

SUPPORTING INFORMATION

Sum rule for inelastic electron tunneling spectroscopy : an ab initio study of donors (TTF) and acceptors (TCNE, TCNQ and DCNQI) parallel-oriented on Cu(100)

Shiri R. Burema, Marie-Laure Bocquet*.

Ecole Normale Supérieure de Lyon, Laboratoire de Chimie, CNRS UMR 5182, 46 Allée d'Italie, 69364 CEDEX07 Lyon, France.

*E-mail: mbocquet@ens-lyon.fr

Height tables are provided : the first four tables are the detailed vibrational analysis and the last four tables are IETS intensities for all modes above 50 meV.

Table 1. Vibrational analysis of TTF/Cu(100) as calculated by the DFT approach used in this study for vibrational modes above 50 meV. The symmetry of the modes is indicated using D2h point group notation for a gas phase molecule. The two thiophene outerends of TTF are arbitrarily numbered '1' and '2' in order to denote the exact location of the described vibration in the molecule. Atoms or groups indicated between []-brackets do not participate in the actual vibrational motion, but serve to clarify the vibrating bond to which is referred.

v (meV)	Mode	Symmetry gas phase
380	2 C-H stretch thiophene 1	B2u
380	2 C-H stretch thiophene 2	B2u
378	2 C-H stretch thiophene 1	B1g
378	2 C-H stretch thiophene 2	B1g
173	[thiophene 1]C=C[thiophene 2] stretch	Ag
147	C=C in plane torsion thiophene 1	B1g
146	C=C in plane torsion thiophene 2	B1g
146	C=C stretch thiophene 1 + C=C stretch thiophene 2	Ag
145	C=C stretch thiophene 1 + C=C stretch thiophene 2	B2u
129	C=C stretch thiophene 1	B2u
129	C=C stretch thiophene 2	B2u
111	C=C out of plane torsion thiophene 1 + C=C out of plane torsion thiophene 2 + [thiophene 1]C=C[thiophene 2] in plane torsion	Au
109	C=C out of plane torsion thiophene 1 + C=C out of plane torsion thiophene 2 + [thiophene 1]C=C[thiophene 2] in plane torsion	Au

109	C=C out of plane torsion thiophene 1 + C=C out of plane torsion thiophene 2 + [thiophene 1]C=C[thiophene 2] in plane torsion	Au
91	Ring stretch thiophene 1 + ring stretch thiophene 2	B3u
91	Ring stretch thiophene 1 + ring stretch thiophene 2	Ag
90	Ring stretch thiophene 1 + ring stretch thiophene 2	B2u
87	Ring stretch thiophene 1 + ring stretch thiophene 2	B2u
83	Ring stretch (Kékulé) thiophene 1 + ring stretch (Kékulé) thiophene 2	B3u
82	Ring stretch (Kékulé) thiophene 1 + ring stretch (Kékulé) thiophene 2	B1g
72	Ring breathing thiophene 1 + ring breathing thiophene 2	Ag
71	Ring breathing thiophene 1 + ring breathing thiophene 2	B2u
67	In plane bent thiophene 1 + in plane bent thiophene 2	B3u
66	In plane bent thiophene 1 + in plane bent thiophene 2 + [thiophene 1]C=C[thiophene 2] in plane torsion	B1g
59	[thiophene 1]C=C[thiophene 2] out of plane torsion	B3g
58	In plane bent thiophene 1 + in plane bent thiophene 2	Ag
52	In plane bent thiophene 1 + in plane bent thiophene 2	B2u

Table 2. Vibrational analysis of TCNE/Cu(100) as calculated by the DFT approach used in this study for vibrational modes above 50 meV. The symmetry of the modes is indicated using D_{2h} point group notation for a gas phase molecule.

v (meV)	Mode	Symmetry gas phase
261	4 CN stretch	Ag
261	4 CN stretch	B2u
253	4 CN stretch	B3u
250	4 CN stretch	B1g
163	2 C-(CN) ₂ stretch (asymmetric)	B1g
154	2 C-(CN) ₂ stretch (asymmetric)	B3u
145	2 C-(CN) ₂ in-plane-bent (scissoring)	Ag
121	2 C-(CN) ₂ in-plane-bent (scissoring)	B2u
76	2 C-(CN) ₂ in-plane-bent (scissoring)	Ag
72	2 C-(CN) ₂ in-plane-bent (scissoring)	B2u
68	4 C-CN in-plane bent (rocking) + C=C stretch	Ag
68	4 C-CN in-plane bent (rocking) + C=C in plane bent (torsion)	B1g
63	4 C-CN out-of-plane bent (wagging) + C=C out-of-plane bent (torsion)	B3g
59	4 C-CN in-plane bent (scissoring)	B3u
57	4 C-CN out-of-plane bent (wagging)	B1u

Table 3. Vibrational analysis of TCNQ/Cu(100) as calculated by the DFT approach used in this study for vibrational modes above 50 meV. The symmetry of the modes is indicated using D_{2h} point group notation for a gas phase molecule.

v (meV)	Mode	Symmetry gas phase
388	4 C-H stretch Ph	Ag
387	4 C-H stretch Ph	B3u
385	4 C-H stretch Ph	B1g
385	4 C-H stretch Ph	B2u
265	4 C-N stretch	Ag
264	4 C-N stretch	B2u
255	4 C-N stretch	B1g
255	4 C-N stretch	B3u
197	C-C stretch Ph	Ag
190	C-C stretch Ph	B1g
184	C-C stretch Ph	B2u
176	C-C stretch Ph	B3u
166	C-C ring stretch (Kékulé) Ph	B3u
162	C-C ring twist Ph	B1g
159	C-C ring breathing Ph	Ag
158	C-C in plane bent Ph	B2u
153	1 C-(CN) ₂ stretch (asymmetric)	B1g
153	1 C-(CN) ₂ stretch (asymmetric)	B3u
147	C-C in plane bent Ph	Ag
138	C-C in plane bent Ph	B3u
128	2 C-(CN) ₂ in plane bent (scissoring) + C-C in plane bent Ph	B2u
124	2 C-(CN) ₂ in plane bent (scissoring) + C-C in plane bent Ph	Ag
122	2 C-(CN) ₂ in plane bent (scissoring) + C-C in plane bent Ph	B2u
116	C-C out-of-plane bent Ph	Au
115	C-C out-of-plane bent Ph	B3g
100	C-C out-of-plane bent Ph	B1u

99	C-C out-of-plane bent Ph	B2g
92	2 C-(CN) ₂ stretch (symmetric) + C-C in plane bent Ph	Ag
88	C-C out-of-plane bent Ph	B3g
80	4 C-CN in plane bent (scissoring) + Ph frustrated translation (in plane)	B2u
78	C-C in plane bent Ph	B1g
77	4 C-CN in plane bent (scissoring) + C-C in plane bent Ph	Ag
69	4 C-CN out-of-plane bent (wagging)+ C-C out-of-plane bent Ph	B1u

Table 4. Vibrational analysis of DCNQI/Cu(100) as calculated by the DFT approach used in this study for vibrational modes above 50 meV. The symmetry of the modes is indicated using D2h point group notation for a gas phase molecule. This is an approximation to the actual C2h symmetry of this compound in order to facilitate comparison with the other fragments. For completeness, C2h notation is used in brackets.

v (meV)	Mode	Symmetry gas phase
387	3 C-H stretch	B1g (Ag)
387	3 C-H stretch	B1g (Ag)
384	3 C-H stretch	B1g (Ag)
384	3 C-H stretch	B1g (Ag)
257	2 N-C-N stretch (asymmetric)	B2u (Bu)
254	2 N-C-N stretch (asymmetric)	Ag (Ag)
191	C-C stretch Ph	Ag (Ag)
186	C-C stretch Ph	B1g (Ag)
180	2 N-Ph stretches + C-C stretch Ph	B2u (Bu)
171	2 N-Ph in-plane bent (torsion)+ C-C stretch Ph	B3u (Bu)
164	2 N-C-N stretch (symmetric) + C-C stretch Ph	Ag (Ag)
163	C-C stretch (Kékulé) Ph	B3u (Bu)
161	2 N-C-N stretch (symmetric) + C-C stretch Ph	B2u (Bu)
157	C-C ring twist Ph	B1g (Ag)
142	C-C ring breathing Ph	Ag (Ag)
137	2 N-C-N stretch (symmetric) + C-C in-plane bent Ph	B2u (Bu)
134	2 N-C-N stretch (symmetric) + C-C in-plane bent Ph	B3u (Bu)
134	2 N-C-N stretch (symmetric) + C-C in-plane bent Ph	B3u (Bu)
122	C-C in plane bent Ph	B2u (Bu)
109	C-C out of plane bent Ph	Au (Au)
109	C-C out of plane bent Ph	B3g (Bg)
100	2 N-C-N in plane bent (scissoring)+ C-C in plane bent Ph	Ag (Ag)
98	2 N-Ph out-of-plane torsion + C-C out of plane bent Ph	B1u (Au)
97	C-C out of plane bent Ph	B2g (Bg)
92	2 N-C-N in plane bent (scissoring) + C-C in plane bent Ph	B2u (Bu)
83	2 C-N-Ph out-of-plane bent (twisting) + C-C out of plane bent Ph	B3g (Bg)
79	2 N-C-N in plane bent (scissoring) + C-C in plane bent Ph	B1g (Ag)

76	2 C-N-Ph in plane bent (scissoring) + C-C in plane bent Ph	B1g (Ag)
69	2 N-C-N in plane bent (scissoring) + Ph frustrated translation (in plane)	B2u (Bu)
64	2 C-N-Ph out-of-plane bent (wagging) + C-C out of plane bent Ph	B1u (Au)
60	2 N-C-N out-of-plane bent (wagging)	B1u (Au)
59	2 N-C-N out-of-plane bent (wagging)	B3g (Bg)

Table 5. IETS relative intensities η in % per vibration mode in meV of TTF/Cu(100) as calculated by the IETS approach used in this study for vibrational modes above 50 meV. Two positions above the molecule have been quoted : on center and off center (above the functional groups) ones.

ν (meV)	η on center (%)	η off center (%)
380	0.1	5.7
380	0.0	3.6
378	0.0	10.1
378	0.0	8.7
173	1.5	0.5
147	0.1	1.3
146	0.1	0.2
146	0.1	0.5
145	0.1	0.3
129	0.5	1.1
129	0.1	0.1
111	0.9	0.6
109	0.3	1.4
109	0.4	1.5
91	0.3	0.1
91	0.0	0.0
90	0.2	1.3
87	0.6	1.2
83	0.1	2.1
82	0.0	0.3
72	0.0	0.0
71	1.0	1.2
67	0.1	0.2

66	0.2	0.2
59	1.2	2.3
58	0.2	0.9
52	0.3	1.6

Table 6. IETS relative intensities η in % per vibration mode in meV of TCNE/Cu(100) as calculated by the IETS approach used in this study for vibrational modes above 50 meV. Two positions above the molecule have been quoted : on center and off center (above the functional groups) ones.

ν (meV)	η on center (%)	η off center (%)
261	0.0	0.1
261	2.4	0.9
253	0.1	0.2
250	0.1	0.0
163	0.1	0.4
154	0.1	0.1
145	0.1	0.2
121	2.0	1.3
76	0.0	0.1
72	0.8	0.6
68	0.3	0.6
68	0.2	0.4
63	2.0	1.0
59	0.3	0.2
57	0.4	0.3

Table 7. IETS relative intensities η in % per vibration mode in meV of TCNQ/Cu(100) as calculated by the IETS approach used in this study for vibrational modes above 50 meV. Two positions above the molecule have been quoted : on center and off center (above the functional groups) ones.

ν (meV)	η on center (%)	η off center (%)
388	0.1	0.1
387	0.1	0.0
385	0.0	0.0
385	0.0	0.0
265	0.0	0.0
264	4.0	0.6
255	0.1	1.0
255	0.0	0.0
197	0.1	4.7
190	1.4	0.1
184	0.1	0.1
176	0.2	0.0
166	0.0	0.1
162	0.1	0.0
159	0.1	1.8
158	0.3	0.2
153	0.1	0.5
153	0.0	0.1
147	0.0	0.8
138	0.1	0.0
128	0.2	0.4
124	0.3	2.3
122	0.0	0.7
116	0.4	0.0
115	1.7	0.7
100	0.1	0.8
99	0.1	0.1
92	0.1	0.5

88	0.1	1.0
80	0.1	0.3
78	0.2	0.0
77	0.0	0.2
69	0.8	9.0

Table 8. IETS relative intensities η in % per vibration mode in meV of DCNQI/Cu(100) as calculated by the IETS approach used in this study for vibrational modes above 50 meV. Two positions above the molecule have been quoted : on center and off center (above the functional groups) ones.

ν (meV)	η on center (%)	η off center (%)
387	0.1	0.0
387	0.1	0.0
384	0.1	0.0
384	0.0	0.0
257	0.2	1.1
254	0.3	0.5
191	0.1	1.1
186	1.4	0.1
180	1.0	0.4
171	0.0	0.1
164	0.3	0.4
163	0.3	0.2
161	0.2	0.7
157	0.2	0.0
142	4.1	0.2
137	0.3	0.3
134	0.0	0.2
134	2.2	0.2
122	0.1	0.1
109	0.6	0.1
109	2.4	0.2
100	1.6	0.2
98	0.7	0.3
97	0.4	0.1
92	0.3	0.8
83	0.0	0.2
79	0.1	0.3
76	0.4	0.1

69	0.1	0.2
64	0.3	0.2
60	2.0	1.5
59	0.3	0.5