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

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| State | Active space  (a’,a”) | State-average  (A’,A”) | CASSCF | CASPT2  NOIPEA | CASPT2  IPEA | SC-NEVPT2 | PC-NEVPT2 | CASPT3  NOIPEA | CASPT3  IPEA |
| 1A’’(n,\*) | (1,5) | (1,3) | 3.478a | **3.461** | **3.581** | **3.829** | **3.839** | **3.662** | **3.660** |
| 1A’(,\*) | (2,4) | (4,0) | 8.849b | **6.278** | **6.931** | **6.433** | **6.123** | **7.045** | **7.178** |
| 1A’’(n,\*) | (1,5) | (1,3) | 6.760a,c | **6.341** | **6.787** | **7.100** | **7.070** | **6.804** | **6.880** |
| 1A’(n,3s) | (2,4) | (4,0) | 7.201b | **6.983** | **7.213** | **7.049** | **7.008** | **7.155** | **7.196** |
| 1A’(2,\*2) | (2,4)  (6,4) | (4,0)  (3,0) | 7.909b  8.454d | **7.746**  **7.528** | **8.101**  **7.961** | **8.328**  **8.006** | **8.302**  **7.846** | **7.950**  **7.906** | **8.022**  **7.979** |
| 3A’’(n,\*) | (1,5) | (1,3) | 3.249a | **3.150** | **3.278** | **3.509** | **3.520** | **3.399** | **3.392** |
| 3A’(,\*) | (2,4) | (4,0) | 3.888b | **3.777** | **4.006** | **4.102** | **4.089** | **3.911** | **3.962** |
| 3A’(,\*) | (2,4) | (4,0) | 5.888b | **5.929** | **6.203** | **6.436** | **6.430** | **6.020** | **6.097** |
| 3A’’(n,\*) | (1,5) | (1,3) | 6.673a,c | **6.207** | **6.647** | **6.936** | **6.906** | **6.664** | **6.743** |

a Using reference (6e,6o) active space including valence , nO and 3pz orbitals. b Using reference (6e,6o) active space including valence , nO and 3s orbitals. c Substantial Rydberg and doubly-excited character. d Using reference (10e,10o) active space including valence , σCC, σCO, σ\*CC, σ\*CO orbitals.