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

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| State | Active space  (a’,a”) | State-average  (A’,A”) | CASSCF | CASPT2  NOIPEA | CASPT2  IPEA | SC-NEVPT2 | PC-NEVPT2 | CASPT3  NOIPEA | CASPT3  IPEA | MS-PT2  IPEA | XMS-PT2  IPEA |
| 12A”(p,n) | (9,2) | (1,1) | 3.529a | **3.405** | **3.390** | **3.346** | **3.311** | **3.320** | **3.327** | **–** | **–** |
| 22A”(n,p\*) | (9,2) | (1,2) | 5.459a | **4.796** | **4.924** | **4.914** | **4.781** | **4.808** | **4.859** | **–** | **–** |
| 22A’(p,p\*)b | (9,2) | (2,0) | 5.908a | **5.484** | **5.663** | **5.700** | **5.665** | **5.599** | **5.645** | **–** | **–** |
| 32A’(n,3s) | (10,2) | (3,0) | 5.789c | **6.196** | **6.188** | **6.158** | **6.161** | **6.180** | **6.179** | **–** | **–** |
| 42A’(n,3p) | (12,2) | (6,0) | 6.297d | **6.202** | **6.378** | **6.399** | **6.335** | **6.331** | **6.374** | **6.708** | **6.719** |
| 52A’(n,3p) | (12,2) | (6,0) | 6.178d | **6.729** | **6.698** | **6.674** | **6.698** | **6.715** | **6.706** | **6.848** | **6.986** |
| 62A’(s,n) | (12,2) | (6,0) | 8.158d | **7.641** | **7.694** | **7.711** | **7.629** | **7.639** | **7.662** | **7.630** | **7.626** |
| 32A”(p,3s) | (10,2) | (1,3) | 7.112c | **7.409** | **7.580** | **7.580** | **7.558** | **7.534** | **7.570** | **–** | **–** |
| 42A”(n,3p) | (10,4) | (1,4) | 7.050e | **7.540** | **7.556** | **7.518** | **7.516** | **7.563** | **7.564** | **–** | **–** |
| 14A’(p,p\*) | (9,2) | (2,0) | 4.509a | **4.426** | **4.548** | **4.571** | **4.571** | **4.508** | **4.540** | **–** | **–** |
| 12A”(p,3s) | (10,2) | (1,1) | 6.751c | **7.254** | **7.331** | **7.319** | **7.357** | **7.351** | **7.359** | **–** | **–** |

a Using reference (11e,11o) full valence active space. b Involving strong double (np,p\*n) character. c Using reference (11e,12o) full valence active space plus one 3s orbital. d Using reference (11e,14o) full valence active space plus one 3s, one 3pz and one 3py orbitals. e Using reference (11e,14o) full valence active space plus one 3s and two 3px orbitals.