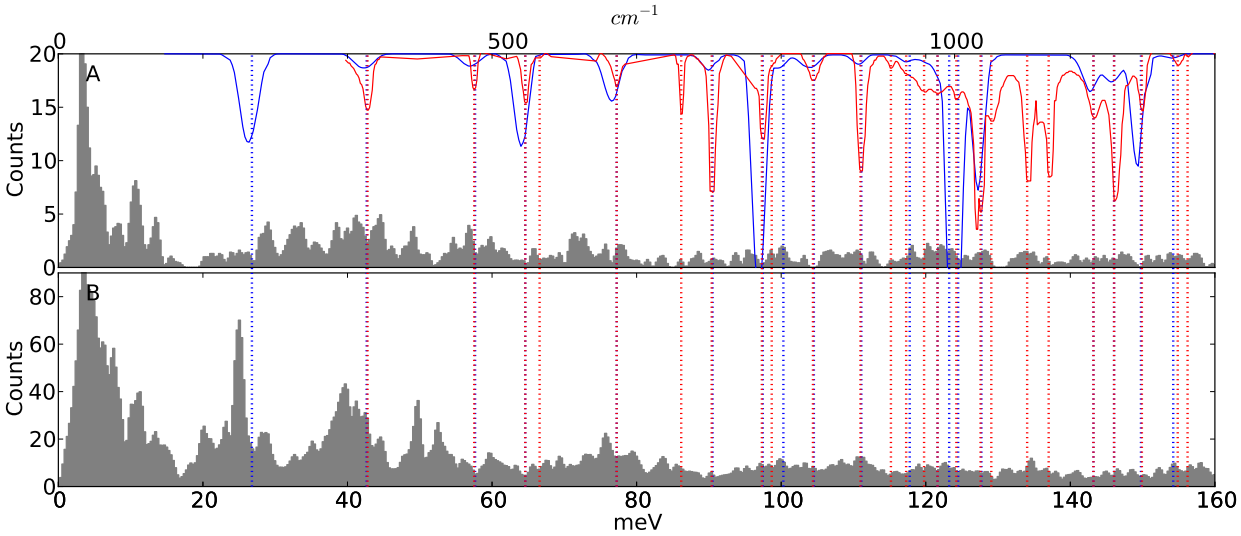

Figure S6 Histograms of peaks in $\frac{d^2I}{dV^2}$ at $V > 0$ from toluene junctions (reference). The junction conductances were approximately $10^{-2}G_0$. Only symmetric peaks/dips are included in the histograms. A) Histograms constructed using peak positions from a single opening trace. B) Histograms constructed using peak positions from 6 different opening traces (including the histogram in "A"). Raman (blue) and IR (red) spectra of toluene are overlaid and peak positions are indicated with vertical dashed lines. Peak positions above 60 meV are equally distributed.