**Table.** MRPT/aug-cc-pVTZ vertical transition energies (eV) of thiophene.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| State | Active space  (a1,b1,b2,a2) | State-average  (A1,B1,B2,A2) | CASSCF | CASPT2  NOIPEA | CASPT2  IPEA | SC-NEVPT2 | PC-NEVPT2 | CASPT3  NOIPEA | CASPT3  IPEA |
| 1A1(,\*) | (0,3,0,2) | (3,0,0,0) | 6.112a | **5.210** | **5.842** | **5.921** | **5.841** | **5.787** | **5.889** |
| 1B2(,\*) | (0,5,0,2) | (1,0,2,0) | 6.937b | **5.886** | **6.352** | **6.203** | **6.100** | **6.353** | **6.439** |
| 1A2(,3s) | (1,3,0,2) | (1,0,0,1) | 5.697c | **6.067** | **6.278** | **6.204** | **6.195** | **6.098** | **6.159** |
| 1B1(,3py) | (0,3,1,2) | (1,1,0,0) | 6.019d | **5.896** | **6.214** | **6.202** | **6.189** | **6.096** | **6.165** |
| 1A2(,3py) | (0,3,1,2) | (1,0,0,1) | 6.054d | **5.976** | **6.321** | **6.414** | **6.401** | **6.214** | **6.284** |
| 1B1(,3s) | (1,3,1,2) | (1,2,0,0) | 5.780e | **6.284** | **6.575** | **6.719** | **6.714** | **6.441** | **6.506** |
| 1B2(,3px) | (0,5,0,2) | (1,0,2,0) | 6.805b | **7.031** | **7.287** | **7.286** | **7.251** | **7.131** | **7.196** |
| 1A1(,\*) | (0,3,0,2) | (3,0,0,0) | 8.288a,f | **6.849** | **7.621** | **7.591** | **7.391** | **7.563** | **7.714** |
| 3B2(,\*) | (0,3,0,2) | (1,0,1,0) | 3.676a | **3.708** | **3.975** | **4.146** | **4.133** | **3.839** | **3.895** |
| 3A1(,\*) | (0,3,0,2) | (3,0,0,0) | 4.972a | **4.393** | **4.853** | **4.877** | **4.844** | **4.789** | **4.870** |
| 3B1(,3py) | (0,3,1,2) | (1,1,0,0) | 5.863d | **5.639** | **5.974** | **5.989** | **5.976** | **5.876** | **5.943** |
| 3A2(,3s) | (1,3,0,2) | (1,0,0,1) | 5.651c | **6.012** | **6.222** | **6.149** | **6.141** | **6.045** | **6.106** |

a Using reference (6e,5o) active space including valence  orbitals. b Using reference (6e,7o) active space including valence  and two 3px orbitals. c Using reference (6e,6o) active space including valence  and 3s orbitals. d Using reference (6e,6o) active space including valence  and 3py orbitals. e Using reference (6e,7o) active space including valence , 3s and 3py orbitals. f Strong double-excitation character.