COMPUTATIONAL APPROACHES TO THE DETERMINATION OF THE MOLECULAR GEOMETRY OF ACROLEIN IN ITS $T_1(n, \pi^*)$ STATE

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The spectroscopically derived inertial constants for acrolein (propenal) in its $T_1(n, \pi^*)$ state[a] were used to test predictions from a variety of computational methods. One focus was on multiconfigurational methods, such as CASSCF and CASPT2, that are applicable to excited states. We also examined excited-state methods that utilize single reference configurations, including EOM-EE-CCSD and TD-PBE0. Finally, we applied unrestricted ground-state techniques, such as UCCSD(T) and the more economical UPBE0 method, to the $T_1(n, \pi^*)$ excited state under the constraint of C_s symmetry. The unrestricted ground-state methods are applicable because at a planar geometry, the $T_1(n, \pi^*)$ state of acrolein is the lowest-energy state of its spin multiplicity. Each of the above methods was used with a triple zeta quality basis set to optimize the $T_1(n, \pi^*)$ geometry. This procedure resulted in the following sets of inertial constants:

Inertial constants (cm^{-1}) of acrolein in its $T_1(n, \pi^*)$ state

Method	*A*	*B*	*C*	Method	*A*	*B*	*C*
CASPT2(6,5)[b]	1.667	0.1491	0.1368	UCCSD(T)[b]	1.668	0.1480	0.1360
CASSCF(6,5)	1.667	0.1491	0.1369	UPBE0	1.699	0.1487	0.1367
EOM-EE-CCSD	1.675	0.1507	0.1383				
TD-PBE0	1.719	0.1493	0.1374	**Experiment**[a]	1.662	0.1485	0.1363

The two multiconfigurational methods produce the same inertial constants, and those constants agree closely with experiment. However the sets of computed bond lengths differ significantly for the two methods. In the CASSCF calculation, the lengthening of the C=O and C=C bonds and the shortening of the C—C bond are more pronounced than in CASPT2.

[a] Previous talk

[b] O. S. Bokareva *et al.*, *Int. J. Quant. Chem.* **108**, 2719 (2008).