Supporting Information

Infrared laser spectroscopy of the CH_3OO radical formed from the reaction of CH_3 and O_2 within a helium nanodroplet

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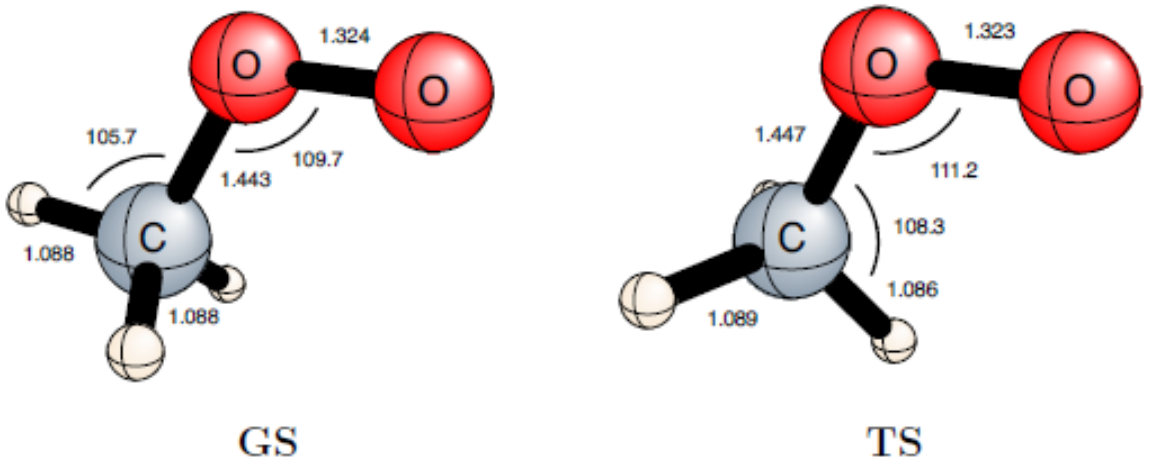

Figure S1: Optimized geometry for the ground-state and transition-state at the CCSD(T)/cc-pVTZ level of theory. Bond lengths are shown in Angstroms and bond angles in degrees.

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Table S1: Focal Point analysis of the CH_3OO torsional barrier in the $(X)^2A''$ electronic state.[a]

Basis set	ΔE_eHF	+δMP2	+δCCSD	+δCCSD(T)	NET
cc-pVTZ	+1.36	-0.66	+0.33	-0.08	[+0.95]
cc-pVQZ	+1.38	-0.69	+0.33	-0.08	[+0.94]
cc-pV5Z	+1.38	-0.69	[+0.33]	[-0.08]	[+0.94]
CBS LIMIT	[+1.38]	[-0.70]	[+0.33]	[-0.08]	[**+0.93**]
ΔE_t(final) = ΔE_t[CBS CCSD(T)] + Δ_{ZPVE}[CCSD(T)/cc-pVTZ]					
ΔE_t(final) = 0.93 – 0.21 = **0.72 kcal mol^{-1}**					

[a]Energies shown in kcal mol^{-1}. Delta (δ) denotes the change in relative energy (ΔE_e) with respect to the preceding level of theory.

Note: The barrier for torsional rotation (0.72 kcal mol^{-1}), has a suggested accuracy of ±0.1 kcal mol^{-1}. This can be deduced from looking at the focal-point table, where we see oscillatory convergence to within 0.08 kcal mol^{-1}.

Ground-State: (Cartesian Coordinates)
H -1.97621996614 0.487796731042 0.0
C -1.1661393889 -0.238632305755 0.0
O 0.0526172527545 0.534467925974 0.0
O 1.09753254814 -0.278193009495 0.0
H -1.19623505374 -0.856855813713 0.895207315689
H -1.19623505374 -0.856855813713 -0.895207320981

Ground-State Frequencies [CCSD(T)/cc-pVTZ]:
0.0000i
0.0000i
0.0000i
0.0000i
0.0000
0.0000
149.7274
493.5895
949.3199
1144.0846
1160.2828
1212.0275
1449.0832
1484.1431
1497.6945
3061.9382
3159.3911
3168.8276
ZPVE: 27.0619 kcal/mol

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Transition State: (Cartesian Coordinates)

H	-0.925965420482	1.29146315085	0.0
C	-1.17814575391	0.234897748448	0.0
O	0.053280041967	-0.525593962184	0.0
O	1.10782046825	0.272944428453	0.0
H	-1.73678128951	-0.0393094821325	-0.893941920592
H	-1.73678128951	-0.0393094821325	0.893941920592

Transition-State Frequencies [CCSD(T)/cc-pVTZ]:

142.6587i
0.0000i
0.0000i
0.0000i
0.0000
0.0000
0.0000
533.7710
941.3993
1126.2488
1138.5946
1229.6803
1437.7611
1486.6697
1496.9888
3059.1017
3148.8551
3182.0058

ZPVE: 26.8489 kcal/mol

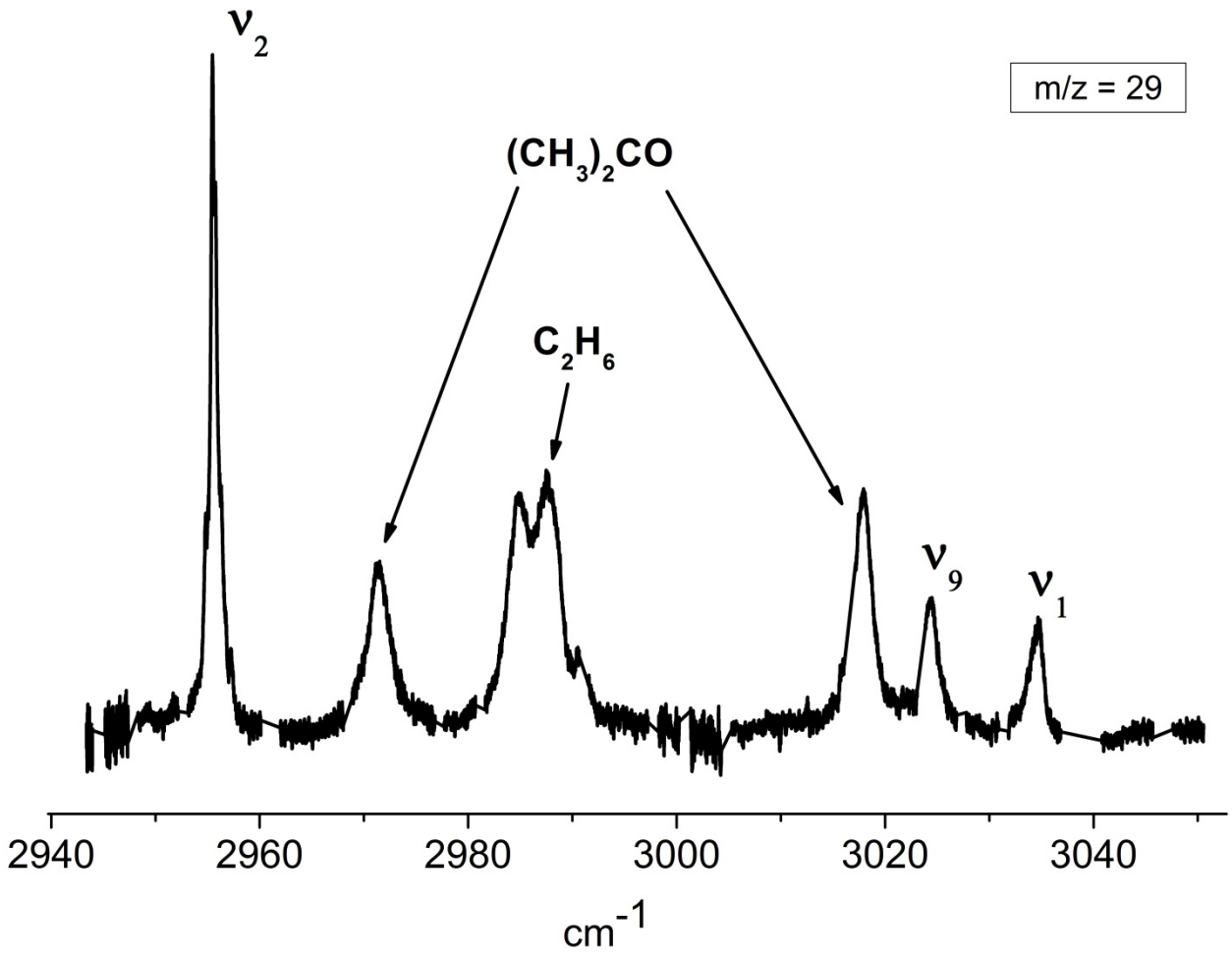

Figure S2: Survey Spectrum of the CH stretch region by measuring the depletion in mass channel m/z = 29. Two acetone bands as well as an ethane band are observed in addition to the three transitions reported in this manuscript for CH_3O_2.