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

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 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 |
| 1A2(n,\*) | (2,2,1,0) | (1,0,0,1) | 2.717a | **2.332** | **2.578** | **2.563** | **2.546** | **2.530** | **2.599** |
| 1B2(n,3s) | (4,2,1,0) | (1,0,2,0) | 4.802b | **5.480** | **5.603** | **5.689** | **5.719** | **5.606** | **5.639** |
| 1A1(,\*) | (2,2,2,0) | (3,0,0,0) | 6.941d | **5.981** | **6.424** | **6.380** | **6.241** | **6.259** | **6.403** |
| 1B2(n,3pz) | (4,2,1,0) | (1,0,2,0) | 5.573b | **6.400** | **6.509** | **6.595** | **6.623** | **6.493** | **6.525** |
| 1A1(n,3py) | (2,2,2,0) | (3,0,0,0) | 6.245d | **6.415** | **6.661** | **6.565** | **6.522** | **6.498** | **6.593** |
| 3A2(n,\*) | (2,2,1,0) | (1,0,0,1) | 2.517a | **2.095** | **2.341** | **2.339** | **2.320** | **2.313** | **2.379** |
| 3A1(,\*) | (2,2,0,0) | (2,0,0,0) | 3.517c | **3.286** | **3.481** | **3.483** | **3.482** | **3.427** | **3.482** |

a Using reference (6e,5o) active space including valence , nO, σCO and σ\*CO orbitals. b Using reference (6e,7o) active space including valence , nO, σCO, σ\*CO, 3s and 3pz orbitals. c Using reference (4e,4o) active space including valence , σCO and σ\*CO orbitals. d Using reference (6e,6o) active space including valence , nO, σCO, σ\*CO and 3py orbitals.