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

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 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 | MS-CASPT2 | XMS-CASPT2 | QD-NEVPT2 |
| 1A2(,3s) | (1,3,0,2) | (1,0,0,1) | 4.489a | **5.230** | **5.436** | **5.505** | **5.514** | **5.229** | **5.284** | **–** | **–** | **–** |
| 1B1(,3py) | (0,3,1,2) | (1,1,0,0) | 5.215b | **6.072** | **6.260** | **6.314** | **6.320** | **6.024** | **6.083** | **–** | **–** | **–** |
| 1A2(,3pz) | (2,3,0,2) | (1,0,0,2) | 4.887c | **6.024** | **6.157** | **6.416** | **6.441** | **5.970** | **6.009** | **–** | **–** | **–** |
| 1B2(,\*)d | (0,4,0,2) | (1,0,2,0) | 7.735e | **6.362** | **6.617** | **6.650** | **6.619** | **6.377** | **6.450** | **6.374** | **6.363** | **6.462** |
| 1A1(,\*) | (0,3,0,2) | (3,0,0,0) | 6.470f | **5.836** | **6.414** | **6.584** | **6.527** | **6.342** | **6.425** | **–** | **–** | **–** |
| 1B2(,3px)d | (0,4,0,2) | (1,0,2,0) | 5.818e | **6.110** | **6.755** | **6.709** | **6.483** | **6.822** | **6.924** | **6.923** | **6.935** | **6.896** |
| 3B2(,\*) | (0,3,0,2) | (1,0,1,0) | 4.242f | **4.299** | **4.566** | **4.760** | **4.743** | **4.438** | **4.494** | **–** | **–** | **–** |
| 3A2(,3s) | (1,3,0,2) | (1,0,0,1) | 4.466a | **5.207** | **5.410** | **5.478** | **5.487** | **5.201** | **5.256** | **–** | **–** | **–** |
| 3A1(,\*) | (0,3,0,2) | (3,0,0,0) | 5.518f | **5.036** | **5.501** | **5.600** | **5.563** | **5.404** | **5.488** | **–** | **–** | **–** |
| 3B1(,3py) | (0,3,1,2) | (1,1,0,0) | 5.183b | **6.032** | **6.220** | **6.273** | **6.280** | **5.983** | **6.042** | **–** | **–** | **–** |

a Using reference (6e,6o) active space including valence  and 3s orbitals. b Using reference (6e,6o) active space including valence  and 3py orbitals. c Using reference (6e,7o) active space including valence , 3s and 3pz orbitals. d Assignment based on orbital extension at CASSCF level and on oscillator strengths at MRPT level. e Using reference (6e,6o) active space including valence  and 3px orbitals. f Using reference (6e,5o) active space including valence  orbitals.