COMPUTATIONAL INVESTIGATION OF THE $T_1(n, \pi^*)$ STATE OF 2-CYCLOHEXEN-1-ONE

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We have used several computational methods, including TDDFT and EOM–EE–CCSD, to determine the equilibrium geometry and harmonic vibrational frequencies of 2-cyclohexen-1-one (CHO) in its $T_1(n, \pi^*)$ excited state. Atom displacement vectors for the normal modes indicate that the lowest-frequency vibration, ν_{39}, is best described as a ring-twisting motion, whereas ν_{38} is a ring-bending vibration consisting mainly of C-5 displacement toward and away from the plane in which the other heavy atoms lie. These updated descriptions are transposed with respect to those in the previous literature.[a] The table below shows that the EOM–EE–CCSD harmonic frequencies generally agree well with fundamentals obtained spectroscopically.[b] In particular, the ν_{39} frequency determined by EOM–EE–CCSD is more accurate than the TDB3LYP result, with errors of +2% and +20%, respectively. This outcome is traceable in part to a larger ν_{39} reduced mass calculated by EOM–EE–CCSD, stemming from a less planar O=C–C=C dihedral angle (170.4° via EOM–EE–CCSD vs. 177.4° via TDB3LYP).

Low-frequency fundamentals (cm^{-1}) for CHO in its $T_1(n, \pi^*)$ state

Mode	Description	TDB3LYP/cc-pVTZ	EOM–EE–CCSD/cc-pVDZ	Experiment[b]
39	ring twist	119.6	101.4	99.5
38	bend (inversion of C-5)	255.9	272.0	253.2
37	C=C twist	306.9	223.0	247.8
36	C=O wag	359.0	340.2	345.5

The success of EOM–EE–CCSD in this application could be due to its ability to describe multiconfigurational wavefunctions within a single-reference formalism.

[a] T. L. Smithson and H. Wieser, *J. Chem. Phys.* **73**, 2518 (1980); M. Z. M. Rishard, E. A. Brown, L. K. Ausman, S. Drucker, J. Choo, and J. Laane, *J. Phys. Chem. A* **112**, 38 (2008).

[b] Previous talk.